Continuous RAFT Miniemulsion Polymerization of Styrene in a Train of CSTRs

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Reversible addition fragmentation transfer (RAFT) miniemulsion polymerization of styrene in a train of continuous stirred tank reactors (CSTRs) is described. It is observed that the polydispersity of the polymer decreases as the number of CSTRs in the train increases, as has been derived theoretically. Furthermore, the CSTRs do not reach steady state, which has been attributed to, at least in part, slow oligomerization of monomer and capping by RAFT agent in the feed. Particle nucleation in a CSTR is found to be less effective than in a batch reactor. This is attributed to a "dry-out" mechanism, which is observed to be more significant in a CSTR than in batch, leading to a "nongrowing" population of dormant chains. Experimental evidence for the presence of this "nongrowing" population is also provided. © 2005 American Institute of Chemical Engineers *AIChE J,* 51: 1009–1021, 2005

Keywords: miniemulsion, reversible addition fragmentation chain transfer (RAFT), continuous stirred-tank reactor (CSTR), controlled/living polymerization

Introduction

Over the last several years, living/controlled radical polymerization has allowed the synthesis of well-defined polymers, such as block copolymers in robust radical polymerization systems[1]. One of the most versatile of these new techniques is reversible addition-fragmentation transfer (RAFT) polymerization[2], Figure 1.

RAFT polymerizations are controlled because of the presence of a rapid exchange reaction that is driven by a RAFT agent with a leaving (R) group that cleaves homolytically very easily. The result is a high rate of reinitiation of dormant radicals, which in turn leads to a constant number of chains during the polymerization. Provided the exchange reaction is much faster than propagation (that is, the transfer constant is high), all the chains will grow at essentially the same rate. Typically, there is no preference for the direction of fragmentation because the intermediate species is symmetric. As such, the equilibrium constant for the reaction as a whole is unity. The effectiveness of the RAFT agent depends on its transfer constant, which is determined by the nature of the Z and R groups. The most common are the dithioester compounds (shown in Figure 1), where R is a free-radical leaving group capable of reinitiating the polymerization and Z is a group that modifies the activity of the RAFT agent. Because the RAFT agent is always an integral part of a growing polymer chain, when bimolecular terminations occur, there is no buildup of the free control agent as is seen in atom transfer radical polymerization (ATRP), and nitroxide-mediated radical polymerization (NMRP). However, since RAFT involves free-radical intermediates, bimolecular terminations of chains formed from initiator-derived radicals will ultimately occur to some extent, forming dead polymer. To achieve the narrow molecular-weight distributions characteristic of living polymerizations, the initiator concentration, and, therefore, the number of initiator-derived chains, is usually minimized.

RAFT can also be applied with emulsion/miniemulsion polymerization techniques, which offer many advantages over homogeneous polymerization systems, including higher production rates due to segregation of radicals, an easy to handle product due to its low viscosity at high polymer contents and a "green" product consisting of polymer particles dispersed in

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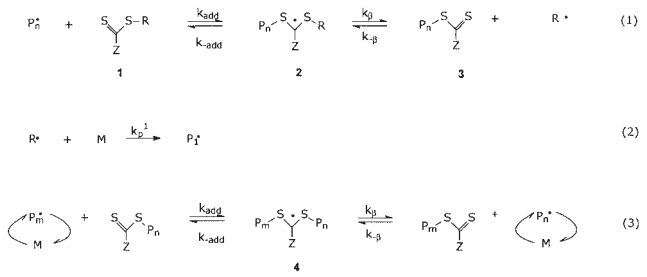

Figure 1. RAFT polymerization.

(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 from which it was formed 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 to recreate 1, and (3) Equilibrium between propagation polymeric radicals and dormant polymeric RAFT agents.

water and, thus, low in VOCs. Due to the hydrophobicity of most RAFT agents, miniemulsion polymerization has proven to be the most easily applicable emulsion polymerization technique[1,3-4], although successful applications of RAFT in seeded,[5,6] and *ab initio* systems[7] have also been reported.

One of the drawbacks of living free-radical polymerizations is that the product is relatively expensive, although it is to be expected that it may be less costly than the currently available well-defined polymers 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 costs is through production in continuous processes, such as in continuous stirred-tank reactors (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. So far, the reports in the literature about living radical polymerization concern primarily batch and semi-batch processes and little has been reported on living radical polymerization in a continuous process [8]. Here we focus on the application of RAFT miniemulsion polymerization in a CSTR and train of CSTRs, although recently we have also reported the use of RAFT miniemulsion polymerization in tube reactors[9,10]. Another publication is dedicated to the use of RAFT miniemulsion polymerization in a CSTR train for the production block copolymers.[11]

The combination of living free-radical polymerization and a CSTR is, at first glance, not a very logical one. After all, obtaining a narrow molecular weight distribution (MWD) has often be a primary goal of academic studies of living free-radical polymerization. However, a CSTR exhibits a residence-time distribution (RTD), and this will likely have a large effect (broadening) on the MWD. The lifetime of a growing/dormant polymer chain in a living process is equal to the residence time in the reactor and, therefore, some chains will reside in the reactor a long time and others a very short time, which will lead to a broad MWD. For that reason, the use of a single CSTR will not often be preferred. In a previous article we theoretically derived that for an ideal living polymerization, the use of a train of CSTRs should reduce the polydispersity[12]. Here we test if this hypothesis is actually valid for a RAFT miniemulsion system. The results of styrene RAFT miniemulsion polymerizations in a train of 3 CSTRs are reported. These results are then compared to what is theoretically expected if a miniemulsion polymerization performed in a CSTR train could simply be considered as a large collection of very small batch reactors (the monomer droplets/polymer particles) with different residence times. In order to make this comparison, the results of a separately performed batch miniemulsion polymerization have to be integrated over the RTD. First, some theoretical background on residence-time distributions in CSTRs, and the impact on living polymerizations is provided.

Residence-time distributions in CSTR trains

The residence-time distribution function for a train of n CSTRs is given by[13]

$$E(\theta') = \frac{(n)^n}{(n-1)!}(\theta')^{n-1}e^{-n\theta'} \tag{1}$$

in which θ' is the dimensionless residence time t/τ. τ is the average residence time and is defined as V/Q, the ratio of the volume of the reactor V and the volumetric flow rate Q. In a previous publication,[12] we have shown that the polydispersity of the residence-time distribution (1) can be expressed as

$$D_{\mathrm{RTD}} = 1 + \frac{1}{n} \tag{2}$$

In an "ideal" living polymerization, in which there is a linear relationship between time and degree of polymerization, DP (that is, DP=constant · t with a polydispersity of 1), Eq. 2 will also be valid for the polydispersity of the chain length distribution of the polymer produced in the CSTR train, indicating that the MWD will narrow with increasing the number of CSTRs in the train.

In practice, however, "ideal" systems do not exist and, therefore, it is not likely that a RAFT miniemulsion polymerization performed in a CSTR train will obey the "ideal" profile predicted by Eq. 2. As will be shown later, the polymer produced in such systems in batch does not have a polydispersity of 1, and the relationship between degree of polymerization and time is not a linear one, at least not into infinity. However, the results of a batch experiment performed under the same conditions as used in the CSTR train give the relationship between residence time and conversion, molecular weight and polydispersity, assuming that the number of particles that are nucleated in batch and the CSTR is the same, and that the initiator concentration does not change significantly with time. According to the method used in the work of Samer et al.[14], it can be calculated that indeed the number of particles in a CSTR is expected to be the same as in batch in the system used here. Since the temperature used in this work is 70°C and sodium persulfate is used as the initiator, it can also be calculated that with the residence times used here, the initiator concentration stays relatively constant. Therefore, integration of the realistic relations between time, conversion, M_n and polydispersity obtained from a batch experiment over the RTD of the CSTR train can be used to obtain the data to be expected from the CSTR train, assuming the CSTR train behaves like a large collection of individual batch reactors with different

