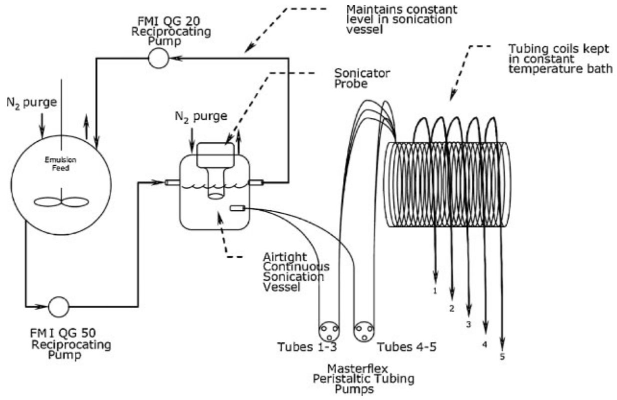
Continuous Miniemulsion Polymerization

F. Joseph Schork,* Juchen Guo

Most miniemulsion polymerizations are carried out in batch reactors. However, continuous reactors or continuous reactor trains can provide a high level of consistency when operated at steady state. In this feature article, progress in continuous miniemulsion polymerization will be reviewed. Special attention will be given to issues of monomer diffusion and secondary nucleation. A large portion of the paper will be devoted to controlled radical polymerization for two reasons. First, this is a relatively new field, particularly when continuous reactors are considered, and second, for controlled radical polymerization in continuous reactors, the molecular weight distribution of the product is a direct function of the reactor residence time distribution.



Introduction

Miniemulsion polymerization is mostly carried out in batch reactors, which give the maximum flexibility and adaptability to specialty products. There are cases, however, when a continuous system might be appropriate. Products made in continuous reactors tend to have a lower manufacturing cost. In the case of copolymers, a continuous stirred-tank reactor (CSTR) gives a constant copolymer composition distribution (CCD), rather than the composition drift seen in a batch reactor. (Semibatch copolymerization can alleviate the composition drift, but cannot eliminate it altogether.) If the particle size distribution is narrow, or the molecular weight is not strongly affected by particle size, a CSTR will give a constant molecular weight distribution (MWD). (As discussed later, this is not the case in living or controlled polymerizations.) CSTR trains can be used to provide high-throughput and high-monomer conversion, while retaining many of the benefits of a single CSTR.

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Tubular reactors exhibit the same kinetic behavior as batch reactors, and so there are no kinetic advantages of using a tubular reactor. However, a tubular reactor operating at steady state will provide a consistent product, quite probably, at a lower cost than a batch reactor. In addition, heat transfer is extremely efficient in a tubular reactor due to the high surface-to-volume ratio.

Reactor configurations involving both CSTR and tubular reactors can be envisioned. For instance, tubular reactors are often used as pre-reactors and/or post-reactors in a CSTR train. Finally, continuous reactors can be used to investigate kinetics in ways that batch reactors cannot. This paper summarizes the work to date on miniemulsion polymerization in continuous reactors. Both free radical and controlled free radical chemistries will be considered, since the effects of residence time distribution (RTD) on these two chemistries are very different.

Miniemulsion Polymerization

Mechanism

In this paper, for the purpose of clearly distinguishing between conventional emulsions and miniemulsions, the

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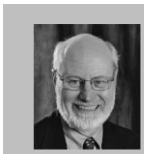

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term macroemulsion will be used for the former. The mechanisms of macroemulsion and miniemulsion polymerization are schematically shown in Figure 1. From a classic point of view, a macroemulsion polymerization reaction can be divided into three intervals. Interval I presents particle nucleation and is believed to take place when radicals enter monomer-swollen micelles in the aqueous phase as single mono-radicals or oligo-radicals. These micelles form primary particles by prolongation of the entering monomers. End of Interval I is signified by the disappearance of free micelles in the aqueous phase. During Interval I, nucleation in monomer droplets can be ignored, because the total droplet surface area is relatively small. Interval II involves polymerization within the primary particles with monomers supplied by diffusion from the droplets. Interval III begins when the monomer droplets disappear and continues to the end of the reaction.

The significant difference of miniemulsion to macroemulsion is the much smaller droplet size (0.01–0.5 μm). Hence, the droplet surface area in miniemulsion systems is very large compared to macroemulsion. With intentional preparation, little free surfactant is present in the form of micelles as most of the surfactant is adsorbed at the droplet surface. Because of the large surface area in miniemulsion polymerization systems, particle nucleation is primarily via radical (mono- or oligo-) entry into monomer droplets which are the polymerization loci in miniemulsion polymerization.

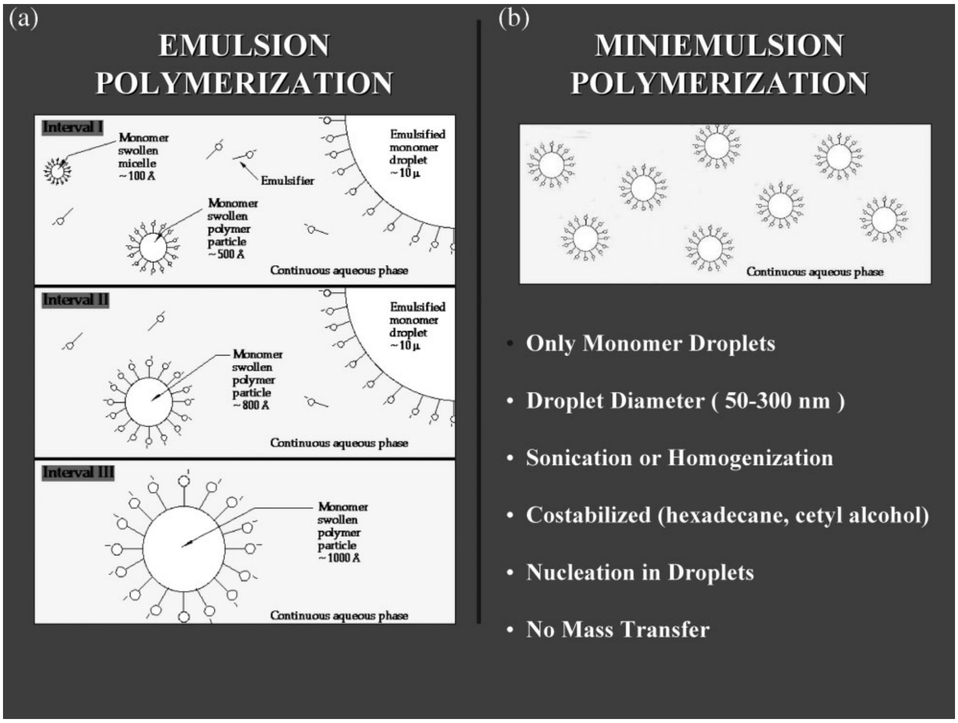

Figure 1. (a) Macroemulsion versus (b) miniemulsion polymerization.[1]

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A miniemulsion is created by the application of high shear force to a macroemulsion, and a distribution of droplet sizes is resulted. Even with surfactant to prevent droplet coalescence, monomers will, over time, diffuse from the smaller monomer droplets into the larger ones. This process of small droplet degradation is referred as Ostwald ripening,[3] and the reduction in interfacial area (energy) is the driving force. If Ostwald ripening is allowed to continue unchecked, creaming of monomers will occur as the droplet sizes become large enough for Stokes law creaming to occur. A costabilizer (also referred to in earlier works as a cosurfactant or hydrophobe) functions to limit Ostwald ripening by retarding monomer diffusion from the smaller droplets to the larger ones. Costabilizers should be highly insoluble in the aqueous phase and highly soluble in the monomer droplets so that they will not diffuse out of the droplets. Under these conditions, diffusion of monomer out of the droplets increases concentration of the costabilizer resulting in increased free energy, which can balance the reduced interfacial energy to limit Ostwald ripening. Ostwald ripening will still proceed, but on a much longer time scale, which is unimportant since the time scale of polymerization is usually hours. The stabilized miniemulsion is shown in Figure 2. In their original discovery of miniemulsion polymerization, Ugelstad et al.[4] used either cetyl alcohol (CA, water solubility estimated at 6×10^{-8})[5] or hexadecane (HD, water solubility estimated at 1×10^{-9})[5] as a costabilizer. Other researchers have used polymer, chain transfer agents, and monomers as costabilizers.[6–14]

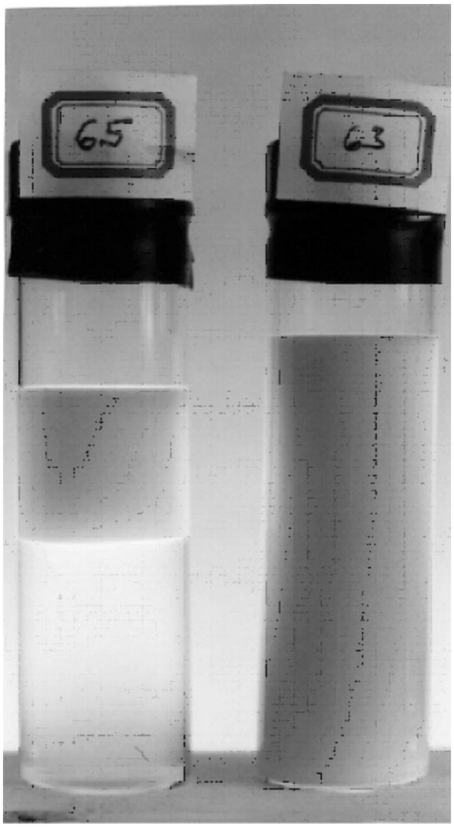

Figure 2. Macroemulsion and miniemulsion after 3 h.[1]

Monomer Transport Effects

Macroemulsion polymerization relies on transportation of monomer from the monomer droplets to the polymerization loci. This transport process is driven by the equilibrium monomer swelling. For monomer transport in macroemulsion polymerization, the following assumptions may be made: (i) The limiting resistance is transported from the monomer droplets into the aqueous phase; (ii) Transport out of the monomer droplet can be modeled with an overall mass transfer coefficient. It is driven by the difference between the saturation concentration of monomer and the actual concentration in the aqueous phase in equilibrium with the polymerization particles: (iii) Diffusion across the aqueous phase is driven by forced convection (stirring) and not the rate-determining step; (iv) The very large interfacial area of the polymerization particles (relative to monomer droplets) will insure that monomer transport from the aqueous phase into the particles is not the limiting step.

