Controlled Free Radical Polymerization in Water-Borne Dispersion Using Reversible Addition−Fragmentation Chain Transfer

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ABSTRACT: A novel approach to conducting controlled free radical polymerization in water-borne organic dispersions using reversible addition−fragmentation chain transfer (RAFT) has been studied. The novel approach in this study focused on eliminating monomer and oligomer transport and comprised two fundamental steps: the synthesis of dithiobenzoate-end-capped styrene oligomers in bulk followed by emulsification of these oligomers to yield a polymerizable water-borne dispersion. Dithioesters that act as chain transfer agents in the RAFT process were synthesized in situ. The free radical polymerization of the dithiobenzoate-end-capped styrene oligomers in the water-borne organic dispersion proceeded in a controlled manner; molar mass increased in a linear fashion with increasing conversion, while polydispersities remained low. The familiar red layer formation associated with RAFT polymerization in conventional emulsions was not observed under these conditions. The effects of changing the costabilizer (hydrophobe) and the degree of polymerization of the emulsified oligomers were investigated. Better control was achieved with a less hydrophilic costabilizer and for the shorter of the oligomers tested.

Introduction

A vast range of synthetic materials are commercially produced by employing conventional free radical polymerization. Up to 50% of these free radical polymerization reactions are conducted in emulsions.[1] This combines the desirable features of the free radical process[2] (compatibility with a wide range of monomers, conventional reaction conditions, and tolerance of trace amounts of water and impurities) with those of emulsions, e.g., high conversions and reaction rates, excellent reaction heat dissipation, and low solvent content.

Termination of growing radicals and chain transfer are, however, features inherent to the mechanism of free radical polymerization. Chain transfer and termination of propagating radicals lead to a loss of control over molar mass and chain architecture as well as broadening of the molar mass distribution. These aspects may adversely affect the mechanical properties of the final material and lead to poor performance of the resulting latex in its ultimate application. Furthermore, termination of growing radicals means that there is no possibility of reinitiation of these species at a later stage, for example, in the preparation of block or gradient copolymers.

These limitations have led to the research field of controlled free radical polymerization (CFRP). Techniques such as reversible addition−fragmentation chain transfer (RAFT),[3] atom transfer radical polymerization (ATRP),[4,5] catalytic chain transfer,[6] nitroxide-mediated radical polymerization,[7] and degenerative chain transfer[8] have become common terminology among researchers worldwide. The common principle of these techniques is that the concentration of active, propagating radicals is kept very low by converting the propagating radicals to various dormant states, depending on the technique that is being used. This reduces the probability of termination, since the rate of termination is strongly dependent on the active radical concentration. Most of the chains are dormant, which allows control over molar masses, and subsequently the possibility of synthesizing polymers with complex architectures, since the suppression of termination reactions allows a “living” system.

One of the most robust and versatile techniques used to obtain control over the free radical polymerization process is RAFT.[3,9] In this technique organic compounds such as dithioesters and trithiocarbonates are used as chain transfer agents. The RAFT process is effective for a wide range of functional monomers and does not require stringent reaction conditions. The mechanism of the RAFT process is shown in Scheme 1.

In this process, initiator-derived primary radicals [I$^\bullet$] react with monomer units [M] to form oligomeric radicals [R$^\bullet$], which undergo addition to the carbon−sulfur double bond of the dithioester chain transfer agents. The resulting species then loses the group P, a good homolytic leaving group, as a radical capable of initiating a polymerization reaction or propagating further. Equilibrium is then established between active (propagating) and dormant polymer chains via the addition (rate coefficient k_{add}) and fragmentation (rate coefficient $k_{-\mathrm{add}}$) steps.

To gain acceptance in industry, techniques such as RAFT and other CFRP techniques must be successful in emulsion systems. Emulsions used in industry today are mostly water-based. This is in accord with the global trend toward being more environmentally friendly, as well as often offering additional advantages, such as easy processing of the latexes. The kinetics of emulsion polymerization is much more complex than that of conventional solution polymerizations. Therefore, a great deal of research effort has gone into improving the efficiency of these CFRP techniques in aqueous systems, in terms of obtaining a linear increase in molar mass with conversion and narrow molar mass distributions.[10−15]