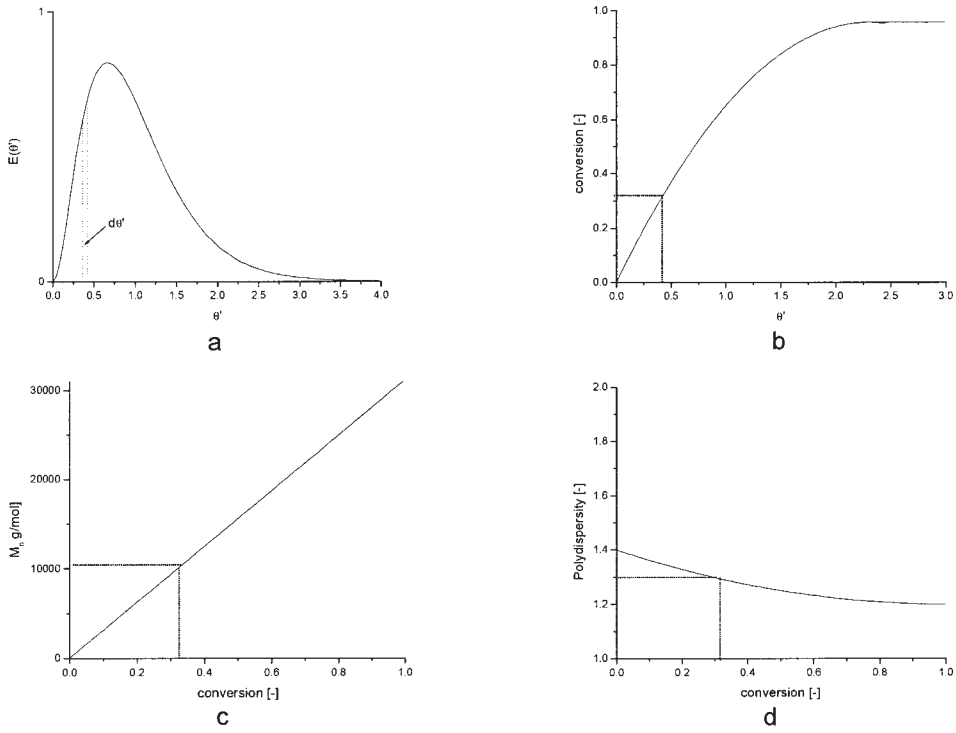

Figure 2. Illustration of integration of data obtained from batch experiments over the RTD of a CSTR train.

(a) Residence-time distribution for 3 CSTRs in series, (b) conversion vs. dimensionless residence time θ', (c) Mn vs. conversion, and (d) polydispersity vs. conversion. The RTD gives the distribution of residence times of the individual droplets/particles, whereas the batch data give the conversion, Mn and polydispersity for a particle/droplet with a certain residence time, so integration over the whole residence time would give the outcome of a CSTR train miniemulsion polymerization, provided that each particle can be considered as an individual batch reactor.

residence times. This is illustrated in Figure 2, and by a following set of equations.

Figure 2a shows the RTD of a train of three CSTRs. Since a RAFT miniemulsion polymerization is a segregated system, the RTD gives you the residence time distribution of miniemulsion droplets or particles. Figures 2b, 2c and 2d show the conversion as a function of the dimensionless residence time in the batch experiment x (θ'), the relation between M_n and conversion M_n (x), and the relation between polydispersity (PD) and conversion $PD(x)$, respectively. As conversion is solely a function of θ', $M_n(x)$ and $PD(x)$, can also be expressed as M_n (θ') and $PD(\theta')$, respectively.

Using this information from the batch experiment and integrating it over the RTD, the following can now be derived for the conversion, M_n, M_w and PD in a CSTR train

$$x_{\mathrm{CSTR}} = \int_0^\infty E(\theta')x(\theta')d\theta' \tag{3}$$

$$M_{n,\mathrm{CSTR}} = \frac{\int_0^\infty E(\theta')x(\theta')d\theta'}{\int_0^\infty \dfrac{E(\theta')x(\theta')}{M_n(\theta')}d\theta'} \tag{4}$$

$$M_{w,\mathrm{CSTR}} = \frac{\int_0^\infty M_n(\theta')\mathrm{PD}(\theta')E(\theta')x(\theta')d\theta'}{\int_0^\infty E(\theta')x(\theta')d\theta'} \tag{5}$$

$$\mathrm{PD}_{\mathrm{CSTR}} = \frac{M_{w,\mathrm{CSTR}}}{M_{n,\mathrm{CSTR}}} \tag{6}$$

Experimental

Materials

Inhibitor in styrene (J.T.Baker) was removed using Aldrich Inhibitor remover for *tert*-butylcatechol. Hexadecane (Aldrich, 99%), sodium persulfate (Aldrich, 98+%), and sodium dodecyl sulfate (ICN Biomedicals, Ultra pure) were used as received. De-ionized water was used in all cases. The RAFT agent, 1-phenylethyl phenyldithioacetate (**I**, Figure 3), was synthesized according to literature procedures[15], using the following materials without further purification: Carbon tetrachloride (Aldrich, 99.9%), benzyl chloride (J.T.Baker, 99.9%), carbon disulfide (J. T.Baker, 99.9%), magnesium turnings (Lancaster, 99+%), methanol (J.T.Baker, 100.0%), ethyl ether (Fischer, certified A.C.S., anhydrous), and *p*-toluene sulfonic acid monohydrate (Aldrich, 98%). The RAFT agent was characterized by ^{1}H NMR, and no evidence of impurities was observed.

Oligomeric RAFT agent was prepared by heating styrene (57.4 g), RAFT **I** (5.0 g) and AIBN (0.15 g) for 5 h at 70 °C under nitrogen. Conversion reached 14%, and the oligomers were recovered by precipitation in cold (approximately 18 °C) methanol, followed by filtration and washing with cold methanol. According to end-group analysis by ^{1}H NMR, M_n is 802

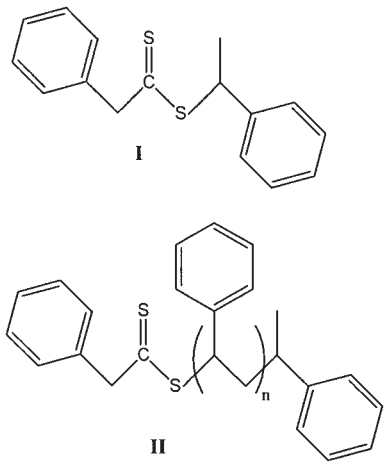

Figure 3. I, 1-phenylethyl phenyldithioacetate, in the text also referred to as "monomeric" RAFT; II "oligomeric" RAFT, obtained by oligomerization of I with styrene.

g/mol, whereas GPC gives an M_n of 649 g/mol. A second batch was prepared the same way, resulting in oligomers with an M_n of 706 g/mol (NMR) and 558 g/mol (GPC), respectively.

CSTR train setup

The CSTR train is shown in Figure 4. The train, including the miniemulsion feed, was kept under a nitrogen atmosphere. The miniemulsion, consisting of water, surfactant, monomer, hydrophobe (hexadecane) and RAFT agent was fed from a stirred and cooled (using an ice-bath or a Fischer Scientific Isotemp 3016 cooler) 3L flask into reactor 1 (R1) using a FMI valveless piston pump (P1). The initiator solution was fed separately using a kdScientific syringe pump (P2). The CSTRs are 50 mL 3-neck round-bottom flasks with an overflow weir, which maintains the CSTR volume at approximately 40 mL, helped by nitrogen pressure in R1 and gravity forces as shown in Figure 4. All CSTRs were equipped with a condenser, with the condenser of R1 under nitrogen pressure. The CSTRs are heated using an oil bath on IKA Works Ceramag Midi hotplates, stirred at speed 5 with magnetic stirrer bars and controlled by IKA® ETS-D4 Fuzzy temperature controllers. The temperatures in the oil-baths were at 72°C to maintain a temperature of 70°C inside the CSTRs. In order to prevent introduction of oxygen into the system, the overflow weir in R3 was equipped with a Masterflex® pump, operated at a flow higher than the flow rate of the combined feeds.