For monomers that are highly water insoluble, the driving force in assumption (ii) will be considerably small because of the very low monomer saturation concentration in aqueous phase. If such monomers are used in macroemulsion polymerizations, they may not participate significantly in the polymerization of the particles. However, these potential transport limitations can be avoided by using miniemulsion polymerization. As described above, in miniemulsion polymerization, nucleation takes place in the monomer droplets which could be considered as individual reactors. Miniemulsion polymerization does not rely on monomer transport across the aqueous phase in batch reactors. In a discussion of continuous miniemulsion polymerization, monomer transport effects are critical. For instance, in a CSTR emulsion polymerization, monomer droplets will be fed into an environment containing particles at a much higher monomer conversion, creating a significant driving force for monomer transfer. Thus, while monomer transport might be almost eliminated in a batch miniemulsion polymerization, it can only be minimized in a CSTR. In copolymerization, these considerations are compounded by the need to consider the relative rates of monomer transport.

Continuous Miniemulsion Free Radical Polymerization

Homopolymerization in Continuous Stirred-Tank Reactors

Nomura and Harada[15] developed a mathematical reaction model for continuous macroemulsion polymerization based on the assumption of high radical capture efficiency of micelles relative to monomer droplets. They derived the rate of particle formation in a CSTR based on initiation of radicals in aqueous phase. Combining particles formation and surfactants balance, they developed a monomer conversion model, which was proved more accurate than models based on Smith-Ewart Case II theory (zero/one system) by experimental data. They demonstrated that the number of polymer particles produced in a CSTR was a function of residence time (reactor volume divided by volumetric flow rate), and a single CSTR produced much less (57%) polymer particles at a steady state than a batch reactor at the same experimental conditions. This was due in large part to the fact that particle formation and growth occur simultaneously in a CSTR.

The first attempt on continuous miniemulsion polymerization was a mathematical model based on theoretical consideration for miniemulsion polymerization of methyl methacrylate (MMA) with an oil-soluble initiator in CSTR by Chen et al.[16] In their model development, they assumed that monomer miniemulsion was pre-filled in the CSTR, aqueous monomer dispersion was fed into the CSTR and the initiator was fed with additional monomer separately. They also assumed that there were free micelles in the aqueous phase and droplet nucleation and micelle nucleation (occurring when oil-soluble radicals desorbed from monomer droplets) coexisted. They concluded that miniemulsion polymerization was a special case for general macroemulsion polymerization, but no experimental data were available. The first experimental work was carried out by Barnette and Schork[17,18] to polymerize MMA in a single CSTR with a water-soluble initiator via miniemulsion polymerization. This work demonstrated the significance of the droplet nucleation mechanism of the miniemulsion polymerization. Since nucleation took place in the monomer droplets and there was no or little micelles existing in the aqueous phase, miniemulsion polymerization did not suffer the oscillation of conversion, which could be often found in CSTR macroemulsion polymerization, caused by the competition for surfactants between growing particles and radicals in aqueous phase needing free micelles for nucleation. Also, this work determined that at a relatively moderate residence time, the steady state conversion from CSTR miniemulsion polymerization is two-fold higher than that from the corresponding macroemulsion one.

A simplified mathematical model to differentiate CSTR macroemulsion and miniemulsion polymerizations was developed by Samer and Schork[19] using the similar approach of Nomura and Harada's as described above. In this simplified analysis, it was assumed that the amount of radicals captured by particles and droplets is proportional to the ratio of particle and droplet diameters and the radical capture rate is independent. This assumption is reliable when polymer particles still closely resemble monomer droplets with respect to composition and surface characteristics. For CSTR miniemulsion polymerization, the maximum particle generation is limited by the concentration of monomer droplets in the feed because of predominant droplet nucleation. From their model, the nucleation efficiency (defined as the number of particles divided by the number of droplets in the feed) approached unity for residence times greater than 30 min, which means that the number of particles generated in CSTR miniemulsion polymerization is nearly identical to that in batch under similar conditions. It is a theoretical interpretation of the experimental finding by Barnette[17] that the steady state conversion in a CSTR miniemulsion polymerization of MMA was approximately twice than that in a CSTR macroemulsion polymerization.

Aizpurua and Barandiaran's work[20] confirmed lack of oscillations in CSTR miniemulsion polymerization for vinyl acetate (VAc) under a wide range of surfactant and initiator concentrations. The number of particles in miniemulsion polymerization depends much less on surfactant concentration than that in macroemulsion polymerization does. They demonstrated that the monomer droplet nucleation mechanism brought the feasibility of miniemulsion polymerization as a strategy to eliminate the oscillatory behavior of CSTR macroemulsion polymerization. Aizpurua et al.[21] successfully used polymeric costabilizers (polyvinyl acetate and polystyrene) in the CSTR miniemulsion polymerization of VAc at high solid levels. The reactants were fed into a CSTR by two streams. One was a monomer miniemulsion (mixture of monomer, surfactant, costabilizer, and most of the water) and the other an aqueous solution of initiator. The experiments successfully eliminated conversion oscillations, indicating droplet nucleation in miniemulsion polymerization in CSTR. These results are particularly significant, since, as fresh miniemulsion droplets containing polymeric costabilizer are introduced into a CSTR, they must compete to retain their monomer with existing particles that may contain converted polymer. The fact that the particle number in the CSTR was approximately same as the droplet number in the feed suggested that the droplet number (if not droplet size distribution) was conserved. They also found that for high solid content emulsion polymerization in CSTR, miniemulsion could reduce the viscosity of the reactants notably at the

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beginning process, preventing initial mixing and heating problems.

Homopolymerization in Plug Flow Reactors (PFR)

In Samer and Schork's CSTR miniemulsion polymerization modeling work mentioned above,[19] they also modeled macro- and miniemulsion polymerization in a PFR/CSTR train. For macroemulsion polymerization, particle nucleation and growth compete with each other for surfactants in a CSTR. Hence, the number of particles formed in a CSTR only is a fraction of that generated in a batch reactor under the same conditions. Their results showed that adding an upstream PFR to a CSTR dramatically enhanced the particle formation and the polymerization rate in the CSTR. In fact, a single CSTR was found to produce only 20% the number of particles generated in a PFR/CSTR train with the same total residence time as the CSTR alone. In contrast, since miniemulsions are dominated by droplet nucleation, the use of a PFR "pre-reactor" had a negligible effect on the polymerization rate in the CSTR miniemulsion polymerization. There was no notable difference between the number of particles generated in a single CSTR and that generated in a PFR/CSTR train with the same total residence time. This confirms Barnette's[17,18] experimental observation that a PFR in front of a CSTR eliminated conversion oscillations in macroemulsion polymerization, but only resulting in a higher steady state monomer conversion in miniemulsion polymerization.

Durant[22] used a PFR to carry out a miniemulsion polymerization with solid content in the industrially relevant range. Ouzineb et al.[23] used a PFR to obtain miniemulsion latexes with high solid content of poly (methyl methacrylate) (PMMA) and copolymer of MMA and butyl acrylate (BuA). This work demonstrated that the miniemulsion polymerization in PFR could eliminate the fouling and demixing problems associated with the presence of monomer droplets in concentrated systems in PFR macroemulsion polymerization because of its droplet nucleation mechanism. High solid content (60%) latexes of PMMA and poly(MMA-*co*-BuA) could be achieved in PFR with miniemulsion polymerization.

Copolymerization in Semibatch Reactors

Semibatch miniemulsion polymerization will be discussed here, even though this is a review of continuous miniemulsion polymerization, since many of the monomer transport issues that are important in CSTR polymerization are also seen in semibatch systems.