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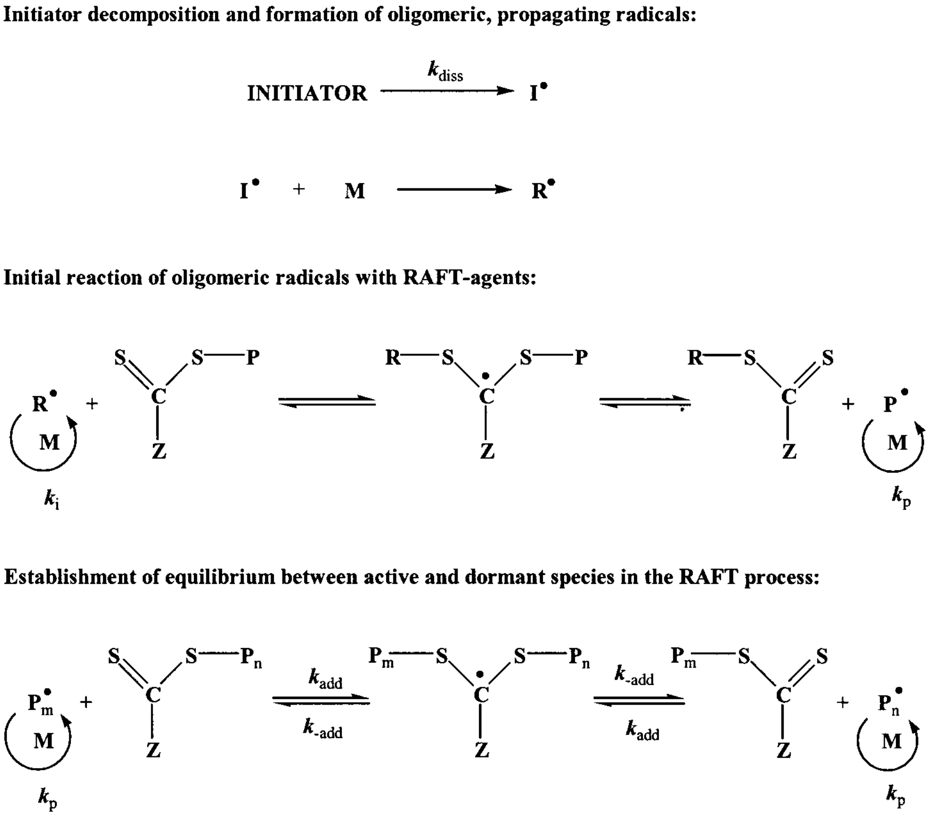
Scheme 1. Elementary Reactions of the RAFT Process

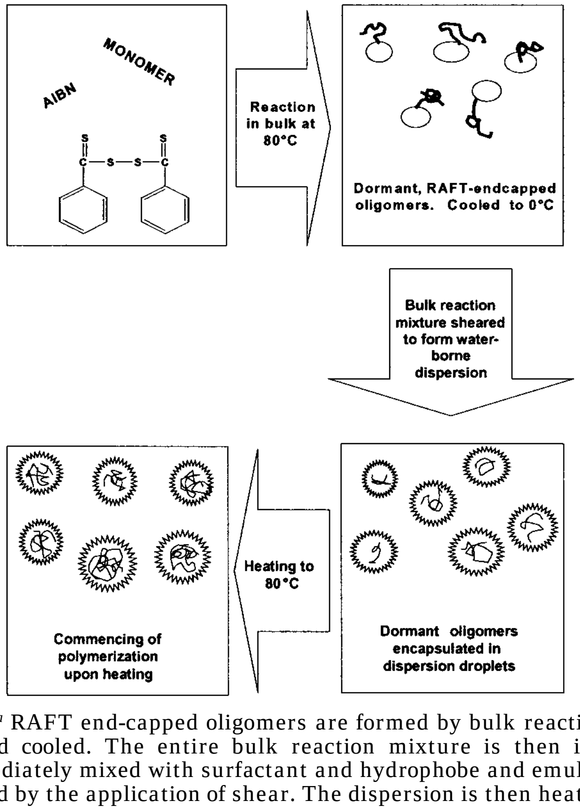


RAFT polymerization in emulsions has also received much attention.[16,17] A common feature of these efforts has been a phase separation resulting in the formation of a red layer. Analysis of this layer has shown it to consist of monomer-swollen, dithiobenzoate-end-capped oligomers.[18] It was suspected that, due to their water insolubility, these oligomers have difficulty being transported across the aqueous phase to nucleation sites.