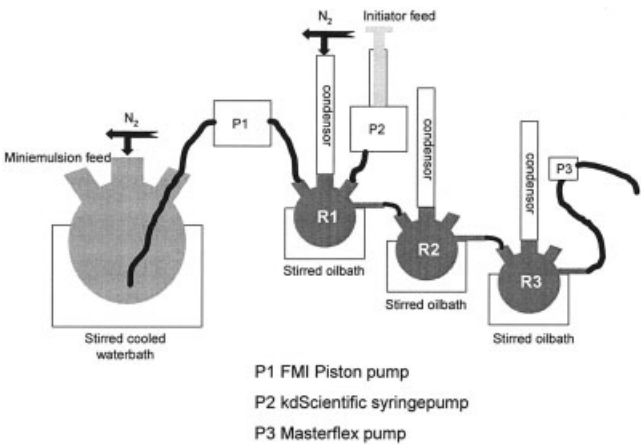

Figure 4. Optimized CSTR train.

Experiments were started after the CSTRs and miniemulsion feed were kept under nitrogen for about 1 h. The CSTRs were filled with miniemulsion and initiator solution (same mass ratio as the mass flow ratio at which pumps P1 and P2 will be operated during the experiment) and pumps P1 and P2 were started.

Samples (approximately 0.6 mL) from the feed and CSTRs were taken through a rubber septum using a 1-mL syringe. Samples were quenched in glass vials, coated on the inside with hydroquinone. Vials were coated on the inside by drying 1 or 2 droplets of hydroquinone dissolved in acetone. Conversion was determined by gravimetry and the same samples were subsequently used for GPC. Separate samples were taken for particle size analysis.

Miniemulsion preparation, polymerization conditions and recipe

The miniemulsion was prepared by adding a mixture of styrene, hexadecane (hydrophobe) and RAFT agent to a mixture of sodium dodecyl sulfate and deionized water. The mixture was then homogenized for 7 min using a Virtis Cyclone I.Q.[2] at 10,000 rpm. After that, the emulsion was sonicated via a Fischer Model 30 Sonic Dismembrator operated at 70% power output for approximately 2 h, while being cooled in an ice-bath. The initiator solution was prepared by dissolving sodium persulfate in water.

In all experiments the monomer/water mass ratio was ~0.25, and the monomer to RAFT molar ratio was ~300. The SDS concentration was ~0.018 M based on water, 2.3 wt % hexadecane was used based on the amount of monomer, and the initiator concentration was ~2 mM based on water. In Table 1 a typical recipe with corresponding flow rates is shown.

GPC

The dried polymer was dissolved in tetrahydrofuran (THF, J. T. Baker) and filtered through a 0.2 μm syringe filter. GPC analyses were carried out using three columns (American Polymer Standards styrene-divinylbenzene 100 Å, 1,000 Å, and 10^5 Å) mounted in a Waters WAT038040 column heater set at 30 °C. The columns were connected to a Viscotek™ GPCMax pump/autoinjector, a Waters 410 refractive index detector, a LDC Milton Roy Spectromonitor 3000 UV detector (at 311 nm), and calibrated against 10 narrow polystyrene standards

Table 1. Typical Recipe and Flow Rates for a RAFT Miniemulsion Polymerization Performed in a Train of CSTR's

Miniemulsion Feed		Initiator Feed	
Water	1182.2 g	Water	200.3 g
SDS	6.62 g	SPS	2.41 g
Styrene	294.2 g		
Hexadecane	6.91 g		
RAFT I	2.52 g		
Flow Rate	0.35 mL/min	Flow Rate	0.804 mL/h

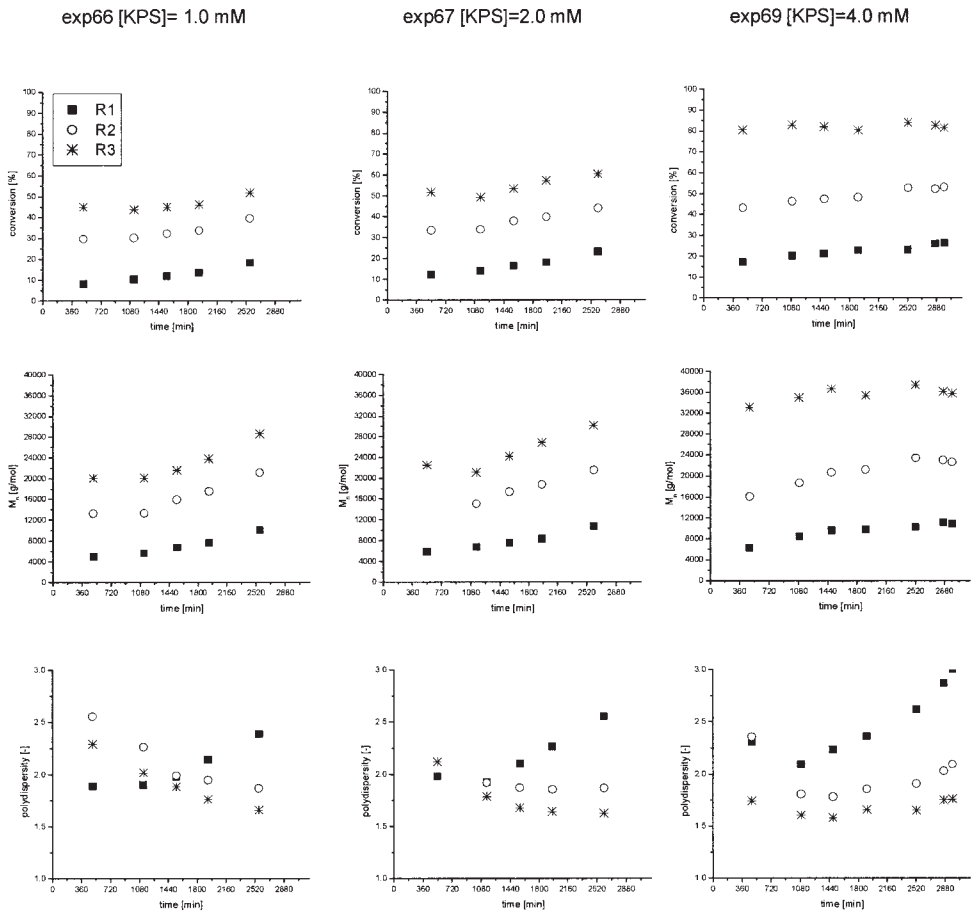

Figure 5. Conversion, Mn and polydispersity vs. time for a styrene miniemulsion polymerization at 70°C in a CSTR train with a potassium persulfate concentration of 1 mM (exp66), 2 mM(exp67) and 4 mM(exp69), respectively.

The average residence time is 106 min per reactor. The feed in these experiments was cooled with ice and the initiator was not fed separately, as it was already present in the feed.

(Polymer Laboratories; M_n = 580–200K, M_w/M_n = 1.02–1.16). THF was used as the eluent at a flow rate of 1 mL/min, and the injection volume was 100 μL.

Particle Size Analysis

Particle sizes were determined using quasi-elastic light scattering (QELS, Protein Solutions DynaPro99 with DynaPro DCS v 5.26 software). The radius reported is the mass average radius. For the calculation of particle numbers, a volume average radius is required. Since the software does not provide a volume average radius, the mass average radius was used as an estimate of the volume average radius.

Results and Discussion

Optimization of the experimental setup

Initially, the CSTR train miniemulsion polymerizations were performed by using a miniemulsion in which all ingredients, thus, also the initiator, were combined into the feed and the feed was kept at room-temperature and under a nitrogen atmosphere. In this case a large increase in conversion over time in the reactors was observed. Using an initiator concentration of 1 mM, it was found that after 15 h (the system should be at steady state by then, since the average residence time was only about 90 min per reactor) the conversion in R1, R2 and R3 was 32%, 53%, and 61%, respectively, while after 29 h conversion had increased to 46%, 81 and 84%, respectively. The feed was also monitored for conversion and it was found that polymerization of the feed was responsible for this large increase in conversions. At about t=17 h, the feed contained a measurable amount of oligomers, reaching 25% conversion at 40 h.