Controlling copolymer composition has long been of prime interest in polymer reaction engineering. Mayo and Lewis[24] studied the kinetics of copolymerization and developed an equation to describe the relationship between the monomer molar concentrations at the site of propagation and reactivity ratio of monomers for the homogeneous copolymerization, such as bulk or solution polymerization. Because of possible difference in reactivity ratios of different monomers, the desired copolymer composition may not be obtained spontaneously. To resolve this problem, semibatch polymerization (both solution and macroemulsion) has long been used to produce copolymers of desired composition distribution. This may be done in either of the following two ways: first (in binary polymerization) the more reactive monomer may be fed in a semibatch manner while the less reactive monomer may be pre-charged in a batch manner. This will result in a higher concentration of the less reactive monomer at the locus of polymerization, and the less reactive monomer could be higher in polymer formation than would be the case for batch polymerization. Alternatively, the reaction may be run monomer-starved. In this case, the monomers are fed in the desired ratio, but at a slow rate. The polymerization rate is then controlled by the rate of monomer feed. Since polymerization occurs under monomer-starved condition, the copolymer composition will be that of the comonomer feed. For semibatch macroemulsion and miniemulsion polymerizations, issues of transport of the monomers to polymerization loci must be considered for both methods. Also, the decision must be made as whether to feed neat monomer, a macroemulsion of monomer droplets, or a miniemulsion of monomer droplets. In general, neat monomer feed will result in the formation of the fewest new particles, while miniemulsion feed will result in the most. Depending on the goals of the polymerization, formation of new particles during the semibatch feeding may be desirable or undesirable.

In 1991, Tang, et al.[25] studied seeded semibatch polymerization of BuA with both neat monomer feed and miniemulsion feed. They found that miniemulsion feeding produced a large number of new particles. It was also found that the faster the feed rate the larger is the population of small particles produced. Their study suggested that miniemulsions can be used to control the particle size distribution of a polymer latex system by adjusting monomer droplet numbers in miniemulsion feed and feeding rates. Unzue and Asua[26] studied the semibatch miniemulsion terpolymerization of BuA, MMA, and VAc. They successfully produced latex with 65% solid content. It is well known that semibatch polymerization can be an effective method of making high solid latex. They demonstrated that miniemulsion feeding could be effective to enhance the solid content, because a miniemulsion feed is likely to produce much more additional particles to bring on a broad particle size distribution (PSD), which was already indicated by Tang's work.[25]

Ouzineb et al.[27] used a two-step semibatch seeded miniemulsion polymerization to produce polystyrene and polystyrene/poly(butyl methacrylate) blend latexes of high solid content (75 wt.-%) and low viscosity. In the first step, they created initial larger seed particles via miniemulsion polymerization, and in the second step, they adjusted the solid content and viscosity of the product by adding second smaller seed particles and polymerizing the two populations together.

Wu and Schork[28] compared miniemulsion and macroemulsion polymerization of three copolymerization systems. VAc/BuA, VAc/dioctyl maleate (DOM), and VAc/*N*-methylol acrylamide (NMA) were selected to be carried out via macroemulsion and miniemulsion copolymerizations in batch and semibatch processes to study the effect of water solubility and reactivity ratio. For the VAc/BuA system, the reactivity ratio of BuA is much higher than that of VAc, but the water solubilities of VAc and BuA are similar. For the VAc/DOM system, the reactivity ratios are close, but the water solubilities are very different. For the VAc/NMA system, NMA is highly water soluble and has a much higher reactivity ratio than VAc. The semibatch miniemulsion polymerization involved two stages: miniemulsion batch stage followed by semibatch stage. The batch stage was continued up to a monomer conversion of about 80%, and then the semibatch stage was started by beginning the feed of monomer emulsion (miniemulsion or macroemulsion, and separate initiator solution at set flow rates simultaneously) into the reactor. For the systems of VAc/BuA and VAc/DOM, the particle number increased with increase in conversion throughout the reaction for both macroemulsion and miniemulsion batch runs. This was taken to indicate that new particle nucleation takes place via homogeneous nucleation throughout these reactions because of the relatively high water solubility of VAc and BuA. Investigation of the copolymer composition demonstrated the important effect of monomer transport on the copolymerization. In macroemulsion polymerization, use of an extremely water-insoluble (defined as solubility $<10^{-2}$ wt.-% in water at ambient temperature) comonomer, such as DOM, resulted in preferential consumption of the more water-soluble monomer early in the polymerization due to faster transport of the more water-soluble monomer to the polymerizing particles. In contrast, the miniemulsion system tended to more closely follow the integrated Mayo Lewis equation of the bulk copolymerization, indicating less influence of mass transfer. Because of the dominating droplet nucleation mechanism, each nucleated monomer droplet could be considered as an individual reactor. Likewise, for the semibatch operation, the influence of monomer was seen in the difference between macroemulsion and miniemulsion feeds. For extremely water-insoluble monomers, the miniemulsion feed mode lessens the departure of the copolymer composition from the feed composition during semibatch polymerization. However, this is accomplished by simultaneously broadening the PSD due to the broad droplet size distribution introduced by the miniemulsion feed.

Wu et al.[29] also investigated miniemulsion and macroemulsion copolymerization of VAc and vinyl versatate (VEOVA) in batch and seeded semibatch manners. At room temperature, the water solubility of VAc is 2.58 wt.-%, and vinyl versatate is 7.5×10^{-4} wt.-%. The extreme difference in water solubility between the two monomers might effect the copolymerization, due to the different efficiencies of mass transfer in aqueous phase. For semibatch copolymerizations, polyvinyl acetate seed particles (20% of the total solid content) were produced via miniemulsion or macroemulsion polymerization, and the feed was added in four different strategies as VAc/VEOVA miniemulsion; VAc/VEOVA macroemulsion; VAc miniemulsion/neat VEOVA, and VAc macroemulsion/neat VEOVA. It was designed to investigate the effects of monomer transport and feeding strategies on the reaction rate, particles size distribution, MWD, copolymer composition, and glass transition temperature (T_g) of the resultant copolymer. As their results indicated, the particle size distributions of the final latexes were affected by the residual surfactant in the seed latex, which tended to facilitate homogeneous nucleation during the entire feeding period. The monomer feed rate determined the polymerization rate and had little effect on copolymer composition. The polymer compositions with different monomer feeding modes tended to be identical at very low feed rate. For all runs (batch and seeded semibatch), the thermal analysis of resultant polymers showed that only one glass transition temperature could be found. This corresponded to the T_g of VAc/VEOVA copolymer. Lower glass transition temperatures were found for the semibatch runs, perhaps due to slightly better VEOVA incorporation. Feeding of neat monomer or a macroemulsion of monomer to a miniemulsion did not differ substantially from the equivalent semibatch feeding into a macroemulsion. The semibatch feeding of a miniemulsion tended to cause an increase in the particle number (due to partial nucleation of the monomer droplets in the feed) and copolymer compositions that more closely followed the Mayo-Lewis equation.

Copolymerization in a Continuous Stirred-Tank Reactor

In 1986, Schuller[30] modified the Mayo-Lewis equation for predicting copolymer composition to account for the solubilities of monomers in the aqueous phase during macroemulsion polymerization. Samer and Schork[31] adopted Schuller's model and substituted a pseudo-monomer partition coefficient for the water solubility to take account of extremely water-insoluble monomers

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which could not be saturated in the polymerizing particle as Schuller assumed. They studied copolymerization of MMA and an extremely water-insoluble monomer, 2-ethylhexylacrylate (EHA, water solubility <0.01 wt.-% at room temperature) via miniemulsion and macroemulsion polymerization in a batch reactor and a single CSTR to examine emulsion polymerization kinetics for monomers of very different water solubilities. In their CSTR experiments, two separate feed streams, monomer emulsion (macro- or mini-) and initiator aqueous solution were fed at constant rates. Both the macroemulsion and miniemulsion polymerization data in CSTR showed good agreement with their modification of Schuller's model.

In Samer and Schork's study, their batch macro- or miniemulsion polymerization results suggested that batch miniemulsion copolymerization led to a more water-insoluble monomer (EHA) incorporated in the copolymer, than batch macroemulsion copolymerization did. However, the same behavior was not observed in the CSTR, although the steady state total monomer conversion increased from macroemulsion to miniemulsion. For miniemulsion polymerization, the amount of EHA incorporated in the copolymer decreased from batch reactor to CSTR. They suggested this observation could be explained by the fact that in miniemulsion polymerization in CSTR, at least a part of monomers in the feed needed to diffuse to the monomer-starved existing polymerizing particles across the aqueous phase. Hence, unlike the exclusive droplet nucleation in batch miniemulsion polymerization, which incorporates water-insoluble monomer at the locus, the CSTR miniemulsion polymerization favors the more water-soluble monomer to incorporate in the resulting copolymer. However, this does not preclude miniemulsion copolymerization in a CSTR for extremely water-insoluble monomers. In spite of the fact that the water-insoluble monomer composition in the continuous miniemulsion is less than that predicted, the composition of miniemulsion copolymer might be more uniform than the macroemulsion copolymer where the possibility of significant micelle nucleation could lead to two separate homopolymers or copolymers of various compositions.

Samer and Schork[32] also studied the role of high shear force in the continuous miniemulsion polymerization. The costabilizer (HD or PMMA in this study) alone could not be sufficient to insure predominant droplet nucleation. They revealed the possibility of utilizing mechanical homogenizer replacing bench work scale sonicator in scale-up process.