Two options, both intent on bypassing interval II in conventional emulsion polymerization, are available for researchers to pursue, in order to overcome the problems associated with water-phase transport. The first is elimination of transport of water-insoluble components by polymerizing in miniemulsion[3,18,19] and by using starved-feed conditions.[20] The second option is the facilitation of transport by using "associative vehicles", such as water-soluble sugars[21] or solvents,[22] to improve transport across the aqueous phase in conventional emulsion systems.

Our approach was to first synthesize the troublesome, dithiobenzoate-end-capped oligomers in bulk. The bulk reaction mixture was to be then transferred to a water/surfactant/cosurfactant mixture and sheared to yield an oligomer-containing, polymerizable miniemulsion. The dithio moieties would then be situated on an oligomer that was beyond its limiting degree of polymerization for water solubility and encapsulated in a miniemulsion droplet. Additional stability was provided through equilibrium swelling of the oligomers by monomer, ensuring further preservation of the droplets. The addition of polymer to miniemulsions for additional stability has been well described in the literature.[23-25] Polymerization could then recommence upon heating of the resulting miniemulsion. A flow diagram of this approach is shown in Scheme 2.

Scheme 2. Flow Diagram of the Novel Approach to Preparing an Organic Water-Borne Dispersion Followed in This Study[a]



[a] RAFT end-capped oligomers are formed by bulk reaction and cooled. The entire bulk reaction mixture is then immediately mixed with surfactant and hydrophobe and emulsified by the application of shear. The dispersion is then heated to reaction temperature to recommence RAFT polymerization.

RAFT agents were synthesized in situ by reacting bis(dithiobenzoyl) disulfide and 2,2′-azobis(isobutyronitrile) (AIBN) in the presence of styrene monomer. This

Table 1. Conversion and SEC Results of RAFT-End-Capped Styrene Oligomers Synthesized by in Situ RAFT Bulk Reaction of AIBN (0.162 g), Bis(dithiobenzoyl) Disulfide (0.201 g), and Styrene (26.25 g) at 80 °C after 60 and 80 min

reaction time bulk (min)	$\bar{M}_n$	$\bar{M}_w$	PDI
60	3400	4200	1.23
80	7100	9800	1.39

eliminated time-consuming and laborious purification of the final dithioesters, which are usually viscous oils.

Experimental Section

Chemicals. Styrene (Acros Organics, 98%) was extracted with two equal aliquots of a 0.3 M aqueous KOH solution to remove inhibitors and distilled at reduced pressure. The middle fraction was collected and stored over molecular sieves (4 Å) at 2 °C for no longer than 1 week for later use.

Azobis(isobutyronitrile) (AIBN, Delta Scientific, 98%), was recrystallized from methanol. The water that was used was distilled and deionized (DDI). Sodium lauryl sulfate (SLS, BDH, 90%), 1-hexadecanol (cetyl alcohol, Acros Organics, 96%), *n*-hexadecane (Acros Organics, 99%), bromobenzene (Fluka, 99%), carbon disulfide (Aldrich, 99.9%), dimethyl sulfoxide (DMSO, Saarchem, 99.5%), and hydroquinone (Aldrich, 99%) were used as received.