To prevent polymerization of the feed, an experiment was performed in which the feed was not kept under a nitrogen atmosphere but under normal air. Since the feed was fed only very slowly into R1, it was expected that retardation/inhibition due to the small amount of oxygen that is introduced this way would be minimal. When the results of this experiment were compared to the results of an experiment with the same recipe in which the feed was kept under nitrogen, it was found that conversions were much lower as a result of the oxygen introduced. The experiment in which the feed was kept under air reached conversion of 7%, 27%, and 39% after 19 h in R1, R2 and R3, respectively, whereas the experiment in which the feed was kept under nitrogen reached 28%, 55 and 67% after the

same time in R1, R2, and R3, respectively. This means that the feed cannot be kept under air because this will cause significant retardation/inhibition, while keeping it under nitrogen will cause polymerization of the feed. Hence, to prevent polymerization of the feed, the feed has to be kept cool or the initiator has to be fed in separately into the reactor. Therefore, first a series of polymerizations of styrene utilizing a train of three CSTRs with varying initiator concentration were performed. In these experiments, all ingredients were combined and the feed was cooled with ice. Later, two experiments in which the feed was cooled with ice and the initiator was fed separately using a syringe pump were performed.

In Figure 5 the results of the experiments with the combined cooled feed at various initiator concentrations are shown. The average residence time was 106 min per reactor. The conversion time profiles are increasing with time at all 3 initiator concentrations, while the conversion of the feed, which was monitored gravimetrically, was less than 1% after 48 h. Since conversion is increasing with time, also an increase with time for M_n is observed. The polydispersity on the other hand showed different trends. The polydispersity increased with time in R1 although it decreased in R2 and R3, although in the experiment with the highest initiator concentration the polydispersity in R2 and R3 increased again toward the end. For R1, however, the polydispersity might not be very accurate as M_n is generally low in R1. Since in R1 the residence time distribution is also broad, it means there will be a lot of very low-molecular-weight material $<$ 500 g/mol, which cannot be accurately quantified by the GPC because it starts to overlap with the RAFT agent and hexadecane peaks in the GPC trace, as will be discussed later. Therefore, the GPC trace has to be cut off without taking the lowest molecular weight species into account, while including some overlap from the initial RAFT peak. This could lead to a deviation from the true polydispersity and M_n at low levels of monomer conversion. For the lowest initiator concentration, initially the polydispersity is even below the theoretical limit of 2 for a single CSTR in R1, which is another indication that the polydispersity obtained from these low-molecular-weight samples might in reality be higher.

Another important observation can be made looking at the polydispersity profiles. Assuming it takes 4 residence times to reach steady state, which means $4 \times 3 \times 106$ min $= 1272$ min for R3, it can be seen from Figure 5 that beyond this point, in all 3 experiments the polydispersity in R3 is lower than in R2, and the polydispersity in R2 is lower than in R1. This shows that the concept of narrowing the MWD of the polymer by putting CSTRs in series works. In R3 the polydispersity is around 1.7. However, a real steady state is never reached and, therefore, in the next two experiments, the initiator was fed separately into R1 using a syringe pump, so no initiator was present in the miniemulsion feed anymore. It was hypothesized that this change would eliminate polymerization or oligomerization in the feed.

Figure 6 shows the results of two experiments in which the feed was cooled with ice and the initiator was fed into R1 separately using a syringe-pump. In one case [SPS] was 2.8 mM and τ was 128 min per reactor, whereas in the other experiment, [SPS] was 1.8 mM and τ was 90 min per reactor. The trends are similar to those seen in Figure 6, although less pronounced. Conversion and M_n are still increasing in time,

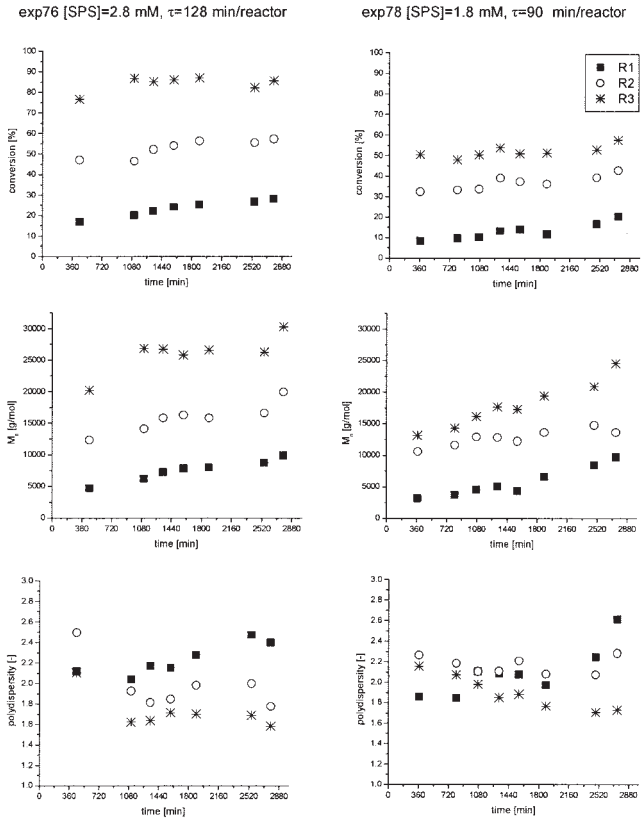

Figure 6. Conversion, Mn and polydispersity vs. time for a styrene miniemulsion polymerization at 70°C in a CSTR train.

The sodium persulfate concentration 2.8 mM(exp76) and 1.8 mM(exp78), respectively, and was fed separately using a syringe pump. The average residence time is 128 and 90 min per reactor, respectively. The miniemulsion feed in these experiments was cooled with ice.

although relatively less than in Figure 5, and again, at times when all three reactors should be at steady state, the polydispersity decreases with increasing CSTR number, although in the second experiment the polydispersities in R1 and R2 are close. Again, the conversion in the miniemulsion feed was always less than 1%. However, since we did not reach a steady state, while the temperature was constant in all three vessels, the initiator feed was constant and the miniemulsion flow rate was constant, the only plausible explanation left was a slow change in the miniemulsion feed itself. Possible changes in the feed include slow degradation of the RAFT agent or slow oligomerization of the feed followed by capping by RAFT agent, resulting in "oligomeric RAFT agent." Another possible change, destabilization of the droplets is less likely, since (a) it was not observed by the eye, and (b) it would lead to a decrease in polymerization rate and, thus, a decrease in conversion, whereas an increase was observed.

Both degradation of the RAFT agent and formation of oligomeric RAFT agent, however, will lead to increasing polymerization rates and, thus, increasing conversions and M_n's. After all, both degradation of RAFT and oligomerization of RAFT will lead to a decreased radical exit rate from the droplets. Degradation will lead to less transfer events and oligomerization will lead to an increased hydrophobicity of the

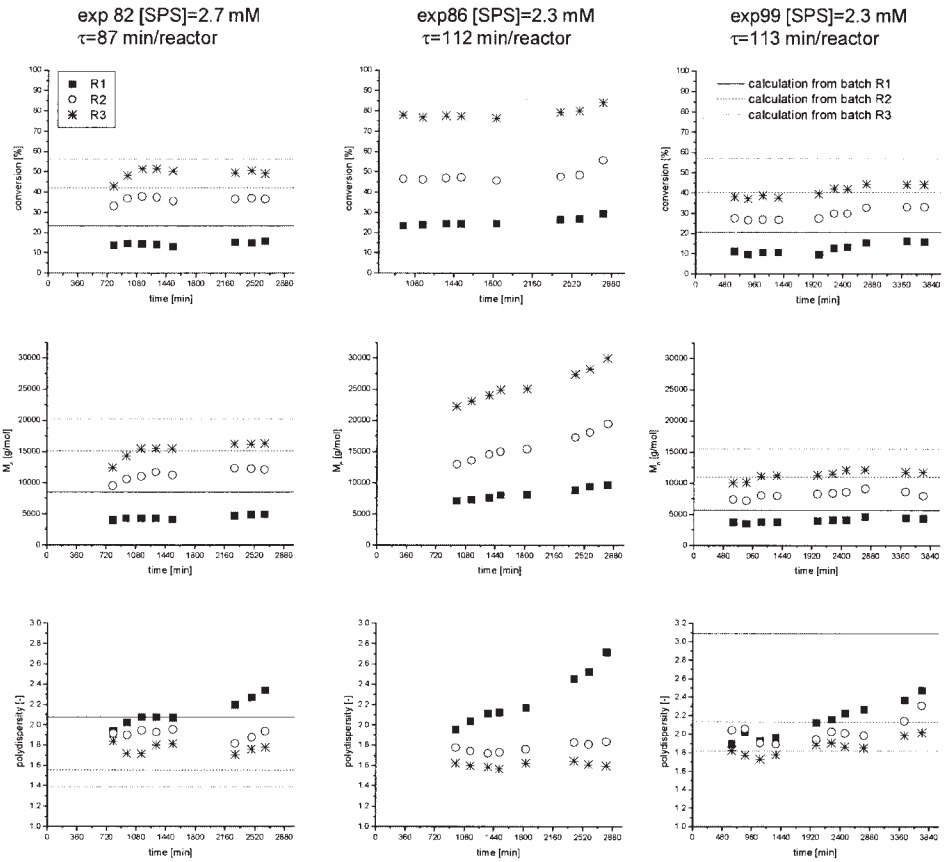

Figure 7. Conversion, Mn and polydispersity vs. time for a styrene miniemulsion polymerization at 70°C in a CSTR train.