Polymerization in a Loop Reactor

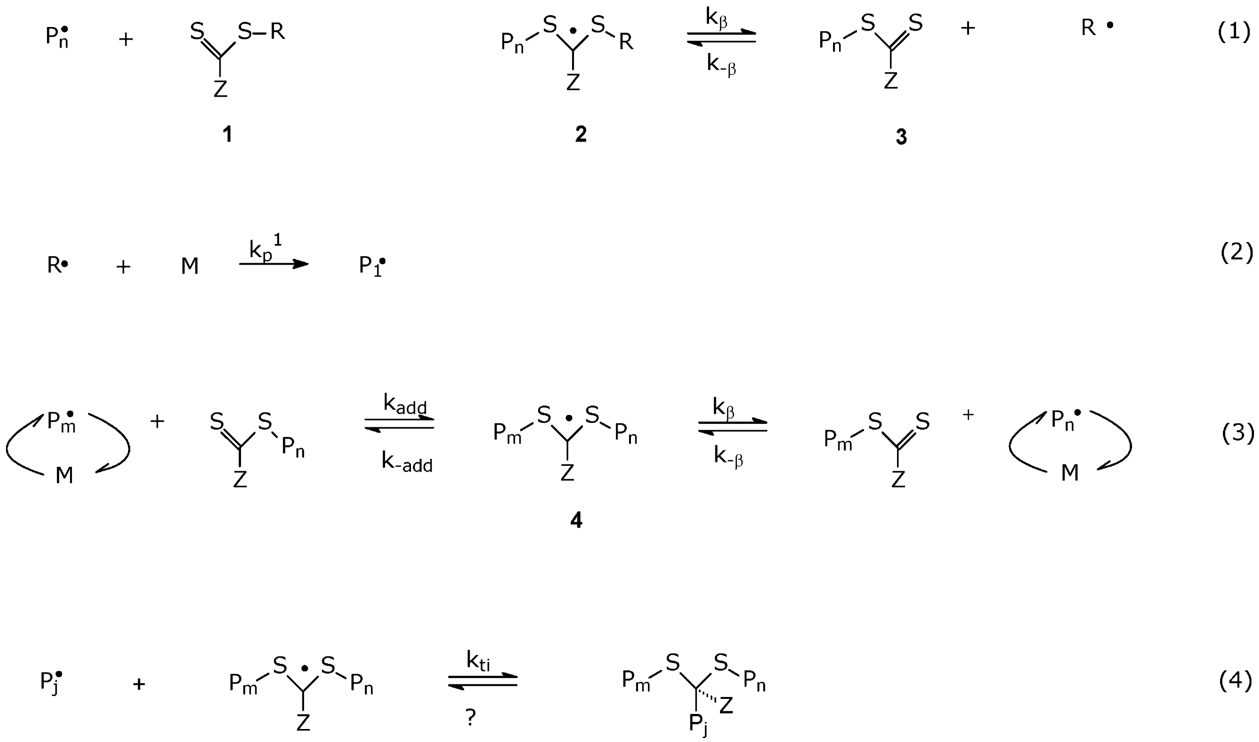
The loop reactor is a reactor system that has been used in pilot plant and small commercial applications of macroemulsion polymerization for many years. It is physically a tubular reactor with very high recycle driven by a pump. Small flows of un-polymerized emulsion are added continuously at one side of the loop, while an equal volumetric flow rate of the finished product is removed from the other. The tubular nature and the high linear velocity in the tube provide effective heat transfer. Since the monomer conversion per pass through the reactor is not large, a significant recycling rate is necessary. Under such conditions the contents of the loop can be considered to be well mixed, and the kinetics approximates that of a CSTR. González et al.[33] have used a loop reactor for the miniemulsion copolymerization of a EHA, MMA, and acrylic acid (AA) copolymer for pressure sensitive adhesives. When compared with similar macroemulsion polymerizations, the miniemulsion product was found to attain the same overall monomer conversation and higher particle number. The miniemulsion product was found to contain lower molecular weight sol fraction, and less gel. This was attributed to reduced chain transfer reaction caused by the fact that, since the miniemulsion costabilizer suppressed monomer diffusion from monomer droplets, the miniemulsion particles had a lower polymer content at the loci of the polymerization. This is in some ways similar to Samer and Schork's[31] results. Remembering that the loop reactor is essentially a CSTR, one can envision new monomer droplets in equilibrium with highly converted polymer particles. Since the miniemulsion costabilizer retards monomer transport, droplets are more likely to survive as particles (giving a higher particle number), and less converted particles are more likely to retain their monomers (giving a lower ratio of polymer to monomer at the locus of polymerization, and therefore less chain transfer to polymer).

RAFT Polymerization

Mechanism

In 1998, Moad and coworkers published a novel free radical polymerization technique[34] involving reversible addition/fragmentation chain transfer mechanism, which they designated as RAFT process. In fact this concept was stemmed from the same researchers' previous published work to produce block copolymers using methacrylate macromonomers as reversible addition/fragmentation chain transfer agents in 1995.[35] However, there was no effective RAFT agent until the invention of a more reactive double bond species, S=C(Z)SR, in their work in 1998. A brief description of the RAFT process is given below, and a schematic representation is given in Scheme 1.

A conventional free radical initiator generates radicals, which can either add to monomer or the S=C moiety of the RAFT agent **1**. In most cases, the addition of small



Scheme 1. RAFT Polymerization Mechanism.[1] (1) Addition of a propagating polymeric radical to the initial RAFT agent **1**, forming the intermediate radical **2**. The intermediate radical can either fragment into the two species it was formed by or into a dormant polymeric RAFT agent **3** and a small radical R˙. (2) The small radical initiates polymerization, forming a polymeric radical, rather than react with **3** forming back **1**. Therefore R should both be a good leaving group and capable of addition to monomer. (3) Equilibrium between propagation polymeric radicals and dormant polymeric RAFT agents. (4) Intermediate radical termination.

carbon-centered radicals to the RAFT agent is rapid and is not rate determining. Therefore, step (1) involves polymeric radical addition to **1** to form an intermediate radical species **2** that will fragment back to the original polymeric radical species or fragment to a dormant species **3** and a small radical, R˙. R˙ can further propagate to form a polymeric radical rather than adding back to **3**. The dormant polymeric species **3** acts similar to a RAFT agent, so growing polymeric radicals can also add to the dithiocarbonyl double bond of the polymeric species **3**, thereby forming an intermediate radical **4**. This intermediate has equal possibility to fragment back into its starting species or into a dormant polymeric RAFT agent and a polymeric radical, in which the dithiocarbonate moiety has been exchanged between the active and dormant polymer chains of the starting species. This equal possibility to fragment to both sides of the equilibrium is a result of the symmetry of **4**. This mechanism of the addition of radicals to the dithiocarbonyl double bond and fragmentation of the intermediate was shown by Moad and coworkers[36] who have observed the intermediate radical directly by electron paramagnetic resonance (EPR) spectroscopy.

Overall, polymer chains with a dithiocarbonate end group are formed. If addition to the dithiocarbonyl double bond is fast compared to propagation, and termination is suppressed by keeping the radical concentration low, all chains will grow in a stepwise process leading to a low polydispersity. The number of chains is determined by the amount of RAFT agents and initiators that has been consumed. Assuming termination by combination, the number of dead chains will be equal to the number of consumed initiators. The number of chains with a dithiocarbonate end group, the dormant chains, is equal to the number of consumed RAFT agents. In order to obtain a high percentage of dormant chains, the probability of termination must be much less than the probability of transfer. Usually this is achieved by keeping the initiator to RAFT agent ratio low. This criterion is especially important in the preparation of block copolymers.[37–39]

If only reactions (1)–(3) in Scheme 1 are considered, there is no reason to assume that the addition of a RAFT agent to a conventional free radical polymerization will have an effect on the polymerization rate, since the equilibrium concentration of propagating radicals will not be affected. However, it has been found that considerable retardation does take place in RAFT polymerizations.[40] Two explanations for retardation have been proposed: (i) slow fragmentation of the intermediate radical;[41] (ii) termination of the intermediate radical (reaction 4 in Scheme 1).[42]

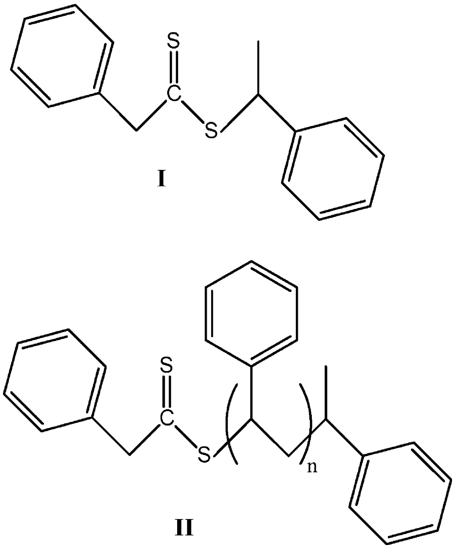
RAFT Process in Miniemulsion Polymerization

In RAFT polymerization, miniemulsion systems are often preferred over macroemulsion systems because of its monomer droplet nucleation mechanism. In 2000, Moad et al.[43] reported the synthesis of controlled polystyrene via miniemulsion using phenyl ethyl dithiobenzoate as RAFT agent in an SDS (surfactant)/CA (costabilizer) stabilized system. Molecular weight increased with conversion and the polydispersity index (PDI) went down to 1.18. No problem of reactant phase stability was reported. de Brouwer et al.[44] and Tsavalas et al.[45] on the other hand were not able to obtain stable latexes using dithiobenzoate RAFT agent in anionic or cationic surfactant stabilized miniemulsion polymerizations. They reported the phase separation as soon as the polymerization started. The separated organic phase consisted of low molecular weight polymer and monomer. However, when nonionic (polymeric) surfactants were used, stable RAFT miniemulsion polymerizations could be performed.[44] Luo et al.[46] later ascribed the phase separation phenomena to a super-swelling state, caused by the large number of oligomers formed at the beginning of the RAFT miniemulsion polymerization. Luo's study also suggested that increasing the amount of costabilizer or using nonionic polymeric surfactants could prevent super-swelling. In de Brouwer and Tsavalas' studies, stable miniemulsion polymerizations of (2-ethyl)hexyl methacrylate (EHMA), styrene, MMA, butyl methacrylate (BMA), and MA were all carried out with nonionic surfactants, namely Igepal890 or Brij98. The polydispersities of the polymers were all below 1.4 and sometimes as low as 1.1 at very high conversions. When a seed latex produced via miniemulsion polymerization was used in either a batch or semibatch RAFT polymerization with a second monomer, block copolymers with a low polydispersity and a high level of block purity were obtained.

