Synthesis of Block Copolymers Using RAFT Miniemulsion Polymerization in a Train of CSTRs

Wilfred W. Smulders, Christopher W. Jones,* and F. Joseph Schork*

School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, 311 Ferst Dr., Atlanta, Georgia 30332

Received June 25, 2004; Revised Manuscript Received September 17, 2004

ABSTRACT: Continuous reversible addition fragmentation transfer (RAFT) miniemulsion block copolymerization of styrene and *n*-butyl acrylate (BA) in a train of continuous stirred tank reactors (CSTRs) is described. It is shown that a train of CSTRs can effectively be used to produce unique (multi)block copolymers. Comparison of gel permeation chromatography (GPC) refractive index (RI) traces and GPC UV traces revealed that the polymer formed has a very high percentage of living chains. The process variables such as flow rate, temperature, and injection point of the second monomer can easily be changed to obtain different block copolymers. The average composition and length of the individual blocks have been determined using ^{1}H NMR, GPC, and mass balances. The advantages and disadvantages of the continuous process for the production of block copolymers are discussed.

Introduction

Current polymers produced via free radical polymerization are made with little control over their structure, which limits their applicability as high-performance materials. The introduction of new living/controlled free radical polymerization (LRP) techniques over the past several years, however, seems to offer promise for overcoming these limitations. Several publications have appeared introducing these new techniques and showing examples of polymers with controlled architectures. Nitroxide-mediated free radical polymerization was introduced first,[1,2] followed by atom transfer radical polymerization (ATRP)[3,4] and reversible addition fragmentation chain transfer (RAFT) polymerization.[5−8] Controlled architectures that have been obtained using RAFT include block copolymers,[9−13] gradient copolymers,[14,15] star-shaped (block co)polymers,[15−17] and polymer brushes.[18,19] Often they also have a narrow molecular weight distribution.

RAFT can easily be applied using emulsion/miniemulsion polymerization techniques at conventional temperatures.[11,20−23] Emulsion/miniemulsion polymerization offers 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 water and thus low in VOC’s. Because of the hydrophobicity of most RAFT agents, miniemulsion polymerization has proven to be the most easily applicable emulsion polymerization technique,[11,20] although successful applications of RAFT in seeded[21,22] and ab initio[23] emulsion systems also have been reported.

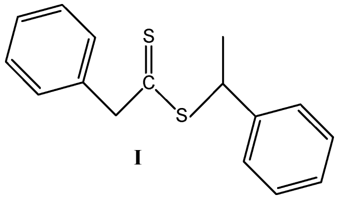
One of the drawbacks of living free-radical polymerizations is that the product is relatively expensive, although it is to be expected that it may be less costly than the currently available well-defined polymers made by anionic or cationic polymerization, which, unlike free-radical processes such as RAFT, require ultrapure and thus expensive reagents. 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 can be operated at steady state, which will yield a consistent product over time and can yield unique architectures which cannot be obtained in batch or semibatch processes. Although there are reports of continuous miniemulsion polymerization in tubular reactors[24] and CSTRs,[25−29] very little has been published in continuous LRP. Zhu et al. carried out continuous ATRP using a packed bed of silica supported control agent[30,31] in a tubular reactor. In addition, we have performed continuous RAFT miniemulsion polymerizations in tubular reactors[32,33] and in a CSTR train.[34] It was shown that narrow molecular weight polymer could be obtained using tubular systems, although, compared to batch, some broadening of the molecular weight distribution (MWD) was observed, likely as a result of axial dispersion. In general, CSTRs are preferred over tubular systems due to the vulnerability of the tubes to plugging. Another advantage of CSTRs is that mixing is better than in tubular reactors, which might be important if a second monomer is fed for (block) copolymer synthesis. A major concern, however, could be the residence time distribution (RTD) exhibited in a CSTR. Since the lifetime of a polymer chain in living systems is equal to the residence time in the reactor, this will broaden the MWD considerably. However, it is not always a narrow MWD that makes living 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 to further process. Moreover, in previous publications it was already derived theoretically[35] and shown experimentally[34] that a train of CSTRs will lead to narrower MWDs. Another advantage of a CSTR train is that higher conversions can be achieved using smaller reactor volumes, which is beneficial for both economic and safety reasons. Moreover, 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. Finally, it

---

* Corresponding authors. E-mail: joseph.schork@chbe.gatech.edu and christopher.jones@chbe.gatech.edu.

10.1021/ma0487204 CCC: $27.50

Scheme 1. 1-Phenylethyl Phenyldithioacetate (I), the RAFT Agent Used



I

has to be noted that a CSTR train can give unique polymers which cannot be made in (semi)batch or tubular systems because a CSTR train can be operated at steady state. This should allow the synthesis of block copolymers with constant copolymer composition within each block, whereas semibatch and tubular systems will show a gradient over the blocks as a result of composition drift.[36] Here we report the synthesis of block copolymers in a continuous free-radical miniemulsion process using a train of CSTRs. To our knowledge, this is the first report dealing with the synthesis of block copolymers in a continuous miniemulsion system.

Experimental Section

Materials. Inhibitor in styrene (J.T. Baker) was removed using Aldrich Inhibitor remover for *tert*-butylcatechol. Inhibitor in *n*-butyl acrylate (BA) (Aldrich) was removed using Aldrich Inhibitor remover for hydroquinone and monomethyl ether hydroquinone. Hexadecane (Aldrich, 99%), sodium persulfate (Aldrich, 98+%), and sodium dodecyl sulfate (SDS) (ICN Biomedicals, ultrapure) were used as received. Deionized water was used in all cases. The RAFT agent, 1-phenylethyl phenyldithioacetate (**I**, Scheme 1), was synthesized according to literature procedures,[37] 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*-toluenesulfonic acid monohydrate (Aldrich, 98%).

Reactor Train. A diagram of the CSTR train is shown in Scheme 2. The train, including the styrene miniemulsion feed and the BA macroemulsion feed (a vigorously stirred water/BA/SDS mixture), was kept under a nitrogen atmosphere. The miniemulsion, consisting of water, surfactant, styrene, costabilizer (hexadecane), and RAFT agent (**I**), was fed from a stirred and cooled (using an ice bath or a Fischer Scientific Isotemp 3016 cooler) 3 L flask into reactor 1 (R1) using a FMI valveless piston pump (P1). The sodium persulfate initiator solution was fed separately using a kdScientific syringe pump (P2). The first two CSTRs are 50 mL three-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 Scheme 2. The third and fourth CSTRs are 100 mL three-neck round-bottom flasks with an overflow weir, which maintains the CSTR volume at approximately 80 mL, helped again by nitrogen pressure in R1 and gravity forces as shown in Scheme 2. All CSTRs are 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 hot plates with magnetic stirring and controlled by IKA ETS-D4 Fuzzy temperature controllers. The temperature in the oil baths was set to 72 °C to maintain a temperature of 70 °C inside the CSTRs. To prevent introduction of oxygen into the system, the overflow weir in R4 was equipped with a Masterflex pump (P4), operated at a flow higher than the flow rate of the combined feeds.