The sodium persulfate concentrations are 2.7 mM(exp82), 2.3 mM(exp86) and 2.3 mM(exp99), respectively, and was fed separately using a syringe pump. The average residence time is 87, 112 and 113 min per reactor, respectively. The droplet size in the third experiment was larger than in the second experiment. The miniemulsion feed in these experiments was cooled with a chiller at a constant temperature of 9°C. Solid and dotted lines show the projected performance of the CSTR series if the miniemulsion can be treated as large collection of small batch reactors with different residence times, as noted in the text.

RAFT agent's leaving group and, thus, a decreased desorption rate. Some RAFT agents are known to slowly degrade under the influence of light[16]. However, these experiments were performed in a fume hood with the lights off most of the time, the miniemulsion was kept in a nontransparent ice-bath and the miniemulsion itself is not transparent, so the RAFT agent is not exposed to much light. Therefore, degradation is the less likely of the two possible explanations, although it cannot be conclusively ruled out. To further minimize any oligomerization of the feed, in the next experiments the feed was cooled in a water-bath, which was held at a constant temperature of about 9°C using a chiller. It was expected that this would reduce the possible oligomerization even more than an ice-bath, because the use of an ice-bath could not prevent the miniemulsion feed from warming up overnight to about 15–20 °C. Furthermore, in the following experiments the feed was monitored both gravimetrically and by GPC to check for oligomerization.

Figure 7 shows the results of three styrene miniemulsion polymerizations in a train of three CSTRs in which the initiator was fed separately and the miniemulsion feed was cooled to a constant temperature of 9°C. In these 3 experiments, the initiator concentration was about the same, and the residence time and the size of the miniemulsion droplets was varied. Compared to the results shown in Figure 6, the data in Figure 7 illustrate that when the miniemulsion feed is cooled at a constant temperature, the conversion-time profiles are even more flat than when the miniemulsion is cooled with ice, although conversion is still slightly increasing over time. Also M_n is still increasing in time, which is related to the increase in conversion, although in exp86 M_n in R2 and R3 increases relatively more than the conversion. The polydispersity profiles are similar to those shown in Figures 5 and 6, with an increasing polydispersity in R1 and either flat or decreasing polydispersities in R2 and R3 with sometimes an increase toward the end. Again, the results show that indeed the polydispersity decreases with increasing the number of CSTRs in the train. Although this confirms the theoretical analysis described in ref. 11, the reason why no steady state is observed remains an important issue. Therefore, in the next section a detailed analysis of the GPC data of both the produced polymer and the feed over time is examined.

GPC of the Miniemulsion Feed

Since steady state is not achieved in the CSTR train, while all flows and temperatures are constant and the experiments run for a much longer time than would be required to reach steady state, changes over time in the feed seem to be the most

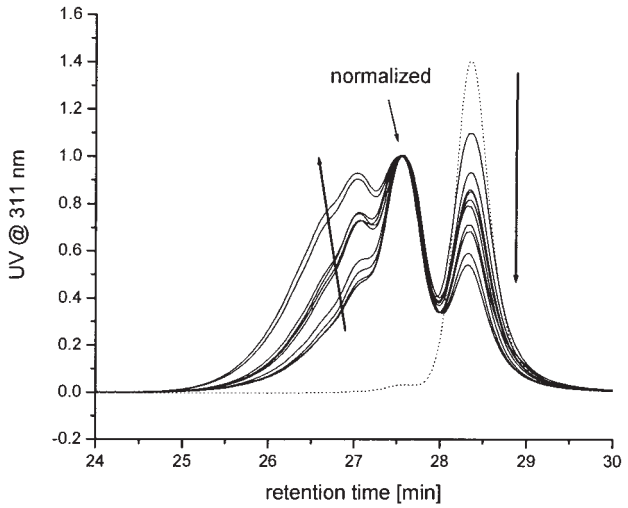

Figure 8. GPC traces from the miniemulsion feed tank over time, obtained from the UV detector, operated at 311 nm in order to monitor the RAFT moiety.

The dotted line represents the feed just after sonification, whereas the solid lines show the traces between 11 and 62 h in the N2 protected and cooled at 9°C miniemulsion feed tank.

plausible explanation. Since the miniemulsion feed in all experiments was monitored gravimetrically, and conversion of the feed was found to be smaller than 1% in all cases, formation of high polymer in the feed can be ruled out as the cause for the increasing conversions and molecular weights observed. It was already rationalized in the previous section that considering the possibilities left (that is, RAFT degradation, formation of oligomeric RAFT agents and miniemulsion instability), formation of oligomeric RAFT species is the most likely to occur.

Because the RAFT agent used here is very reactive (transfer constant ~130 [4]), if radicals are formed in the feed, the radicals cannot add many monomer units before undergoing a transfer reaction with a RAFT agent. This forms an oligomeric RAFT agent and a small radical, which, after adding a few monomer units, will transfer again. Hence, this implies that all RAFT agent molecules slowly could add 1 monomer unit to their leaving group, while this would likely not be observed by gravimetry. After all, since the monomer to RAFT ratio is 300 in these experiments, the addition of 1 monomer unit per RAFT molecule would only give 0.33% conversion of the feed. Indeed, it has recently been reported that a related RAFT agent adds one monomer unit to every RAFT molecule before further polymerization proceeds[17]. A single monomer unit can make the RAFT leaving group much more hydrophobic, leading to a decreased exit rate and increasing polymerization rate and, thus, increasing conversions and molecular weights over time. Therefore, in subsequent experiments, the feed was also monitored by GPC in order to detect changes in the feed.

Figure 8 shows the GPC data of the miniemulsion feed in exp99, although in all experiments in which the feed was monitored by GPC, comparable results were obtained. The data shown represent the UV traces, obtained from the UV detector operated at 311 nm, which detects the RAFT moiety[6], whereas the other ingredients in the feed are invisible at this wavelength. Hence, this signal gives the number distribution of the RAFT agent. The dotted trace in Figure 8 shows that just after sonification, basically all the RAFT agent is still present as **I** (Figure 3), which also indicates that the RAFT agent is not significantly degraded by the high energy of sonification. Figure 8, however, indicates that over time, the RAFT agent in the feed is transformed into a mixture of **I** and oligomerized monomer capped by RAFT, **II** (see Figure 3) with mainly $n=1$, 2 and 3. The elution times of the oligomers correspond to their molar masses, since the lowest molecular weight polystyrene standard, $M_p = 580$, elutes at 26.3 min, and the oligomers with $n = 1$ (MW = 376), n = 2 (MW = 480) and n = 3 (584) elute at approximately 27.5, 27.0 and 26.5 min, respectively. The first sample was taken from the feed tank, which was cooled at 9°C and kept under N_2, after 11 h and shows that already more than half of the RAFT agent **I** has been oligomerized into **II** with mainly n = 1 and some n = 2, whereas this process slowly progresses over time, decreasing the amount of **I** and increasing the amount of **II**. Over time the average number of monomer units in the oligomers **II** also gradually increases. These results show that indeed the composition in the feed is changing and that this change is likely to be responsible for the absence of a steady state in the CSTR train. It is expected that especially the disappearance of **I** will increase the polymerization rate, because the leaving groups of **II** are all very water-insoluble, even with n = 1, so these will all have a very low probability for droplet exit. To test the hypothesis that transformation of **I** into **II** is indeed responsible for an increase in polymerization rate, the results of two experiments, one in which **I** was used and one in which **II** was used as the RAFT agent, are compared in the next section.