Butté et al.[43] were able to perform miniemulsion polymerizations stabilized with SDS/HD using dithiobenzoate and ''pyrrole'' RAFT agents. Although basically the same systems were used, Butté et al. did not observe the phase separation reported earlier by de Brouwer and Tsavalas. In their study, Butté et al. used relatively a larger amount of surfactant and costabilizer. The SDS/monomer and HD/monomer weight ratios in their study were 0.017 and 0.033, and these ratios in de Brouwer's work were 0.01 and 0.01–0.025, respectively. Relatively narrow polydispersities were reported, although broader than in bulk polymerizations. This was ascribed to the presence of dead chains in the oligomer RAFT agent and difference in miniemulsion droplet sizes. The smaller droplets were nucleated first and depleted faster than the monomer, which was then replaced by that coming from larger droplets nucleated later. This led to different RAFT agent concentrations in different particles, thus causing a difference in the average molecular weight among particles and then a broadening of the MWD. Butté found that the polymerization rate of RAFT miniemulsion polymerizations was lower than that of the corresponding nonliving systems. This was supposed to be the result of the exit of the radical formed by the first exchange reaction of the RAFT agent out of the droplets. Even when oligomer RAFT agents were used, which basically should not lead to increased exit, a decrease in polymerization rate was observed, which was ascribed to the presence of monomeric RAFT agent in the oligomer mixture.

In order to prevent the phase separation often observed in macroemulsion RAFT polymerization, Vosloo et al.[48] performed SDS stabilized miniemulsion polymerizations of styrene using dithiobenzoate-end-capped styrene oligomer RAFT agents which were pre-formed in bulk. Two types of costabilizers, HD and CA and two different molecular weight oligomer RAFT agents were used. In none of the miniemulsion polymerizations, phase separation was observed. When HD and the lower molecular weight oligomer RAFT agent were used, the lower polydispersity and molecular weight closer to the theoretical value were achieved.

Lansalot et al.[49] studied the influence of the structure of RAFT agents in styrene miniemulsion polymerizations. Three RAFT agents, (1-phenylethyl)phenyldithioacetate (PEPDTA, Scheme 2), cumyldithiobenzoate (CDB), and (1-phenylethyl)dithiobenzoate (PEDB) were compared. It was shown that PEPDTA did not show retardation in bulk polymerizations, while runs with CDB and PEDB showed a large decrease in the polymerization rate with increasing RAFT agent concentration. This was ascribed to the less stable PEPDTA macro-RAFT radical. When the same RAFT agents were used in styrene miniemulsion polymerizations stabilized by SDS/HD, again the PEPDTA showed much higher polymerization rates than CDB and PEDB. However, polymerization rate was found decreased with increasing PEPDTA concentration. This was assigned to the exit of radicals formed after addition and fragmentation of the initial RAFT agent. This was confirmed by miniemulsion polymerization experiments using oligomer PEPDTA, of which the leaving radical cannot exit to the aqueous phase. In that case, using the same concentration of oligomer PEPDTA as in the experiment with monomeric PEPDTA, the polymerization rate dramatically increased to almost the same polymerization rate as without the RAFT agent.



I

II

Scheme 2. PEPDTA RAFT Control Agent.[51] **I** 1-phenylethyl phenyldithioacetate, "monomeric" RAFT. **II** "oligomeric" RAFT, obtained by oligomerization of **I** with styrene.

RAFT Miniemulsion Polymerization in CSTR

One of the drawbacks of controlled free radical polymerizations is that the product is relatively expensive, although it is to be expected that it will be much cheaper than the currently available products made by anionic or cationic polymerization, which, unlike free radical processes such as RAFT, require ultra-pure and thus expensive ingredients. One way to reduce the cost is production in continuous processes, such as CSTRs and tube reactors. Another advantage of continuous processes is that they yield a consistent product over time, once the process is running at steady state. At a first glance, the combination of controlled free radical polymerization and a CSTR is not a very logical one. Obtaining a narrow MWD has often been a primary goal in controlled free radical polymerization. However, a CSTR exhibits a RTD and will broaden the MWD. The lifetime of a growing polymer chain in a controlled process is equal to the residence time in the reactor and, therefore, some chains will reside a long time in the CSTR and some very short, which will lead to a broad MWD. For that reason the use of a single CSTR will not often be preferred. Schork and Smulders[50] showed theoretically that for an ideal controlled free radical polymerization, the MWD PDI for a single CSTR should be 2.0, and that the use of a CSTR train should reduce the polydispersity according to

$$D_{\mathrm{RTD}} = 1 + \frac{1}{n} \tag{1}$$

where D_{RTD} is the theoretical PDI predicted from the RTD and n is the number of CSTRs in series.

Smulders et al.[51] reported the controlled styrene miniemulsion polymerization, using PEPDTA as the RAFT agent, in a CSTR and a CSTR train. The reactor configuration is shown in Figure 3. He was able to demonstrate that a RAFT miniemulsion polymerization can be performed in a CSTR train, resulting in a polymer with a relatively high PDI (greater than 2) for a single CSTR. The polydispersity was decreased by increasing the number of CSTRs in the train. A slow drift, rather than a steady state was reported, even though the train was operated much longer than the time theoretically required to reach a steady state. This drift was shown to be the result of an oligomerization of the RAFT agent in the feed, leading to slowly increasing polymerization rates over time. This could be alleviated by inline production of miniemulsion of the un-polymerized monomers. Use of intentionally oligomerized RAFT agent (first discussed by Lansalot et al.[49]), resulted in higher rates of polymerization and was reported and was attributed to lower rates of radical exit from the particles. An effort was made to model the reactor as a set of independent reacting miniemulsion particles, each with a residence time drawn from the RTD of a CSTR. The effort

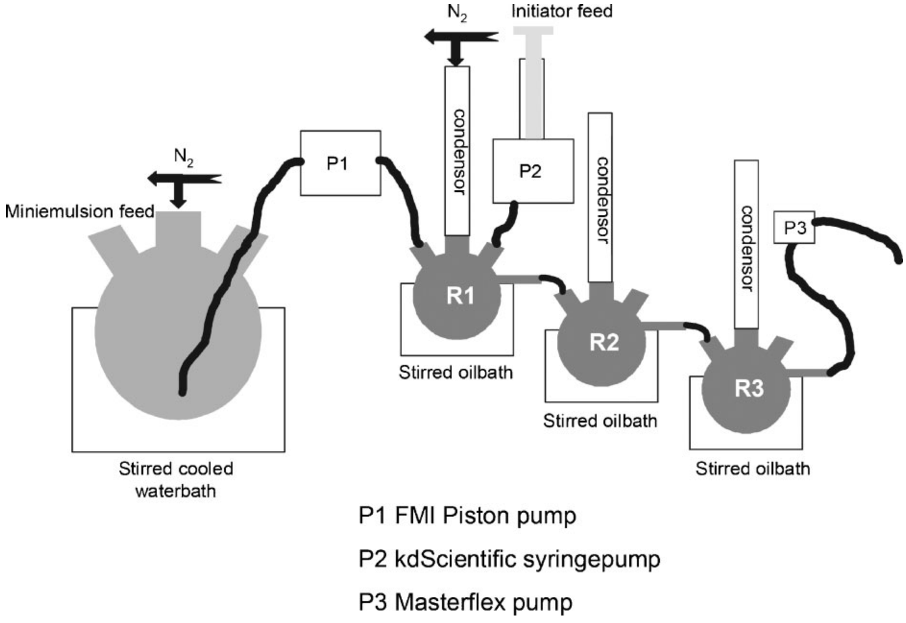


Figure 3. CSTR train for RAFT miniemulsion homopolymerization.[51]

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was only marginally successful, and reinforcing again Samer and Schork's[31] statement that significant intraparticle mass transfer takes place when miniemulsion polymerization is carried out in a CSTR. Also as reported by Samer, nucleation in the batch reactor was more effective than in the CSTR, leading to a higher particle concentration in batch. It was postulated that a portion of the miniemulsion droplets functioned as monomer reservoirs for polymerization before becoming a polymer particles, and that this fraction is larger in a CSTR than in batch. Because in a CSTR there is a large difference in the weight fraction of polymer between the particles, which creates an extra driving force for monomers in miniemulsion droplets to diffuse to polymerization loci. UV GPC data, monitoring the RAFT moiety, revealed that this was indeed the case. Chain extension experiments were carried out in which a polymer was dried, then dissolved in styrene, and polymerized. Chain extension, rather than new chain formation was observed, indicating that the chains were still "living."