The second monomer was fed into either R3 or R2 as a BA/SDS/water macroemulsion using an FMI valveless piston pump (P3). The BA macroemulsion was kept at room temperature and stirred at high speed using a magnetic stirrer. Samples were taken and analyzed gravimetrically to check for polymerization in the BA feed, and it appeared that no polymerization in the feed took place. The monomer to water mass ratio was 0.25, with 2 mM SDS based on water, which is far below the critical micelle concentration.

Experiments were started after the CSTRs, styrene miniemulsion feed, and BA macroemulsion feed were kept under nitrogen for about 1 h. The first two 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. A few hours later the feed of BA into R3 was started by starting P3. Before the first samples were taken, the system was allowed to stabilize overnight. It is important to note that the system never reaches a real steady state as a result of slow oligomerization of the RAFT agent in the feed, as was shown in a previous publication.[34] After sufficient samples were taken to characterize the system, changes in either flow rate, temperature, or injection point of BA were made, and the system was allowed to stabilize again before new samples were taken. In both experiments described here, the reactor train was operated at three different conditions, further referred to as stages 1−3 of exp1 and exp2 (see next section).

Miniemulsion Preparation and Recipe. The miniemulsion was prepared by adding a mixture of styrene, hexadecane (costabilizer), 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 stirred and cooled in an ice bath. The initiator solution was prepared by dissolving sodium persulfate in water.

The monomer/water mass ratio was ~0.25, in both the styrene miniemulsion and the BA macroemulsion, and the monomer to RAFT molar ratio in the styrene miniemulsion was ~300, while the BA macroemulsion feed did not contain any RAFT agent. The SDS concentration in the styrene miniemulsion was ~0.018 M based on water, and 2.3 wt % hexadecane was used based on the amount of monomer. The initiator feed rate was set such that the concentration in R1 was ~3 mM based on water. In the reactor in which the BA macroemulsion was fed and the reactors downstream of this reactor, the initiator concentration was about 1.5 mM, since the styrene and BA are fed at about the same flow rate and the BA was fed without additional initiator. In Table 1 the recipe with corresponding flow rates and reactor temperatures for the two experiments in the three different stages are shown.

Analysis. *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, 1000, 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, and a LDC Milton Roy Spectromonitor 3000 UV detector (analyzing at 311 nm) and calibrated against 10 narrow polystyrene standards (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.

NMR. Copolymer composition analysis was determined by ^{1}H NMR using a 300 MHz Varian Gemini, operated at room temperature. Extensively dried copolymer was dissolved in $CDCl_3$ at a concentration of ~4 wt %. Peak areas of the proton resonances at δ = 6.3−7.4 ppm (phenyl of styrene, 5H) and δ = 3.4−4.1 ppm (methylene of BA, 2H) were taken to calculate copolymer composition. A typical ^{1}H NMR spectrum is shown in Figure 1.

Results and Discussion

Conversion, Molecular Weight, Polydispersity, and Proof of Livingness. The CSTR train in exp1 was started using a flow rate of 0.35 mL/min of both the

Scheme 2. Schematic Setup of the CSTR Train

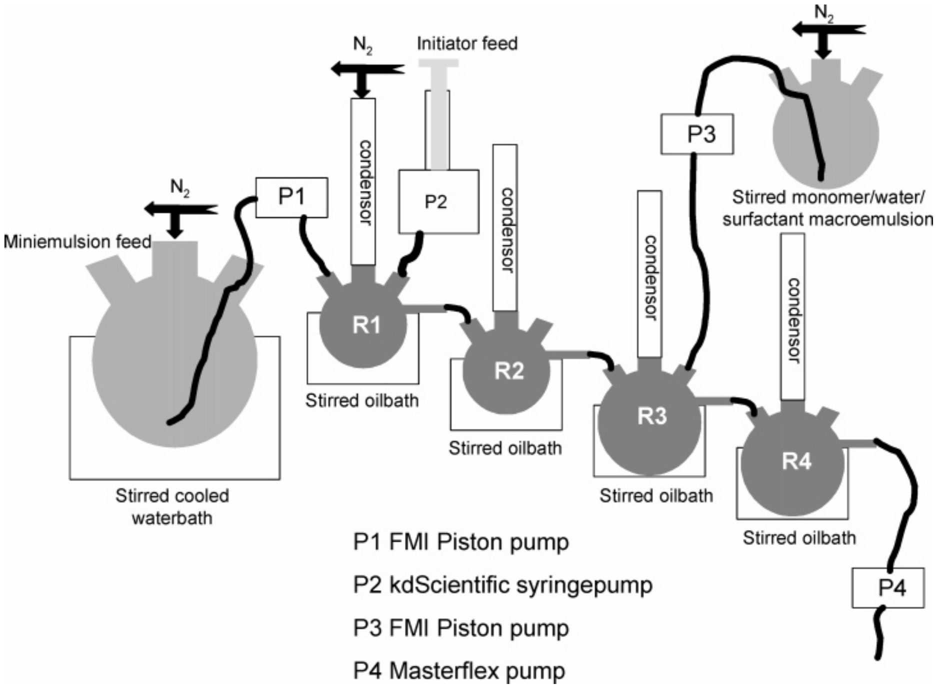


Table 1. Typical Recipe, Oil Bath Temperatures, and Flow Rates for a RAFT Miniemulsion Polymerization with an Additional BA Macroemulsion Feed Downstream, Performed in a Train of CSTRs

styrene miniemulsion feed		SPS initiator feed		BA macroemulsion feed[a]	
water	1469.24 g	water	204.98 g	water	1000.4
SDS	7.96 g	SPS	2.43 g	SDS	0.59
styrene	352.99 g			BA	250.0
hexadecane	8.25 g				
RAFT **I**	3.04 g				

	STY flow rate [mL/min]	SPS flow rate [mL/min]	BA flow rate [mL/min]	reactor temperature[b] [°C]
exp1stage1	0.35	0.018	0.35	72,72,71,71
exp1stage2	0.30	0.018	0.35	72,72,71,71
exp1stage3	0.30	0.018	0.35	72,72,71,71
exp2stage1	0.30	0.015	0.30	72,72,71,71
exp2stage2	0.30	0.015	0.30	77,77,71,71
exp2stage3	0.30	0.015	0.30	74,74,71,71

[a] The BA macroemulsion was fed into R3 in all cases except in stage 3 of exp 1, where the BA was fed into R2. [b] Oil-bath temperatures of R1, R2, R3, and R4, respectively.

styrene miniemulsion feed and the BA macroemulsion feed. The BA was fed into R3. These start-up conditions are referred to as exp1stage1. Because the reactor volumes in R3 and R4 are exactly twice the reactor volumes of R1 and R2, this means that in stage 1 the average residence time was equal in each reactor (40 mL/0.35 mL/min or 80 mL/(0.35 mL/min + 0.35 mL/min), which makes 114 min). The overall conversions for each reactor are plotted in Figure 2. The overall conversions are based on the recipe in which all feeds are combined, i.e., the recipe in R3 and R4. This means that the actual conversions in R1 and R2 are actually about twice as high as plotted in Figure 1, but for the readability of the plot and in order to be able to compare conversions in all reactors, conversions based on the overall recipes are used.