The oligomerization of the feed might also explain why such a large increase in the polydispersity in R1 over time is observed. The low-molecular-weight tail of the polymer formed in R1 overlaps with the high-molecular-weight tail of the RAFT/RAFT oligomers from the feed and with increasing oligomerization in the feed, this overlap increases, which might explain the large increase in polydispersity over time.

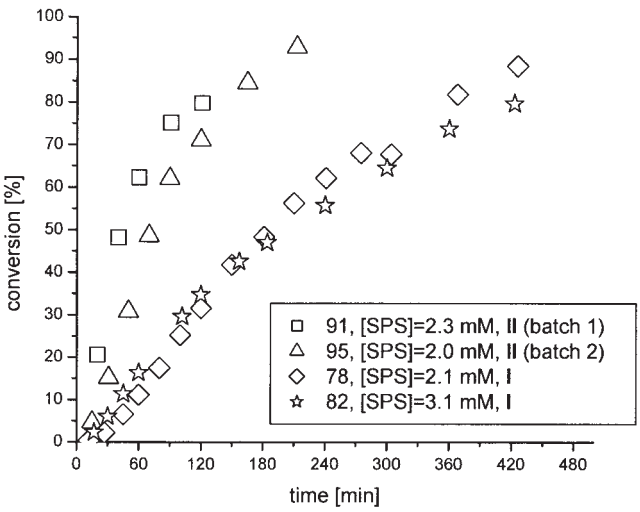

Figure 9. Conversion-time profiles for a series of batch styrene miniemulsion polymerizations at 70°C using both oligomeric RAFT, II, and monomeric RAFT agent I.

Table 2. Exit Rate Coefficients of Batch Miniemulsion Polymerizations of Styrene at 70°C Using Both I and II. For the Calculation, Limit 1 Zero-One Kinetics are Assumed[18]

	$dx/dt \times 10^5$ $[s^{-1}]$[a]	r_m [nm][b]	$N_c \times 10^{17}$ $[dm^{-3}]$[c]	$\bar{n}$ [−][d]	$\rho_{initiator}$ $[s^{-1}]$[e]	k $[s^{-1}]$[f]
exp91	17.2	42.1	7.20	0.084	0.015	0.15
exp95	13.8	59.0	2.65	0.185	0.038	0.13
exp78	5.35	71.7	1.48	0.129	0.069	0.40
exp82	5.73	73.0	1.37	0.146	0.091	0.44

(a) The initial slope at low fractional conversions.
(b) Extrapolated mass average particle ratio. The mass average radius was the closest estimate we had available for the volume average diameter, which is required to calculate the particle number. To obtain an estimate for the actual droplet size, the measured value was extrapolated to 100% conversion, and it is assumed that at the dilution required to measure the particle size, all residual monomer in the particles will be stripped. The extrapolated value is obtained by multiplying the measured value by $(1/x)^{1/3}$, where x is the fractional monomer conversion.
(c) The particle number is calculated using the extrapolated mass average particle radius and the recipe, which gives the amount of water and monomer.
(d) $\bar{n}$ is calculated using the conversion equation[18], using a k_p of 500 L mol^{-1} s^{-1}[20] and C_p is 7.7 M, the monomer concentration in the droplets around 10% conversion, the conversion around which the rate of polymerization was determined.
(e) The entry rate coefficient was estimated according to Gilbert using the following parameters[19]: a k_d of 2.3×10^{-5} s^{-1}[21], a $k_{t,aq}$ of 1×10^9 L mol^{-1} s^{-1}, a $k_{p,aq}$ of 750 L mol^{-1} s^{-1}, a C_w of 4.3 mM and a z of 2.5.
(f) The exit rate coefficient, k, was calculated using $\bar{n}$ and $\rho_{initiator}$ assuming Limit 1[19] zero-one conditions. Limit 1 was assumed because of the high radical flux at 70°C, which should result in aqueous phase termination of most exiting radicals. k is then given by $\rho_{initiator}(1 - 2\bar{n})/\bar{n}$.

Does oligomerization of the feed lead to increased polymerization rates?

Lansalot et al.[4] have shown that the use of oligomeric RAFT agents with the same RAFT moiety as used in this work in miniemulsion polymerization, drastically increased the polymerization rate compared to the "monomeric" equivalent. They used an oligomeric RAFT agent with a relatively high-molecular-weight ($M_n = 2080$) compared to the oligomers we found to be present in our feed tank. However, this should not make a significant difference, since both have a water-insoluble leaving group, so both should have a drastically decreased probability of exit from the droplets. Furthermore, Lansalot et al. used different temperatures, initiator concentrations and surfactant levels from this work. Here, the differences in rate using lower molecular weight oligomers are presented. These oligomers were synthesized (see experimental section) by bulk polymerization in styrene using a high RAFT to AIBN ratio, in order to minimize the formation of dead chains. The oligomers had an M_n around 700 g/mol. Here, the results of a batch polymerization using **I** are compared to the results of a batch polymerization using these oligomers as the RAFT agent. Furthermore, the results of a continuous polymerization in the CSTR train using these oligomers are presented. Since the RAFT agent present in the feed is oligomeric from the start, conversion and M_n are not expected to increase with time, once steady state is reached.

Figure 9 shows the results of a series of batch miniemulsion polymerizations at 70°C in which oligomeric RAFT **II** was used, and the results were compared to batch experiments in which RAFT **I** was used. It can be seen that the polymerization rates in the experiments in which oligomeric RAFT was used are much higher. However, it has to be noted that the final particle size in the experiments with the oligomers was much smaller, even though the miniemulsions were prepared using the same procedure, recipe and scale. So either the oligomers are effective costabilizers[18], which results in a smaller droplet size, or the oligomers enhance nucleation, so more of the initial droplets are being nucleated. Both effects will lead to a smaller particle size. Because the number of particles is not the same in these experiments, looking at the rate of polymerization will not disclose whether or not the rate of polymerization would also be higher if the number of particles was the same in all experiments. However, from the rate of polymerization and the particle size, the average number of radicals per particle $\bar{n}$, can be calculated. Assuming zero-one kinetics, and using a simple analytical estimation for the entry rate coefficient, the exit rate can than be calculated from $\bar{n}$ and the entry rate[19]. The results of these calculations are shown in Table 2.

The data in Table 2 shows that indeed the estimated exit rate coefficient in the experiments in which oligomeric RAFT agents are being used is much smaller than the exit rate coefficient in which **I** was used. This also suggests that when the particle sizes and initiator concentration in all experiments are the same, the experiments with oligomeric RAFT would be faster because of the smaller exit rate coefficient. From these results it is clear that oligomerization in the miniemulsion feed could lead to faster kinetics and it is likely that the increase in time we observe in the CSTR train is indeed at least partially attributable to oligomerization in the feed tank.

The previous results also suggest that when oligomeric RAFT agent **II** is used in a CSTR train instead of monomeric RAFT agent **I,** conversion should no longer increase with time. Figure 10 shows the results of an experiment with the CSTR train in which **II** (batch 2) was used as the RAFT agent, using the same miniemulsion as was used for exp95 in Figure 9.