Analysis. Molar masses were determined using size exclusion chromatography (SEC). Samples were prepared for SEC analysis by drying the polymer in vacuo and redissolving ca. 5 mg of the polymer in 1 mL of THF. The SEC instrument consisted of a Waters 717_{plus} autosampler, a Waters 600E system controller, and a Waters 610 fluid unit. A Waters 410 differential refractometer was used at 35 °C as detector. Tetrahydrofuran (THF, HPLC grade) sparged with IR grade helium was used as eluent at a flow rate of 1 mL min^{-1} and 60 min per sample. The column oven was kept at 35 °C, and the injection volume was 100 μL. Four Phenogel columns (300 mm × 7.80 mm) with respective pore sizes of 100, 10^3, 10^4, and 10^5 Å were used in series. The system was calibrated using six narrow polystyrene molar mass standards in the range of 4000−2000 000 g mol^{-1}, supplied by Pressure Chemical. Molar masses and structures of oligomers were determined using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI−TOF MS). Samples for analysis by MALDI−TOF were prepared as follows: 10 mg of the polymer sample was dissolved in 1 mL of THF, 1 mg of matrix in 1 mL of THF, and 10 mg of dithranol in 1 mL of THF. These three solutions were mixed in a ratio of 1:1:8 (sample:Ag-TFA: dithranol). A 2 μL aliquot of this final solution was loaded into a single well of a gold-coated MALDI plate and air-dried before placement in the vacuum chamber of the instrument. MALDI−TOF MS was carried out on a PerSeptive Biosystems Voyager-DE Pro mass spectrometer operating in linear mode. The instrument was equipped with a nitrogen laser ($\lambda = 337$ nm) and calibrated using a mixture of insulin (bovine, peak at 5734.59 g mol^{-1}), thioredoxin (*E. coli*, peak at 11 674.48 g mol^{-1}), and apomyoglobin (horse, peak at 16 952.56 g mol^{-1}). Silver(I) trifluoroacetate (Ag-TFA) was used as a matrix, and THF was used to dissolve both the matrix and the sample. The accelerating voltage was 20 kV, the grid voltage 94.5%, the guide wire voltage 0.050%, and the pressure 2.66×10^{-7} Torr. Spectra were collected as the averages of 256 scans.

Preparation of Bis(dithiobenzoyl) Disulfide. Synthesis was based on a reaction of Rizzardo et al.[26] Bromobenzene (11.30 g, 0.072 mol) in 30 mL of dry THF was added over a period of 30 min, at 0 °C, to magnesium turnings (2.0 g, 0.082 mol), a catalytic amount of iodine, and bromobenzene (1.26 g, 0.008 mol) in THF (10 mL). The reaction was started by mild heating. CS_2 (6.10 g, 0.080 mol) was added dropwise to the reaction mixture, keeping the temperature below 20 °C. The Grignard product was hydrolyzed with 100 mL of cold, distilled water, and the formed salts, together with excess Mg turnings, were removed by filtration. After removal of THF under reduced pressure the reaction mixture was acidified to pH 1 by the dropwise addition of fuming HCl. The color changed from brown-red to a permanent deep purple. The mixture was extracted three times with 200 mL of diethyl ether. After drying the organic phase over $MgSO_4$, the ether was removed under vacuum. The red oil so obtained was dissolved in 100 mL of absolute ethanol and reacted with DMSO (12.50 g, 0.160 mol) in the presence of a catalytic amount of iodine at room temperature for 1 h. After keeping the reaction mixture at 0 °C for 12 h, the resulting precipitate was filtered, redissolved in ethanol at 40 °C, and recrystallized. After drying, bis(dithiobenzoyl) disulfide (5.20 g, 82%, purity (^{1}H NMR) >90%) was obtained as a purple, crystalline product.

Preparation of Styrene Oligomers in Bulk Using RAFT. Oligomers of different lengths were prepared in separate bulk reactions (a total of four batches, corresponding to the four reactions after emulsification). A typical bulk reaction was prepared as follows: styrene (ca. 26.25 g, 0.252 mol) was degassed for 30 min by bubbling N_2 through the monomer. AIBN (0.162 g, 0.0009 mol) and bis(dithiobenzoyl) disulfide (0.201 g, 0.0007 mol) (the 1.5:1 molar ratio of AIBN to bis(dithiobenzoyl) disulfide compensated for cage effects[27]) were added, and the mixture was degassed for another 30 min. The reaction mixture was kept under N_2 and heated to 80 °C. Thus, the RAFT agent was formed by heating the bis(dithiobenzoyl) disulfide in the presence of AIBN, as shown in Scheme 3.[27]

The degrees of polymerization of the styrene oligomers obtained in bulk were varied by changing the reaction time, with some variability between batches. The reactions were run for 60 min (60 min oligomers, 15−20% conversion) and 80 min (80 min oligomers, similar, higher conversion) before stopping by rapid cooling and exposure to the atmosphere. Samples were taken and precipitated using a 2.5% (m/v) solution of hydroquinone in methanol for SEC analysis. Samples for MALDI−TOF analysis were removed and cooled and dried by careful evaporation of excess monomer to avoid possible complications with the end group analyses. The bulk SEC results and final conversions for the bulk reactions are shown in Table 1.