The data in Figure 2 show that in exp1stage1 an overall conversion of about 60% is achieved in R4. The reactors in which BA is present, R3 and R4, show a higher increase in conversion, as BA has a much higher propagation rate coefficient,[38] k_p, than styrene, which will lead to a higher copolymerization rate. The weight fraction of BA in the polymer, $F_{w,BA}$, obtained from the mole fraction BA determined by ^{1}H NMR (see Figure 1) and the monomer molar masses are also noted in Figure 2. In exp1stage2 the styrene miniemulsion flow was lowered to 0.30 mL/min, such that the conversions in R1 and R2 would be higher before BA was introduced in R3. In stage 3, the flows are equal to those in stage 2; however, the BA macroemulsion was fed into R2 instead of into R3. The conversions and weight fraction of BA in the polymer for exp1stage2 and exp1stage3 are also shown in Figure 2. Figure 3 shows the number-average molecular weight, M_n, and Figure 4 shows the polydispersity in all three stages. M_n and polydispersity were obtained from the refractive index (RI) traces of the GPC using polystyrene standards.

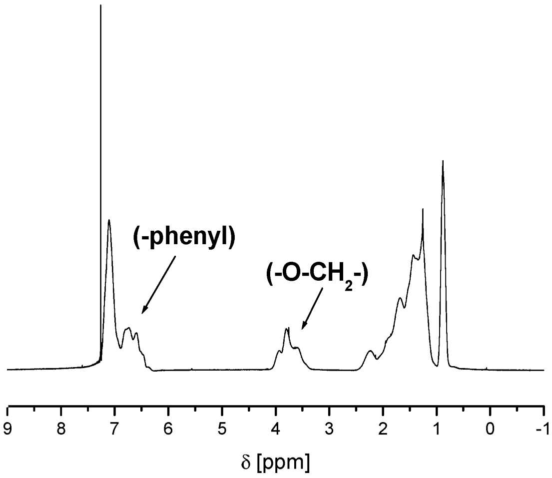


Figure 1. ^{1}H NMR spectrum of copolymer formed in the CSTR train. The area of the methylene peak next to the ester (2H) and the phenyl peak (5H) were used to calculate the fraction of *n*-butyl acrylate and styrene, respectively, in the polymer.

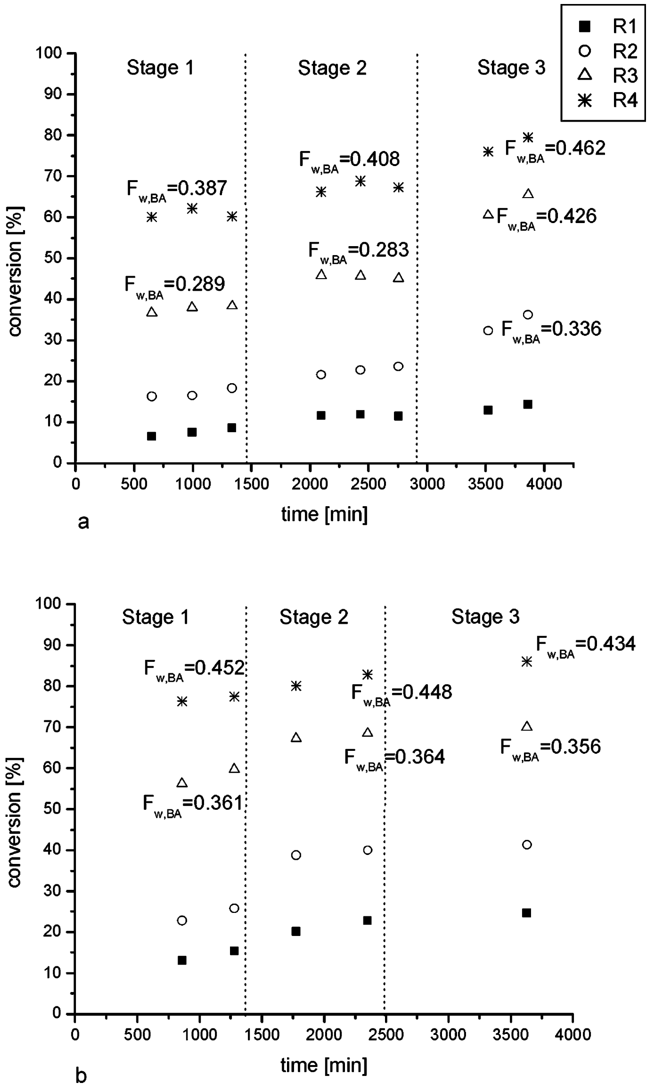


Figure 2. Conversion−time data of the continuous RAFT miniemulsion block copolymerizations in the CSTR train, consisting of four reactors (R1−R4). Conversions are based on the recipes in which all feeds are combined. Conditions of exp1 (a) and exp2 (b) in all three stages can be found in Table 1. Additionally, the weight fractions of *n*-butyl acrylate in the copolymer, obtained from ^{1}H NMR, and the monomer molar masses are noted.