The data presented in Figure 9 illustrated that the polymerization rate in this system is much higher than for the systems in which **I** was used and, therefore, the average residence time per CSTR was shortened to 40.4 min by increasing the flow rate. Figure 10 shows that the profiles have a different shape than the ones shown in Figures 5, 6 and 7, in which **I** had been used. Where Figures 5-7 show increasing or nearly flat profiles, Figure 7 shows profiles that appear to be oscillating, although this would be very unlikely for a miniemulsion system[22]. However, the CSTR train has to be operated for a much longer time to see if this is truly the case, which would require large amounts of **II** because of the high flow rate that was used to avoid starved-feed conditions. This could be a subject of a future publication. Although a CSTR train using **II** also does not lead to a true steady state, the use of oligomeric RAFT results in experiments that no longer show constantly increasing conversions, M_n's and polydispersities. Another observation that can be made is that the polydispersity when **II** is used is much higher than when **I** is used. This is a result of the

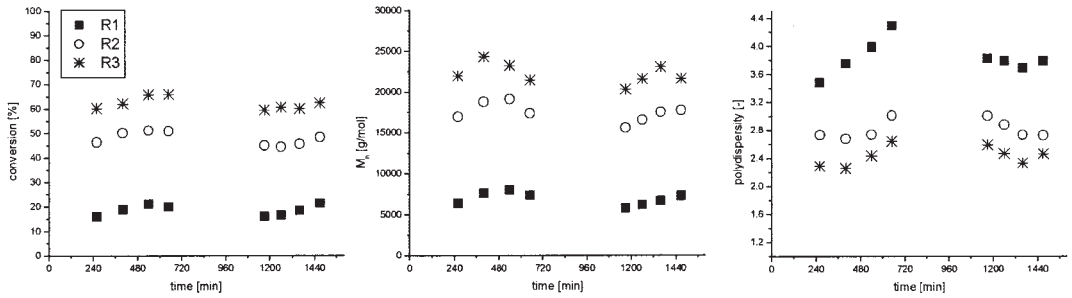

Figure 10. Conversion, Mn and polydispersity vs. time for a miniemulsion polymerization of styrene at 70°C in a 3 CSTR train using oligomeric RAFT agent II (exp95).

overlapping GPC traces of polymer formed and unreacted oligomers, which will always be present because of the RTD. This gives a population of particles that does not have enough time to grow to a length at which its GPC trace is completely separated from the GPC trace of the starting oligomers.

Using the same approach as used for Table 2, also the exit rate coefficients for a CSTR train using RAFT **II** can be calculated. The results, in which exp86 (Figure 7) and exp95 (Figure 10) are compared, are shown in Table 3.

Table 3 shows that the use of oligomeric RAFT in a CSTR train leads to smaller exit rate coefficients. However, the large decrease in the exit rate coefficient in exp95 going from R1 to R2 is unexpected, whereas for exp86 a decrease in the exit rate coefficient is expected, since in R1 more "monomeric" RAFT will be present than in R2. In exp95 the exit rate was expected to stay relatively constant because in all reactors the RAFT moiety is attached to a water-insoluble leaving group. These data suggest that the oligomeric RAFT used in exp95 still contained some "monomeric" RAFT, which is being used up in R1 after which the exit rate coefficient is much lower in R2.

Projection of batch polymerization to a CSTR train

If a miniemulsion could be considered as large collection of small batch reactors, the results from a batch miniemulsion polymerization can be used to calculate the outcome of a CSTR train, using the RTD of the train. The theory behind this has been presented in the Introduction. To carry out these calculations, the batch experiments were performed using miniemulsion taken from the feed tank of the CSTR experiment, such that the data obtained from the batch experiment would represent exactly the miniemulsion used in the CSTR train. The conversion time data of a batch experiment typically have to be fitted using 3 regions (1, 2, 3 in Figure 11): a linear fit to account for the short induction time[1] often observed, a second-order polynomial fit thereafter, and a constant conversion that was assumed after a long enough time. M_n vs. conversion could be fitted linearly, and the polydispersity vs. time can be fitted using a second-order polynomial. As an illustration, Figure 11 shows the fitted data of the batch experiment in exp99. It has to be noted that the *x*-axis of the conversion vs. dimensionless residence time fit of the batch experiment will change if the first, second and third CSTR in the train are being considered, since θ' (R1) = 2 θ' (R2) = 3 θ' (R3).

Assuming that a miniemulsion behaves like a large collection of small batch reactors, the data fits from Figure 11 and Eqs. 1 and 3–6 will give the outcome of a CSTR train experiment. In Figure 7, the outcomes of these calculations are plotted as solid lines for one CSTR, dashed lines for two

[1] Induction, inhibition and rate retardation in RAFT polymerization are topics of active research in several groups. Standardization of the above terms is necessary to allow for facile communication between all parties. We propose to use:
Retardation: A reduction in rate of polymerization. A mechanistic cause is not implied in this definition.
Induction: A delay in the onset of polymerization. A mechanistic cause is not implied in this definition.
Inhibition: A delay in the onset of polymerization caused by the presence of an inhibitor.
Initialization: A delay in the onset of polymerization (or at least a change in the rate of polymerization caused by the tendency of all RAFT moieties to add one monomer unit before any add more) [16]. If monomeric RAFT is not picked up easily in the conversion measurement, this may look like induction.

Table 3. Exit Rate Coefficients of CSTR Train Miniemulsion Polymerizations of Styrene at 70°C Using Both I (exp86) and II (exp95)

	$dx/dt \times 10^5$ [s^{-1}][a]	r_m [nm]	$N_c \times 10^{17}$ [dm^{-3}]	$\bar{n}$ [−][b]	$\rho_{initiator}$ [s^{-1}][c]	k [s^{-1}][d]
exp95 R1	7.4	57.9	2.80	0.091	0.035	0.32
exp95 R2	12.0	61.8	2.31	0.310	0.041	0.051
exp95 R3	5.94	60.2	2.49	0.187	0.037	0.12
exp86 R1	3.48	82.3	1.12	0.128	0.097	0.52
exp86 R2	3.40	81.3	1.16	0.175	0.080	0.30
exp86 R3	4.70	82.8	1.10	0.161	0.078	0.33

a. dx/dt for a CSTR is calculated as follows: $(x_{out} - x_{in})/\tau$.
b. $\bar{n}$ is calculated using the conversion equation[18], using the same values as used in Table 1. The C_p was calculated using: $C_p = C_{p0}(1 - x_{CSTR})$, where C_{p0} is the C_p of a monomer droplet, which is approximately 8.6 M and x_{CSTR} is the fractional monomer conversion in the CSTR.
c. The initiator concentration used to calculate $\rho_{initiator}$ was calculated using $[I] = [I]_0\exp(-k_d\tau n)$, with τ being the average residence time per reactor and n being 1, 2, or 3 for R1, R2, and R3, respectively.
d. The exit rate coefficient, k, was calculated using $\bar{n}$ and $\rho_{initiator}$ assuming Limit 1[18] zero-one conditions. Limit 1 was assumed because of the high radical flux at 70°C, which should result in aqueous phase termination of most exiting radicals. k is then given by $\rho_{initiator}(1 - 2\bar{n})/\bar{n}$.

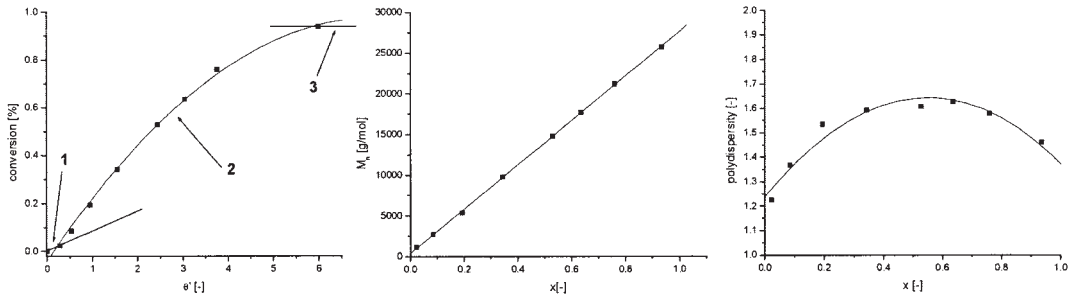

Figure 11. Fits of conversion vs. dimensionless residence time, *Mn* vs. conversion, and polydispersity vs. conversion of a the batch miniemulsion polymerization of exp99.