Block Copolymers Via RAFT Miniemulsion Polymerization in CSTR Train

A narrow MWD is often listed as the goal of a lot of controlled free radical polymerizations. As shown above, one is limited in a single CSTR to a minimum PDI of 2. This may be reduced by using a train of CSTRs. However, it is not always a narrow MWD that makes controlled free radical polymerization attractive. Instead, the ability to produce controlled architectures such as block copolymers is often much more important. In many applications, a narrow MWD is not desirable, as nearly monodisperse polymer can be difficult for further processing. When a CSTR is operated at a steady state, the incorporation of the monomers is in accordance with their reactivity ratios, providing a constant CCD. A train of CSTRs allows the synthesis of (multi)block copolymers by feeding additional monomers in one or more of the downstream CSTRs in the train. Thus, a CSTR train will allow the synthesis of block copolymers with constant copolymer composition within each block. Smulders et al.[52] reported the RAFT miniemulsion copolymerization of styrene and BA in a train of CSTRs. The reactor configuration is shown in Figure 4. A styrene miniemulsion containing the RAFT agent, along with sodium persulfate (SPS, initiator) was introduced into reactor 1. BA, in a macro- (not mini-) emulsion, was fed into either reactor 2 or 3. A macroemulsion was used for the second feed in order to suppress any potential additional droplet nucleation caused by introducing a miniemulsion at the feed point. Steady state was approximated in all reactors, although there was some drift. Molecular weight increased from reactor to reactor, as did overall monomer conversion. However, the polydispersity was relatively broad in all cases and the polydispersity increased in the reactor in which the BA is added. This was attributed to secondary nucleation at the BA feed point, and was remedied by increasing the styrene conversion before adding the BA. When that was done, the polydispersity decreased from reactor to reactor down the train as is predicted by the theory. Monomer conversion versus number-average molecular weight is plotted in Figure 5, and the linearity of the plots indicates a great level of control. Through a combination of analyses, Smulders was able to describe the various blocks formed in the CSTR train. As shown in Table 1, significant differences among the blocks formed in the various reactors were observed, supporting the idea that a CSTR train with downstream monomer addition can

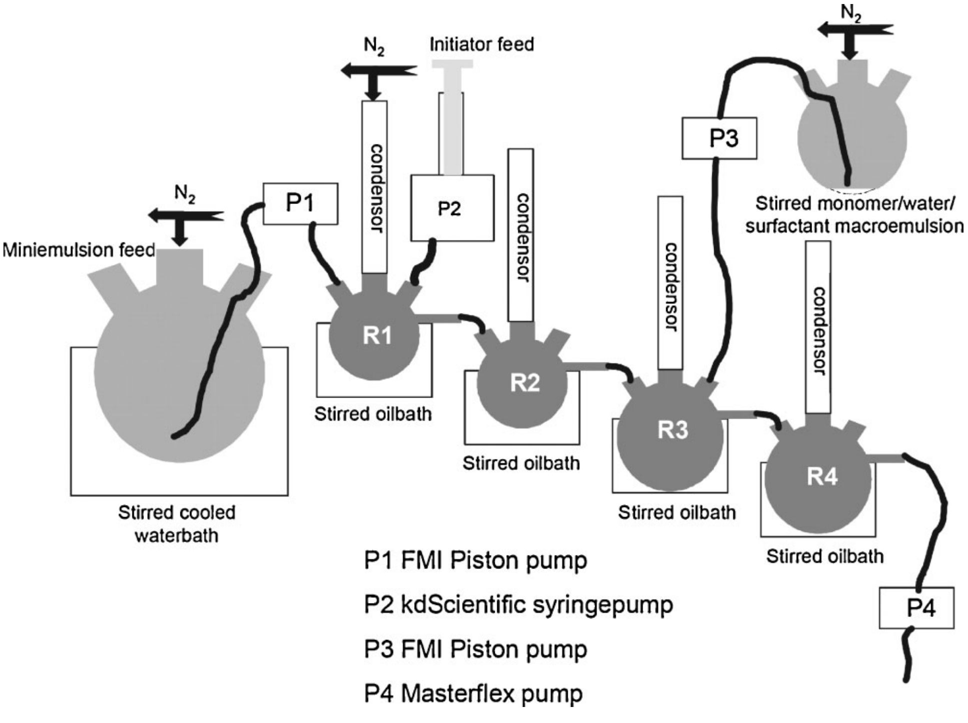

Figure 4. CSTR train for RAFT miniemulsion copolymerization.[52]

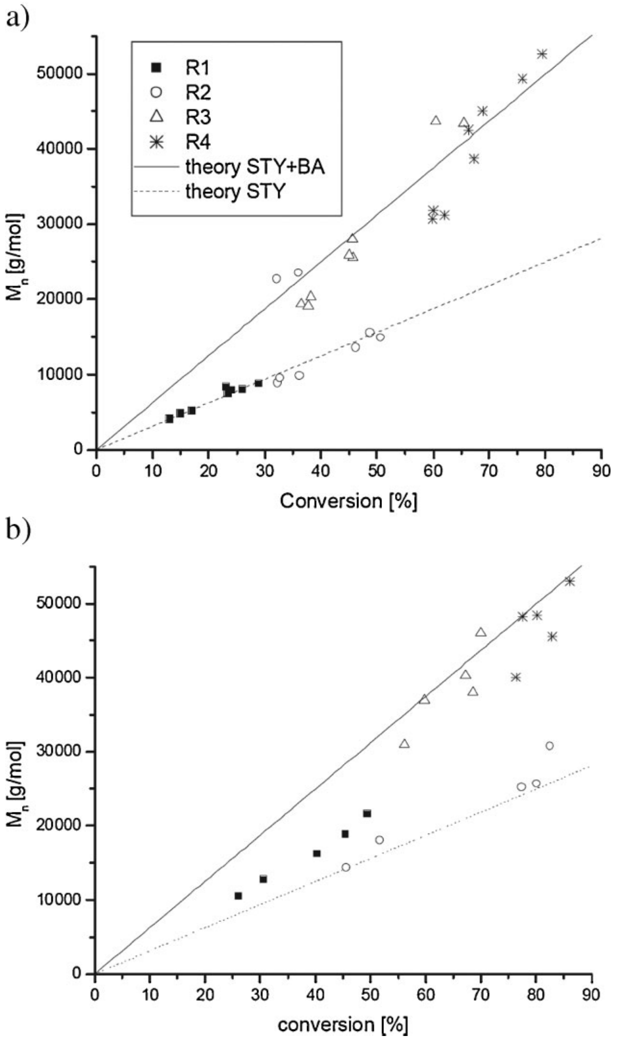

Figure 5. Number-average molecular weight versus conversion of the CSTR RAFT miniemulsion block copolymerization. The solid lines represent the theoretical molecular weights in the reactors in which the styrene and BA feed are combined, whereas the dotted lines represent the conversion in the reactors in which only styrene is present. Conversions in the reactors in which only styrene is present are, other than in the previous figures, based on only the styrene feed and, therefore, are about twice as high. (a) and (b) represents runs at different operating conditions.[52]

be used in a controlled radical polymerization to produce block copolymers with blocks that are internally homogeneous (with respect to CCD) and significantly different to the other blocks.

It is worthwhile discussing the relative intrinsic merits and disadvantages of synthesizing block copolymers via controlled miniemulsion polymerization in a CSTR train. First, the technique allows for the preparation of unique, multi-block copolymers with a constant average composition in each block, materials that cannot be made in the batch and semibatch processes that are commonly used. This is achievable due to lack of composition drift in each reactor. Thus, completely new materials can be made using this technique. The flip-side of these advantages is that the polydispersity in the length of the constant composition blocks will be large and the overall polydispersity of the MWD will also be large compared to batch (although it can be reduced by using multiple reactors). Another limitation could arise from uneven droplet nucleation. Reaction conditions have to be chosen such that the vast majority of the droplets present in reactor 1 are nucleated to limit the potential of block copolymer formation missing the first polymer block. Although the reactors can be operated under conditions that minimize this occurrence, as was done here, the RTD that is inherent in CSTRs will lead to this occurrence to some degree. Finally, this technique could limit the impact of the super-swelling phenomena that have been reported to limit some RAFT miniemulsion polymerizations in batch. Super-swelling at very early stages of the polymerization can lead to droplet instability due to the driving force for diffusion of monomer from the large number of un-nucleated droplets to the small number of droplets that contain oligomeric chains (oligomers are known to be very effective swelling agents).[46] As a few nucleated droplets absorb large amounts of monomer they eventually become unstable and phase separate into an organic layer. In contrast, in RAFT miniemulsion polymerization in a CSTR, there is a much larger number of nucleated droplets. This also leads to a driving force for diffusion of monomer from the monomer droplets to the droplets that contain polymer, although the larger concentration of polymer particles is less likely to result in super-swelling state leading to phase separation.