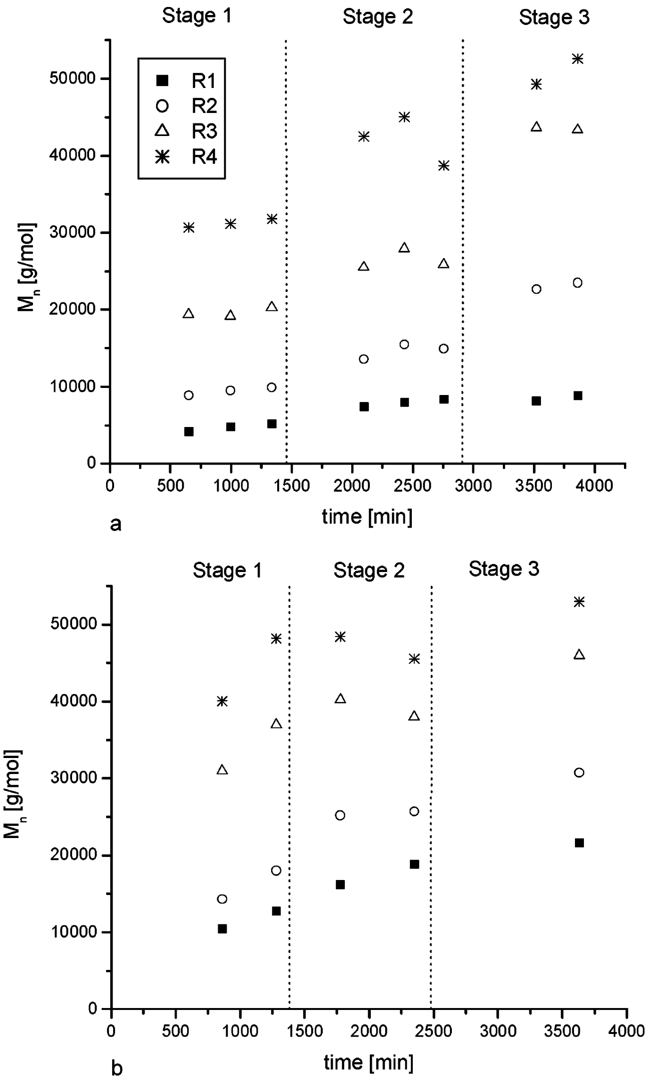


Figure 3. Number-average molecular weight (M_n) vs time data of the continuous RAFT miniemulsion block copolymerization in the CSTR train, consisting of four reactors (R1−R4). (a) represents exp1 and (b) represents exp2. See Table 1 for further details.

Figure 3 shows that in all three stages M_n increases with conversion, which is consistent with a living polymerization. The living nature of the polymerization is further supported by the data in Figure 5, in which the M_n values are plotted against conversion and compared to the theoretical values. Figure 5 shows that the M_n values are close to the theoretical values in all cases. It is important to note that there are two theoretical lines, one for the cases in which only styrene is present in the reactor and one for the cases in which also BA is fed into the reactor, which doubles the theoretical molecular weight. This is another indication that the system is living and that indeed block copolymers are being produced (more conclusive evidence is presented below).

The data in Figure 4 show that the polydispersity is relatively broad in all cases and that the polydispersity increases in the reactor in which the BA is added. For the final material from reactor 4, polydispersities are ~3.3, 2.8, and 3.0 for stages 1, 2, and 3, respectively. However, obtaining a narrow MWD was not the first objective here. Furthermore, it has to be noted that a narrower distribution can be obtained by adding more CSTRs to the train, as was already derived theoretically[35] and shown experimentally for styrene miniemulsion homopolymerizations.[34] This trend is best visible in stage 3, where the polydispersity decreases from about 5.5 in R2 via 3.5 in R3 to 3.0 in R4. It has to be noted though that in exp1stage1 the polydispersity in R3 is lower than in R4, which is opposite of what is expected. Molecular weight polydispersity could also be a consequence of polydispersity in the droplet or particle size distribution (PSD). However, in this work, light scattering was used to measure PDSs, and no unusual polydispersity was observed.

To prove the livingness of the system and thus to prove the formation of block copolymers, the GPC data can be further analyzed. In a living system, the MWD obtained from the RI detector, which detects all polymer, should be identical to the MWD obtained from the UV detector operated at 311 nm, which will detect only the RAFT end group.[22] To obtain a weight distribution from the UV detector, the detector signal at a certain elution time has to be multiplied by the corresponding molecular weight at that elution time, since the UV detector

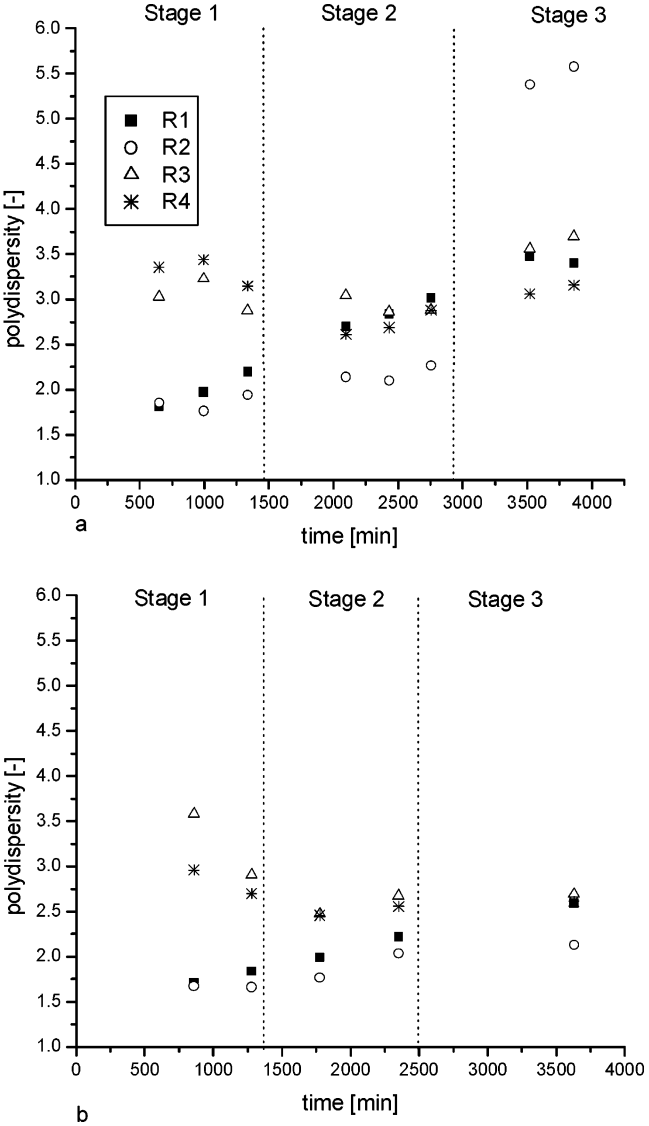


Figure 4. Polydispersity (M_w/M_n) vs time data of the continuous RAFT miniemulsion block copolymerization in the CSTR train, consisting of four reactors (R1−R4). (a) represents exp1 and (b) represents exp2. See Table 1 for further details.