CSTRs, and dotted lines for three CSTRs in two different CSTR train experiments. Figure 7 shows that the conversion in a CSTR train is lower than predicted from batch for one, two and three CSTRs in series. Since the conversion does not match, also the calculated M_n and polydispersity will not match, which is indeed shown in Figure 7. These results indicate that the miniemulsion studied here cannot simply be considered as a large collection of individual batch reactors, but that transport of material between the particles through the aqueous phase takes place. This hypothesis is confirmed when the final mass average particle size of batch experiments are compared to the final particle size in R3 of the CSTR train experiment in which exactly the same miniemulsion was used. In both cases the particle size is extrapolated to 100% conversion, assuming that at the dilution used in light scattering, all monomer is stripped from the particles. To minimize the error introduced by this assumption, R3 was allowed to proceed to high conversions after the CSTR train experiment was stopped. The results are shown in Table 4.

The data in Table 4 shows that indeed the particle size in batch is smaller, even though calculations performed according to Samer et al.[14] using parameters that apply to the conditions in this work, showed they should be the same. A smaller particle size also means that the particle number in batch is higher and, therefore, the polymerization rate in batch will be higher than in a CSTR. This also means that conversions for the CSTR train calculated from batch experiments will be higher than the ones found experimentally, as shown in Figure 7. Table 4 also shows that when oligomeric RAFT agent is used, the particle size and number are almost identical.

The smaller particle size in batch compared to CSTR experiments for **I** means that nucleation in batch is more effective than in a CSTR. A possible explanation is illustrated in Figure 12.

In a batch experiment, all particles will have about the same weight fraction of polymer w_p, so there will be less thermodynamic driving force for monomer to diffuse from 1 particle to another, except Oswald ripening, which has been minimized by the use of hexadecane in the recipe. In a CSTR, however, because of the RTD, there will be large differences in w_p between the particles, creating a thermodynamic driving force for monomer to diffuse from low w_p particles or even monomer droplets without polymer to high w_p particles. If this driving force is large enough, it will "dry out" fresh droplets or particles in the CSTR before they are nucleated, resulting in less particles and a larger particles size in the CSTR. Since hexadecane, the RAFT agent used and polymer are water-insoluble, these "dried out" particles cannot be consumed completely and could remain in the system as a very small inert species, too small to show up in the light scattering particle size data. However, these " dried out"' particles do show up in the in the UV trace at 311 nm of the GPC as a low-molecular-weight "nongrowing" population. The RI detector does not clearly reveal this population, except that it shows some low MW tailing. However, data on this population can be obtained from the UV trace. As stated earlier, the UV signal at 311 nm corresponds to the RAFT moiety, resulting in a number distribution of RAFT terminated chains. If the hypothesis of the "dry out" mechanism is correct, it should mean that the "nongrowing" population in a batch experiment should be smaller than in a

Table 4. Particle Size and Number of Batch Experiments and Corresponding Particle Size and Number in R3 of the CSTR Train Experiment

	Batch		R3 in CSTR Train	
exp, RAFT	r_m [nm]	$N_c \times 10^{17}$ [dm^{-3}]	r_m [nm]	$N_c \times 10^{17}$ [dm^{-3}]
78, I	71.7	1.48	84.2	0.91
82, I	73.0	1.37	80.5	1.02
99, I	84.1	1.02	91.5	0.79
95, II	59.0	2.65	60.2	2.50

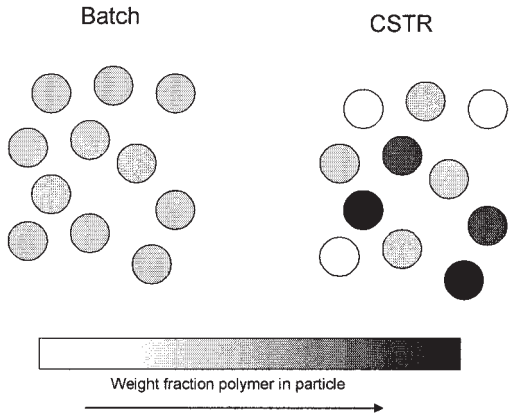

Figure 12. The difference in weight fraction of polymer, wp, in particles in a CSTR, as a result of the residence-time distribution, creates a driving force for monomer to diffuse from low to high wp particles, thereby "sucking dry" fresh droplets or low wp particles, leading to a decreased nucleation efficiency compared to batch.

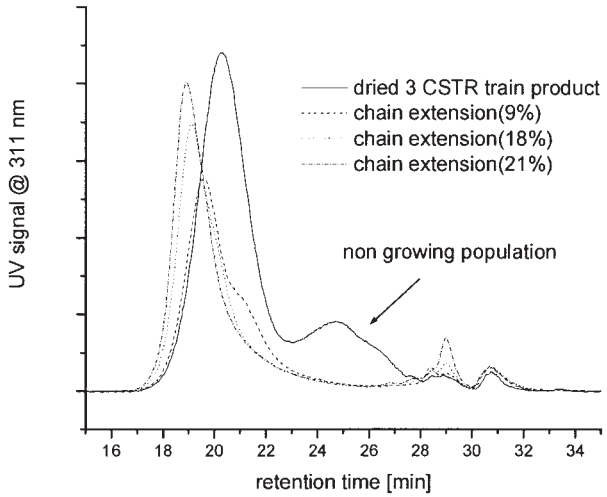

Figure 13. GPC traces of a chain extension experiment with styrene in bulk at 70°C using dried polymer obtained from a 3 CSTR train (solid line).

The dashed line shows that after 9% conversion, the nongrowing population has disappeared.

CSTR train at the same conversion. Unfortunately, the molecular-weight distribution is too broad to quantify the amount of nongrowing material, since the MWD of the polymer is too broad and the nongrowing material also overlaps with the oligomers present in the feed. Furthermore, this "nongrowing" population should disappear in an experiment in which dried polymer is dissolved in monomer and polymerized. This is shown in Figure 13.

Figure 13 shows the UV GPC traces at 311 nm of a chain extension experiment, in which polymer formed in a 3 CSTR train was dried and then dissolved in styrene (1 to 6.8 mass ratio), and heated at 70 °C in the presence of AIBN (2 mM). It is shown that at 9% conversion, the "nongrowing" population has already disappeared, indicating it does not consist of dead polymer chains and indicating that in the styrene miniemulsion polymerizations reported here, indeed a "drying out" process likely takes place. The final particle size suggests that in a CSTR, more particles are being "dried out" than in batch.

Conclusions

It has been shown that a RAFT miniemulsion polymerization can be performed in a CSTR train, resulting in polymer with a relatively high polydispersity (>2) for 1 CSTR. The polydispersity decreases by increasing the number of CSTR's in the train. A steady state has not been reached in the experiments with the CSTR train, even though the train was operated much longer than the time theoretically required to reach steady state. It has been shown that this may be the result of oligomerization of the RAFT agent in the feed, leading to slowly increasing polymerization rates over time. The use of oligomeric RAFT agent in the CSTR showed a different oscillating trend, although it requires future investigation since the experiment was not run long enough to make a definitive characterization of the trend, and the exit rate data indicated that the oligomers still contained monomeric RAFT.

Comparison of batch experiments to CSTR experiments revealed that the miniemulsion in a CSTR does not behave as a large collection of individual batch reactors, but that transport between the particles takes place. 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 "dry out" before becoming a polymer particle, 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 miniemulsion droplets to "dry out". UV GPC data, monitoring the RAFT moiety, was consistent with this hypothesis.

Acknowledgments

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Notation

θ' = dimensionless residence time
$\rho_{initiator}$ = initiator derived entry rate coefficient
τ = average residence time
C_p = monomer concentration in a particle/droplet
C_w = monomer concentration in the aqueous phase
D_{RDT} = polydispersity of the residence-time distribution
DP = degree of polymerization
k = exit rate coefficient
k_d = initiator decomposition rate coefficient
k_p = propagation rate coefficient
$k_{p,aq}$ = aqueous phase propagation rate coefficient
$k_{t,aq}$ = aqueous phase termination rate coefficient
M_n = number-average molecular weight
M_w = weight-average molecular weight
n = number of CSTR's
$\bar{n}$ = average number of radicals per particle
N_c = number of particles per liter of water
PD = polydispersity of the molecular-weight distribution
Q = volumetric flow rate
r_m = mass average particle radius
t = time
V = volume of the CSTR
w_p = weight fraction of polymer in a particle
x = fractional monomer conversion
z = critical chain length for entry

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