Qi et al.[53] studied the lack of complete steady state found in Smulders et al.'s work.[51] Two categories of factors potentially contributing to unstable transients in RAFT miniemulsion polymerization in CSTR trains were examined. Possibilities from equipment design and operation were first checked. When keeping the CSTR train under nitrogen pressure and constant concentration of initiator feed, no significant transients were observed. Possibilities related to the polymerization mechanism were then evaluated. However, such possibilities were ruled out after careful analysis. Therefore, the transients in Smulders' work were attributed to equipment design and operation (and/or impurities) rather than to mechanistic issues associated with RAFT miniemulsion polymerizations. A steady state in RAFT miniemulsion polymerization in a CSTR train was demonstrated.

Tubular Reactors

Russum et al.[54] studied RAFT miniemulsion polymerization in tubular reactors. Since the reactor volume and the

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Table 1. Composition and block lengths of the block copolymers produced in a CSTR train.[52]

		Block 1	**Block 2**	**Block 3**	**Block 4**
stage 1	reactors[a]	(R1 + R2)	(R3)	(R4)	
	STY/BA[b]	100/0	45/55	44/56	
	rel. wt[c]	1	1.11	1.20	
	block length[d]	9.9×10^3	10.4×10^3	11.5×10^3	
stage 2	reactors[a]	(R1 + R2)	(R3)	(R4)	
	STY/BA[b]	100/0	41/59	34/66	
	rel. wt[c]	1	0.92	0.95	
	block length[d]	14.9×10^3	11.0×10^3	12.9×10^3	
stage 3	reactors[a]	(R1)	(R2)	(R3)	(R4)
	STY/BA[b]	100/0	47/53	46/54	37/63
	rel. wt[c]	1	1.72	2.22	1.05
	block length[d]	8.8×10^3	14.7×10^3	19.9×10^3	9.2×10^3

[a] Reactors in which the blocks are formed; [b] Weight fraction styrene in the block/weight fraction BA in the block; [c] Relative weights of the separate blocks obtained from the mass balance, in which the weight of the first block is set to 1; [d] Block lengths as obtained from GPC ($g \cdot mol^{-1}$).

flow rate were low (resulting in laminar flow), one single tubular reactor could not be assumed as a PFR so that reactant samples could not be taken at various points along a single tube. Instead, multiple tubes were used, each with an identical flow rate, but with different lengths as shown in Figure 6. By sampling each tube simultaneously and knowing the residence time of each tube, a plot of conversion versus residence time (or tube length) could be obtained. Figure 7 shows an overlay of the conversion/time curves for batch and tubular reactors with identical recipes. The almost perfect overlay indicates that the kinetics in the tubes is approximately as same as batch reactors. However, the polydispersities from tubular reactor polymerization were consistently higher than

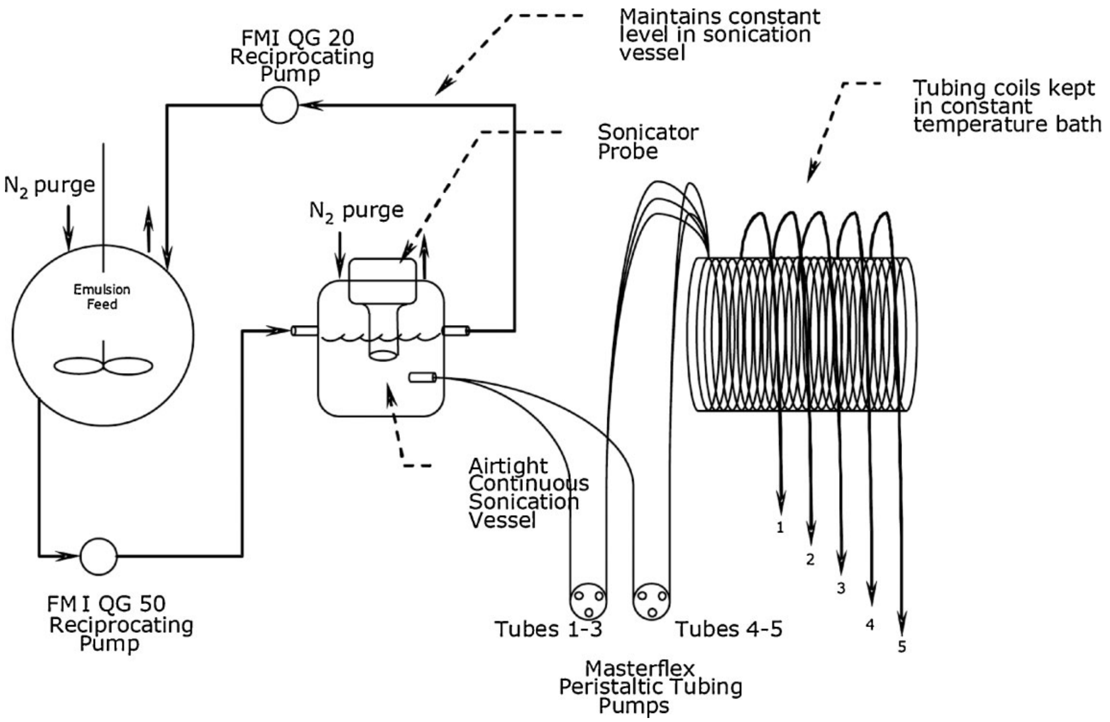

Figure 6. Configuration of the tubular reactor for RAFT continuous miniemulsion polymerization.[54]

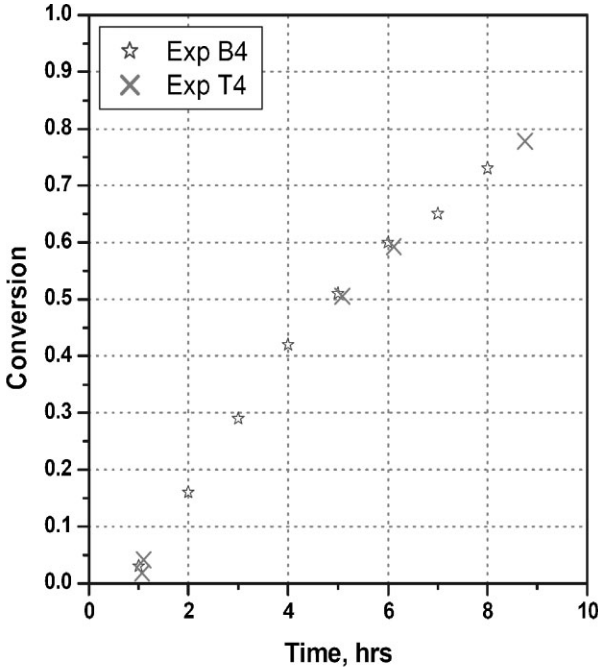

Figure 7. Conversion versus time curves for batch and tubular reactors.

those from the batch, likely owing to back-mixing or axial dispersion causing a broader RTD of the latex particles in the tubes. As typical of miniemulsions, the particle size evolution was flat. Visual inspection of the clear tubing after the experiment revealed no fouling at the conversion reached in this study (approximately 65%).

In a subsequent paper, Russum et al.[55] further investigated RAFT miniemulsion polymerization in the tubular reactors described above. It was demonstrated that a 1:1 molar ratio SDS/Triton X-405 surfactant system provided excellent stability of the styrene RAFT miniemulsions, in both tube and batch, with no visible latex separation or coagulum. The RAFT agent PEPDTA was found to work reasonably well in miniemulsion with styrene. Experiments in the continuous tubular reaction system revealed similar kinetics to batch. However, under the same experimental conditions, reaction in the tube reactor consistently progressed at a slightly faster polymerization rate. As shown in Figure 8, the linearity of the number-average molecular weight with monomer conversion indicates a high degree of livingness. 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 ruled out based on the calculations of initiator decomposition. Small differences in the particle size could cause the discrepancy, and cannot be ruled out. The polydispersity of the polymer produced in the tube reactor was consistently higher than that produced in concurrent batch experiments, which suggested that axial dispersion played a contributing role.

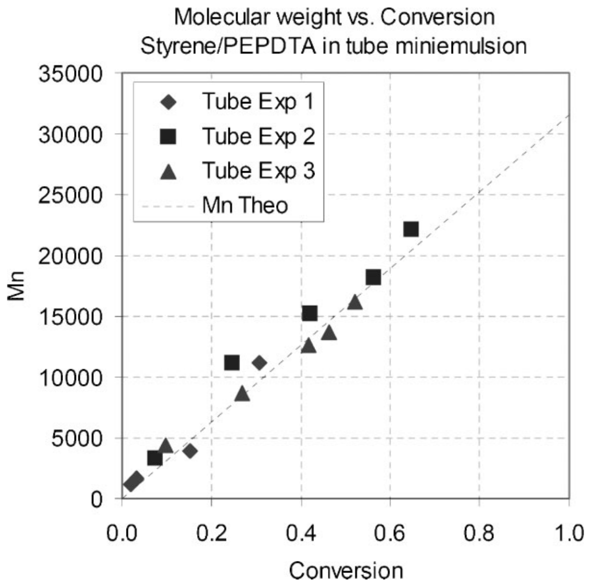

Figure 8. Number-average molecular weight of polymers produced via the styrene/PEPDTA RAFT miniemulsion as a function of conversion.[55]

An underlying population of nongrowing chains which served to broaden the MWD was identified in both batch and tube RAFT miniemulsion polymerizations. 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. 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*-BuA), opening the possibility of employing this system in the production of block copolymers.