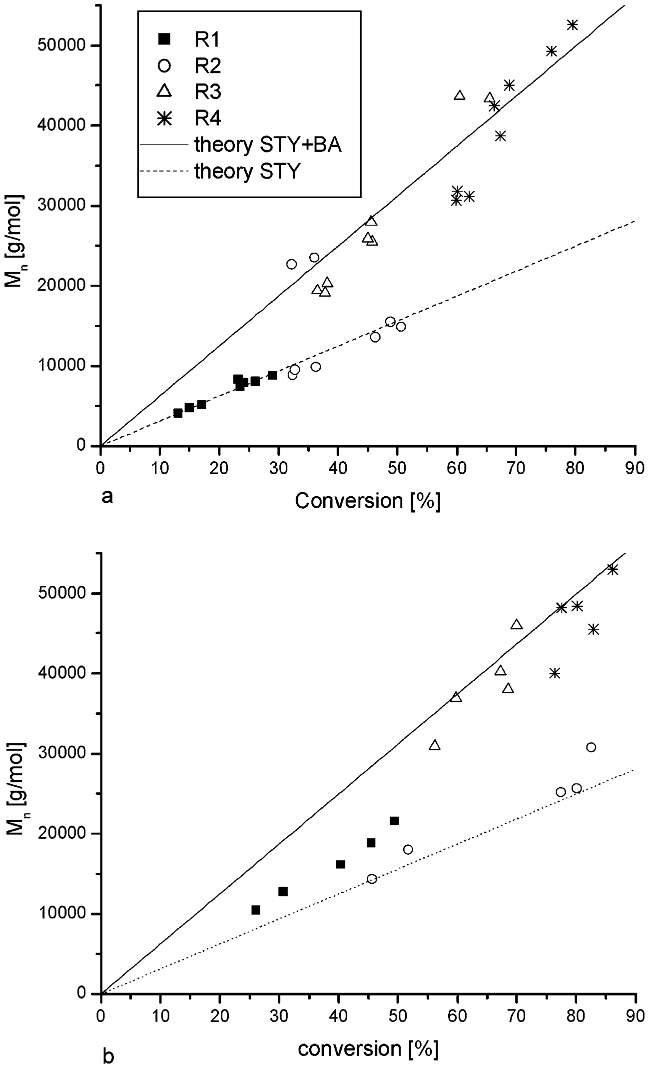


Figure 5. M_n vs conversion of the continuous RAFT miniemulsion block copolymerization and theoretical molecular weights The solid lines represent the theoretical molecular weights in the reactors in which the styrene and BA feed are combined, whereas the dotted lines represent the conversion in the 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) represents exp1 and (b) represents exp2. See Table 1 for further details.

at 311 nm will only give the number distribution, as styrene and BA are invisible at this wavelength. In Figure 6, the molecular weight distribution obtained from the RI detector and the UV detector at 311 nm are shown for reactors R3 and R4 in exp1stage1 and exp1stage2 and for R2−R4 in exp1stage3.

As can be seen in Figure 6, the MWDs are overlapping almost perfectly, indicating almost all chains have a RAFT end group. In stage 3, however, there appears to be some high molecular weight material without a RAFT end group, although it becomes less pronounced going from R2 to R4. Gravimetric analysis of the BA feed showed that no measurable polymerization takes place in the BA feed, so formation of high molecular weight BA homopolymer can be excluded as a cause. But for all three stages the final material formed in R4 appears to be almost exclusively RAFT end-capped polymer, although it has to be noted that the GPC traces do show a bimodality. This issue will be addressed to further in a section below.

It has been shown so far that BA is being incorporated into the polymer chains (^{1}H NMR, Figure 2), that M_n increases with conversion according to theory (Figure 5), and that the polymer formed in R4 contains almost exclusively RAFT end-capped chains (Figure 6). In exp1stage1 and exp1stage2, the polymer in formed in R1 and R2 is styrene homopolymer, and because the system is operated at steady state, with different styrene/BA monomer compositions in R3 and R4, this means that in exp1stage1 and exp1stage2 a three-block copolymer is produced. The first block is a styrene block while the second and third block are styrene/BA copolymer blocks with different average compositions. In stage 3 a four-block copolymer is produced, with a styrene homopolymer block at the beginning of the chain and three consecutive copolymer blocks of different composition. In the next section, the average compositions and length of the blocks are discussed in more detail.

Copolymer Composition and Composition of the Individual Blocks. From a mass balance, conversion data, monomer flow rates, and ^{1}H NMR copolymer composition data it is possible to calculate the average composition of each block, *assuming all polymer is block*

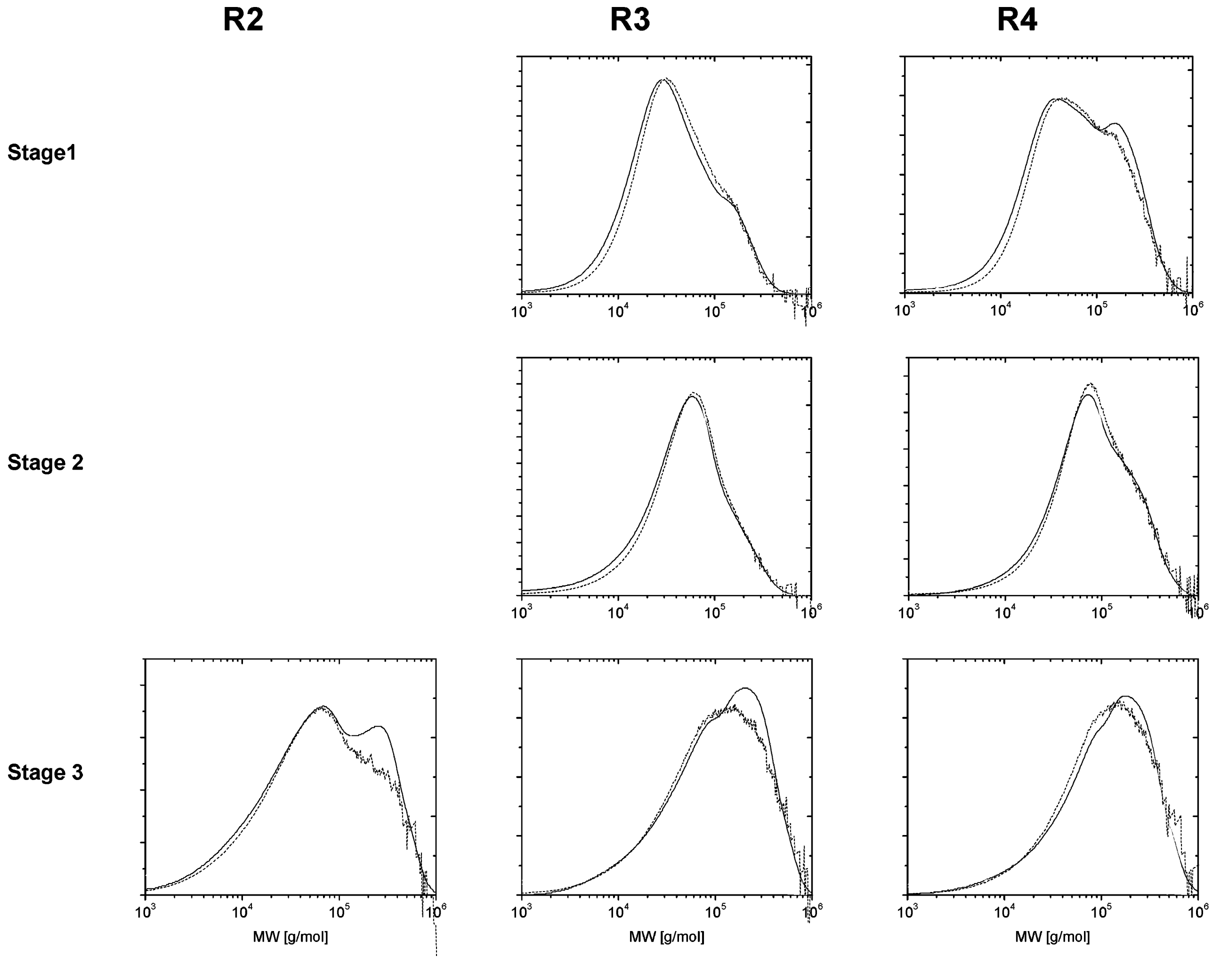


Figure 6. Overlays of copolymer MWDs obtained from the RI detector of the GPC (solid lines) and the UV detector operated at 311 nm (dotted lines) for all three stages in exp1.