The tubular reactors in Russum's studies are lack of plug flow characteristic and it affects the RTD, and consequently, the polydispersity. Russum et al.[56] investigated the flow characteristics of the tubular reactor using a modified dye tracer approach. It was shown that by utilizing an oil-soluble dye, the droplet/particle flow behavior of a miniemulsion could be quantified. Dye tests performed in normal flow at low Reynolds numbers revealed that the reactor was not operating in laminar flow and that the axial dispersion was quite high. RAFT miniemulsion polymerizations conducted in this regime were compared to batch, and the polymer formed was shown to have higher polydispersity than polymer formed in batch. Dye tests carried out in isolated plug flow (obtained by separating plugs of miniemulsion with plugs of nitrogen) demonstrated the near-ideal nature of the

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flow regime. Polymer formed by RAFT miniemulsion polymerizations in this regime was shown to have similar polydispersity as that formed in batch. Taken together this establishes a direct relationship between the RTD and final polydispersity of the polymer formed in a controlled radical miniemulsion polymerization.

Nitroxide-Mediated Radical Polymerization

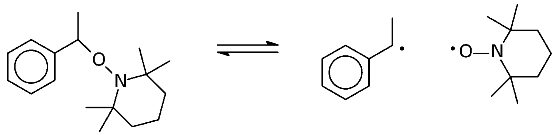
Mechanism

The work of Georges et al.[57] clearly demonstrated the possibilities of nitroxide-mediated controlled radical polymerization (NMP). In processes based on reversible termination, a species is added which prevents bimolecular termination by reversible coupling. In NMP this species is a nitroxide. The mechanism of NMP is based on the reversible activation of dormant polymer chains (P_n-T) as shown in Scheme 3. This additional reaction step in the free radical polymerization provides the living character and controls the MWD. When a dormant species or alkoxyamine dissociates homolytically, a carbon-centered radical and a stable nitroxide radical are formed (Scheme 4). This is a reversible process and at high enough temperatures where dissociation is competitive, the polymeric radicals (Pn $^{\cdot}$) can add to monomer, which allows stepwise growth of the polymer chains.

NMP can be started using an alkoxyamine as an initiator such that, ideally, no other reactions than reversible activation of dormant species and addition of monomer to carbon-centered radicals take place. Upon decomposition of the alkoxyamine in the presence of monomer, polymeric dormant species will form and grow in chain length over time. Otherwise, polymerization can be started using a conventional free radical initiator and a nitroxide. The alkoxyamine will then be formed in situ, when an initiator molecule decomposes and, after adding a monomer unit or two, is being trapped by a nitroxide. Since the nitroxide and the carbon-centered radical diffuse away from each other, termination by combination or disproportionation of two carbon-centered radicals cannot be excluded. This will lead to the formation of dead polymer chains and an excess of free nitroxide. The accumulation of free nitroxide is referred to as the persistent radical effect[58] and slows down the polymerization, since it will favor trapping (radical-radical coupling) over propagation.

$$P_n\!-\!T \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} P_n^{\bullet} + T^{\bullet}$$

Scheme 3. Reversible activation of dormant polymer chains.



Scheme 4. Dissociation of a typical alkoxyamine into a carbon-centered radical (ethylbenzene radical) and a nitroxide (TEMPO)

As with RAFT, NMP will benefit from the segregation effects inherent in a miniemulsion polymerization.

Miniemulsion NMP in Tubular Reactors

Although there are numerous reports of miniemulsion NMP in batch reactors, there is only one report of this reaction carried out in a tubular reactor. Enright et al.[59] reported miniemulsion NMP in a tubular reactor, after forming oligomeric control agent in a batch step. In order to get favorable results with the TEMPO control agent, the reaction was carried out under pressure at 135 °C. Both the tubular polymerizations and batch polymerizations with the same recipe resulted in stable latexes with minimal coagulum. Reaction rates were similar for the two reactors, but the monomer conversion was slightly lower for the tubular reactor. This was attributed to some level of axial mixing in the tube. Conversion versus number-average molecular weight plots indicated good control for both reactors. The PDI remained below 1.5, but unlike Russum et al.'s study,[54] these authors did not see any discernable difference in PDI between the batch and tubular reactors. The slight differences between the RAFT and NMP tubular systems (higher than batch PDI for RAFT; lower than batch conversion for NMP) might be explained by the size and materials of the tubes. The tubing used by Enright et al. was stainless steel and had an inside diameter very close to 1/16 inch and Russum used perfluoroalkoxy (PFA) tubes with inside diameter of 1/16 inch. So it is more likely that any differences in RTD would have to be attributed to differences in Reynolds number due to differences in fluid velocity profile. Chain extension experiments confirmed the living nature of the NMP polymer.

Concluding Remarks

Continuous Stirred-Tank Reactors

CSTRs have very different kinetic behavior than batch or tubular reactors. In general, a single CSTR will give a much lower monomer conversion than a tubular reactor of the same volume. Adding CSTRs in series gives the reactor train an RTD more similar to that of a PFR. (CSTR trains containing five or more reactors approximate PFR behavior.) In free radical miniemulsion polymerization, the

MWD is a weak function of RTD, so the increase in the MWD polydispersity over a batch reactor is not significant. However, if monomer transport between fresh droplets and partially converted particles (or between particles in the reactor and particles in the feed) is significant, a broadening of the PSD can occur, causing a secondary broadening of the MWD. In the case of copolymerization, the CSTR will, by its nature give a constant CCD, with no composition drift. This is less significant in a CSTR train with more of a PFR nature. If the two (or more) monomers in a copolymerization are of markedly different water solubilities, transport of the more hydrophilic monomer for the lower conversion particles in the feed to the higher conversion particles in the reactor can cause a heterogeneous comonomer composition, and hence a broad CCD. In the extreme, this could result in each monomer forming homopolymers in their respective particles.

In the case of controlled radical polymerization in continuous reactor, the polydispersity of the MWD will mirror that of the RTD. For a single CSTR, the theoretical PDI of the RTD is 2.0, so the minimum PDI of the MWD is 2.0, rather than 1.0 as for batch or tubular reactors. CSTR trains narrow the RTD, and hence the MWD. In the case of copolymerization with intermediate feed, monomer transport can cause broadening of the CCD as described above. Monomer transport can result in droplets that could not be nucleated and behaves as monomer reservoirs, trapping the hydrophobic control agent. Since this trapped control agent is not at the locus of polymerization, the molecular weight will be higher than theoretically predicted, or control may be lost all together, resulting in free radical polymerization.

Tubular Reactors

Tubular reactors approximate the kinetics of batch reactors; therefore it is not surprising that free radical miniemulsion polymerization in tubular reactors can be accurately described by batch kinetics where reaction time is replaced by residence time in the reactor. A tubular reactor carrying out a copolymerization will have the same copolymer composition drift as a batch reactor unless there is intermediate feed of one or more of the monomers. This is functionally equivalent to a semibatch reactor. Although studies have not been done on tubular miniemulsion free radical polymerization with intermediate feed, it is safe to conclude that all of the issues found in CSTR polymerization would come into play. These include secondary nucleation of polymer particles at or near the feed point, and/or significant redistribution of monomer between existing particles and the monomer droplets being introduced. Slight variations in RTD due to imperfect plug flow should not cause significant broadening of the MWD since the time interval between terminations is many orders of magnitude less than the reactor residence time. A tubular reactor could be envisioned as a nucleation reactor upstream of a CSTR train as has been done in conventional emulsion polymerization. This might be an important consideration, since in order to get the full benefits of miniemulsion polymerization, it is necessary to nucleate a large fraction of the initial monomer droplets. A tubular reactor might also be used as a finishing reactor at the end of a CSTR train. In this case an additional initiator would be added at the inlet to the tube, or the reaction temperature in the tube would be set to a high value in order to consume the residual monomer. One significant advantage of a tubular reactor is the high surface to volume ratio that provides a very efficient heat transfer. A loop reactor could be envisioned to exploit the heat transfer capabilities (however, the RTD and kinetic of the loop reactor approximate those of a CSTR, not a PFR).

In a truly living polymerization, the molecular weight is a direct function of the residence time. In a PFR which has, by definition, a flat velocity profile and hence a monodisperse RTD, the MWD should have a PDI between 1.5 and 2.0 as in a batch reactor. Any polydispersity in the RTD should result in a polydispersity of the MWD. This was seen by Russum in RAFT polymerization in a tubular reactor,[54,55] but was not seen by Enright in NMP.[59] The CCD can be manipulated in controlled radical polymerization by intermediate feed as with free radical polymerization. Of course, with controlled radical polymerization, one can much more closely approach true block copolymers. It is especially important to suppress secondary nucleation or inter-particle monomer transport, since these phenomena can result in populations of particles containing no control agent. Particles without control agent will polymerize via a free radical mechanism, causing a broad or even bimodal MWD. Similar to CSTR, monomer transport in tubular reactor can result in particle or droplets as monomer reservoirs that were eventually depleted of monomers, retaining only the hydrophobic control agent. Since this trapped control agent is not at the locus of polymerization, free radical polymerization may take place. If the two commoners have substantially different water solubilities, the more hydrophobic monomer may be transported to the more highly converted particles, causing a broadening of the CCD.

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Keywords: continuous reactor; miniemulsion; radical polymerisation; RAFT

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