Table 2. Composition and Block Lengths of the Block Copolymers Produced in the CSTR Train for Exp1

		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 the GPC data [g/mol].

copolymer. This key assumption will be discussed further below. The results of these calculations are shown in Table 2.

The data in Table 2 show that in stage 1 the three-block copolymer is basically a two-block copolymer, since the composition in the second and third block is almost equal. The same applies in stage 3, where the second and third block have an almost equal composition, so the four-block copolymer is in fact a three-block copolymer. In all cases, the weight fraction of BA in the blocks increases in each block, which is expected from the reactivity ratios of styrene and BA. Using these reactivity ratios, $r_{\mathrm{STY}} \sim 0.83$ and $r_{\mathrm{BA}} \sim 0.18$,[39] it can be calculated that the fraction of styrene in the copolymer formed is higher than the fraction of styrene in the monomer mixture. This means that the monomer mixture becomes richer in BA, and therefore, the blocks will become richer in BA if you go downstream in the reactor train, as can be seen in Table 2. In Table 2, the relative average masses of the blocks, as calculated from mass balances (c), are also shown. As can be seen in Table 2, they compare well to the average lengths obtained from the GPC (d).

This shows that a relatively good characterization of the block copolymers can be obtained from ^{1}H NMR data, GPC, and conversion data, assuming that all polymer formed is indeed block copolymer. (The possibility of some homopolymer or secondary block copolymer formation is discussed further below.) The comparison of the RI GPC and the UV at 311 nm GPC data in the previous section already showed that indeed almost all polymer has a RAFT end group. It has to be kept in mind, however, that the values for the block lengths in Table 2 represent average values. As a result of differences in residence times of the different particles, there can be large differences in the lengths of the blocks, which is confirmed by the broad polydispersities in Figure 4. For the copolymer composition this should not apply if the system is at or almost at steady state, such that composition drift is minimal or absent. Therefore, the composition of the blocks will ideally be independent of the residence time if the reactors operate at steady state.

While the livingness of this system implies that the production of homopolymer of the first monomer should not been an issue, it may be possible that a different block copolymer or a homopolymer of the second monomer could be formed under some conditions. For example, if the feed of the second monomer is placed in a reactor near the front of the train and if new chains are initiated in that reactor, these chains will be missing the first block. Additionally, as a consequence of the residence time distribution (RTD), if the conversion is low in the first reactor, some droplets may not be nucleated in the first reactor. When these droplets polymerize in downstream reactors, they will produce different polymer chains as well. Additionally, if there is a large amount of unreacted RAFT agent after the first reactor, this also could contribute to the formation of new polymer chains that do not have the first block. This effect could be tempered in light of the recent data reported by Klumperman[40] on the initialization period in RAFT. Klumperman and co-workers have shown that nearly all the RAFT agent is consumed in batch reactions to form short, oligomeric, or single monomer unit chains capped by RAFT species during the initialization or induction period that is commonly observed in RAFT systems.[40] This indicates that, even for relatively low conversions of monomer one in the first reactor, essentially all of the RAFT agent should be consumed before a second monomer is added in a downstream reactor, assuming all droplets nucleate. While all of these issues warrant future attention, the conditions used in this study were designed to minimize these effects. In particular, conditions were chosen such that theoretically >95% of the droplets were nucleated in the first reactor, minimizing the likelihood of formation of homopolymer or polymers that are missing the first block.[26,27]

Bimodality in the MWD. As mentioned before, the traces shown for the styrene BA block copolymerization in Figure 6 are bimodal. Although the overlays in Figure 6 show that almost all polymer chains have a RAFT end group, the bimodality suggests that the block copolymerization with BA does not proceed ideally. For an ideal block copolymerization, the traces would be monomodal and the polydispersity would decrease going downstream in the train. Here, however, the polydispersity goes up in the reactor in which the BA is fed and decreases again going further downstream the train. In the reactor in which BA is fed, the MWD also becomes bimodal. When a similar experiment is performed in which styrene is fed into R3 instead of BA, this bimodality is not observed, and the polydispersity does not increase in the styrene fed reactor. The polydispersity decreases throughout the train, just as is observed in a homopolymerization without additional second monomer feed.[34,35] The steady-state values of this experiment are shown in Table 3.

Table 3. Steady State Values of a Continuous Styrene Miniemulsion Polymerization in Which Additional Styrene Is Fed into R3[a]

	R1	R2	R3	R4
conversion [%][b]	17	31	57	63
M_n [kg/mol]	18.2	25.7	35.9	39.7
PD	1.98	1.83	1.77	1.69

[a] Reaction conditions are the same as for exp2stage1 in Table 1 with BA being replaced by styrene. [b] Conversion based on combined feeds.

The data in Table 3 show that an additional monomer feed does not necessarily lead to increased polydispersity and bimodality. Furthermore, if one compares the MWDs of exp1stage1 and exp1stage2 in Figure 6, it can be seen that the bimodality becomes less pronounced in exp1stage2. The styrene polymerization in R1 and R2 in exp1stage2 had proceeded to higher conversions than in exp1stage1 before BA was fed into R3. Therefore, it was hypothesized that a low styrene conversion might lead to instabilities and secondary nucleation when the additional BA macroemulsion was fed, leading to a bimodal distribution. Because in a CSTR there will likely be small amounts of unreacted RAFT agent, the polymer formed in the “new” population of particles can still have a RAFT end group, even though the concentration of RAFT in these particles will be low. To test this hypothesis, in a following experiment, referred to as exp2, the styrene homopolymerizations in R1 and R2 were allowed to proceed to higher conversions by increasing the reaction temperature in R1 and R2, before BA was fed into R3. Reaction conditions of the three stages in exp2 are shown in Table 1. The results of exp2 are shown in Figures 2−4, and the MWDs obtained from the RI and UV detector at 311 nm are shown in Figure 7.

Initially, the conditions in exp2stage1 were chosen such that they were close to the conditions in exp1stage2. As can be seen in Figure 7, again bimodal MWDs were obtained. In exp2stage2 the oil bath temperatures in R1 and R2 were increased from 72 to 77 °C. As can be seen in Figure 2b, this led to increased conversions in R1 and R2. The conversion in R2 was now close to 80% (note that it is plotted as 40% in Figure 2b, since the conversions in Figure 2 are based on overall recipes including the BA feed). As can be seen in Figure 7, the bimodality has almost disappeared and also the polydispersity, shown in Figure 4b, decreased.

In exp2stage3 the temperatures in R1 and R2 were decreased to 74 °C, although this did not lead to a decrease in conversion, as can be seen in Figure 2b. This is most likely a result of oligomerization of the RAFT agent in the feed,[34] which results in an increased polymerization rate as a result of a decreased radical desorption (exit) rate and compensates the decrease of polymerization rate as a result of the 3 °C lower reaction temperature. Also in exp2stage3, the bimodality observed in exp1 and exp2stage1 was not visible.

Similar to exp1, it can be shown that also in exp2 a large majority of chains have a RAFT end group. This is shown by the overlays of the UV at 311 nm MWD and the RI MWD in Figure 7, which show a very good match. Also, the M_n values are close to the theoretical values, as shown in Figure 5b, which is another indication for the livingness of the system. It has to be noted though that the M_n values in R1 are all slightly above the theoretical M_n.

Also for the block copolymer formed in exp2, the average block composition and length can be calculated using GPC data, NMR data, and mass balances. These results are shown in Table 4.

As expected, the data in Table 4 show that when R1 and R2 are operated at higher conversions, the weight fraction of BA in the second block increases. This shows that by adjusting temperatures, flow rates, etc., a large variety of block copolymer can be produced, without stopping or changing the continuous CSTR train, which

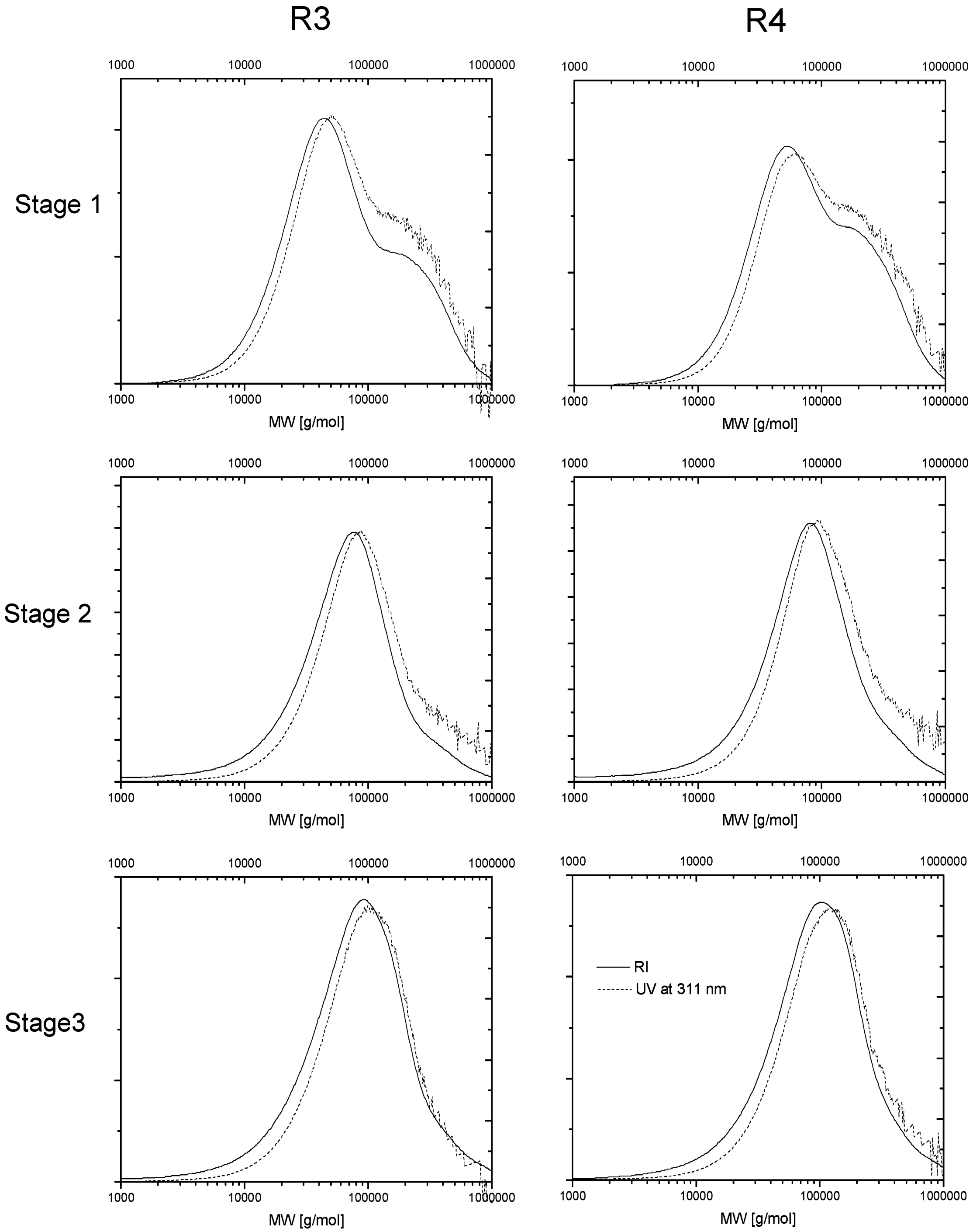


Figure 7. Overlays of copolymer MWDs obtained from the RI detector of the GPC (solid lines) and the UV detector operated at 311 nm (dotted lines) for all three stages in exp2.

makes the CSTR train an attractive process for the continuous production of a variety of specialty polymers in a single setup.

Prospects and Limitations of RAFT Polymerization in CSTRs. As this is the first report of continuous miniemulsion living radical polymerization of block copolymers, it is worthwhile discussing the relative intrinsic merits and disadvantages of this technique. First, the technique allows for the preparation of unique, multiblock 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 a 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 molecular weight distribution 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 where the first polymer block is missing. 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

Table 4. Composition and Block Lengths of the Block Copolymers Produced in the CSTR Train for Exp2

		block 1	block 2	block 3
stage 1	reactors[a]	R1 + R2	R3	R4
	STY/BA[b]	100/0	37/63	24/76
	rel wt[c]	1	1.32	0.69
	block length[d]	18.0×10^3	18.9×10^3	11.3×10^3
stage 2	reactors[a]	R1 + R2	R3	R4
	STY/BA[b]	100/0	12/88	23/77
	rel wt[c]	1	0.71	0.36
	block length[d]	25.7×10^3	12.3×10^3	7.5×10^3
stage 3	reactors[a]	R1 + R2	R3	R4
	STY/BA[b]	100/0	13/87	23/77
	rel wt[c]	1	0.70	0.39
	block length[d]	30.8×10^3	15.2×10^3	7.0×10^3

[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 the GPC data [g/mol].

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 unnucleated particles to the small number that contain oligomeric chains (oligomers are known to be very effective swelling agents).[41] As the 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 particles. 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 droplet rupture. Overall, this monomer transport mechanism can lead to droplets that are "sucked dry" of monomer,[27,33,34] which has implications for the types of polymer chains that will be formed in the system.

Conclusions

It has been shown that a miniemulsion polymerization performed in a CSTR train is an effective way to produce (multi)block copolymers in a continuous way. It was also demonstrated that the composition and block lengths can easily be varied by changing flow rates, temperatures, or the injection point of the second monomer. Comparison of RI GPC data and UV GPC data revealed that the percentage of living chains in the system was very high. Using mass balances, ^{1}H NMR data, and GPC, it was possible to calculate average length and compositions of each block. Low conversions of the initial styrene block led to bimodal distributions in BA block copolymerizations. The bimodality was not observed when styrene was used as the second block (chain extension) or when the first block was allowed to proceed to higher conversion before BA was added. Overall, this polymerization methodology offers the potential for several key advances, including (i) the ability to produce new block copolymers (due to the absence of composition drift) that cannot be made in traditional batch processes and (ii) lower cost production of block copolymers when perfectly sequenced block copolymers are not needed.

Acknowledgment. The authors thank the National Science Foundation for funding this work (CTS-0234658) and James Russum for useful discussions.

References and Notes

(1) Solomon, D. H.; Rizzardo, E.; Cacioli, P. U.S. Patent 4581429, 1985.
(2) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987.
(3) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.
(4) Wang, J. S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901.
(5) Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. PCT Int. Appl. 1998, WO 9801478.
(6) Rizzardo, E.; Thang, S. H.; Moad, G. PCT Int. Appl. 1999, WO 9905099.
(7) Corpart, P.; Charmot, D.; Biadatti, T.; Zard, S.; Michelet, D. PCT Int. Appl. 1998, WO 9858974.
(8) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559.
(9) Chong, Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 2071.
(10) Schellekens, M. A. J.; Klumperman, B.; van der Linde, R. *Macromol. Chem. Phys.* **2001**, *202*, 1595.
(11) de Brouwer, H.; Tsavalas, J. G.; Schork, F. J.; Monteiro, M. J. *Macromolecules* **2000**, *33*, 9239.
(12) Vasilieva, Y. A.; Thomas, D. B.; Scales, C. W.; McCormick, C. L. *Macromolecules* **2004**, *37*, 2728.
(13) Szablan, Z.; Toy, A. A.; Davis, T. P.; Hao, X.; Stenzel, M. H.; Barner-Kowollik, C. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 2432.
(14) Davis, K. A.; Matyjaszewski, K. *Adv. Polym. Sci.* **2002**, *159*, 2.
(15) Rizzardo, E.; Chiefari, J.; Chong, B. Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Thang, S. H. *Macromol. Symp.* **1999**, *143*, 291.
(16) Mayadunne, R. T. A.; Jeffery, J.; Moad, G.; Rizzardo, E. *Macromolecules* **2003**, *36*, 1505.
(17) Stenzel, M. H.; Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 4498.
(18) Baum, M.; Boyes, S.; Granville, A.; Mirous, B.; Sedjo, R.; Brittain, W. J. *Polym. Prepr.* **2002**, *43*, 72.
(19) Brittain, W. J.; Boyes, S.; Granville, A. M. *Abstracts of Papers,* 227th ACS National Meeting, 2004.
(20) Tsavalas, J. G.; Schork, F. J.; de Brouwer, H.; Monteiro, M. J. *Macromolecules* **2001**, *34*, 3938.
(21) Smulders, W.; Gilbert, R. G.; Monteiro, M. J. *Macromolecules* **2003**, *36*, 4309.
(22) Prescott, S. W.; Ballard, M. J.; Rizzardo, E.; Gilbert, R. G. *Macromolecules* **2002**, *35*, 5417.
(23) Ferguson, C. J.; Hughes, R. J.; Pham, B. T. T.; Hawkett, B. S.; Gilbert, R. G.; Serelis, A. K.; Such, C. H. *Macromolecules* **2002**, *35*, 9243.
(24) Ouzineb, K.; Graillat, C.; McKenna, T. *J. Appl. Polym. Sci.* **2004**, *91*, 2195.
(25) Barnette, D. T.; Schork, F. J. *Chem. Eng. Commun.* **1989**, *80*, 113.
(26) Samer, C. J.; Schork, F. J. *Ind. Eng. Chem. Res.* **1999**, *38*, 1801.
(27) Samer, C. J.; Schork, F. J. *Ind. Eng. Chem. Res.* **1999**, *38*, 1792.
(28) Aizpurua, I.; Barandiaran, M. J. *Polymer* **1999**, *40*, 4105.
(29) Aizpurua, I.; Amalvy, J. I.; de la Cal, J. C.; Barandiaran, M. J. *Polymer* **2001**, *42*, 1417.
(30) Shen, Y.; Zhu, S.; Pelton, R. *Macromol. Rapid Commun.* **2000**, *21*, 956.
(31) Shen, Y.; Zhu, S. *AIChE J.* **2002**, *48*, 2609.
(32) Russum, J. P.; Jones, C. W.; Schork, F. J. *Macromol. Rapid Commun.* **2004**, *25*, 1064.
(33) Russum, J. P.; Jones, C. W.; Schork, F. J. *Ind. Eng. Chem. Res.*, in press.
(34) Smulders, W. W.; Jones, C. W.; Schork, F. J. *AIChE J.*, in press.
(35) Schork, F. J.; Smulders, W. *J. Appl. Polym. Sci.* **2004**, *92*, 539.

(36) At the end of the CSTR train, it is common practice to utilize a small tubular reactor to polymerize the remaining monomer. If the conversion is high in the final CSTR, this will lead to only a very short polymer block with composition drift.

(37) Quinn, J. F.; Davis, T. P.; Rizzardo, E. *Chem. Commun.* **2001**, *11*, 1044.

(38) Beuermann, S.; Paquet, D. A., Jr.; McMinn, J. H.; Hutchinson, R. A. *Macromolecules* **1996**, *29*, 4206.

(39) Chambard, G.; Klumperman, B.; German, A. L. *Polymer* **1999**, *40*, 4459.

(40) McLeary, J. B.; Calitz, F. M.; McKenzie, J. M.; Tonge, M. P.; Sanderson, R. D.; Klumperman, B. *Macromolecules* **2004**, *37*, 2383.

(41) Luo, Y.; Tsavalas, J.; Schork, F. J. *Macromolecules* **2001**, *34*, 5501.

MA0487204