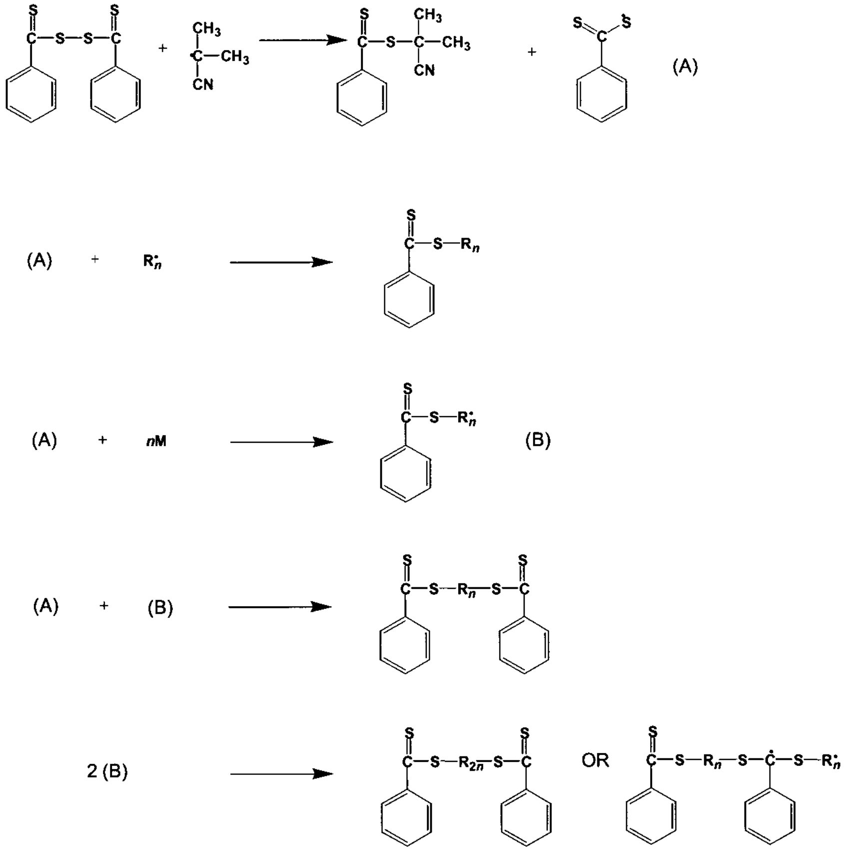
Preparation of Dispersions Employing SLS and *n*-Hexadecane as Emulsifiers. SLS (0.433 g, 0.0015 mol) was dissolved in water (150 g), and *n*-hexadecane (*n*-HD, 1.359 g, 0.0060 mol) was dissolved in the styrene bulk reaction mixture. After combining the two mixtures, the resulting mixture was sheared at 4000 rpm (Silverson L4R high shear mixer) for 1 h.

Preparation of Dispersions Employing SLS and Cetyl Alcohol as Emulsifiers. SLS (0.433 g, 0.0015 mol) and cetyl alcohol (1-HD) (1.455 g, 0.0060 mol) were mixed at 70 °C for 2 h to form an aqueous gel. After cooling, the gel was added to the styrene bulk reaction mixture and sheared at 4000 rpm for 1 h.

Polymerization in Dispersions. After shear, the dispersions were degassed by bubbling through N_2 for 30 min. The temperature was then raised to the reaction temperature (80 °C). Samples were taken to determine the conversion gravimetrically and to determine the molar mass during the course of the reaction by SEC.

A typical reaction example is as follows. *n*-Hexadecane (1.359 g, 0.0060 mol) was dissolved in a solution consisting of the entire reaction mixture of RAFT-end-capped oligomers synthesized by the in situ RAFT bulk reaction of AIBN (0.162 g), bis(dithiobenzoyl) disulfide (0.201 g), and styrene (26.25 g) at 80 °C for 60 min (containing about 20 wt % oligomer). The mixture was dissolved in a solution of SLS (0.433 g, 0.0015 mol) in water (150 g). The resulting mixture was sheared at 4000 rpm for 1 h and heated to 80 °C. After 12 h, the reaction was stopped, and the polymer was isolated by precipitation in a 2.5% (m/v) solution of hydroquinone in methanol to give polystyrene (67% conversion, $\bar{M}_n = 19\,000$, $\bar{M}_w/\bar{M}_n = 1.46$ by SEC).

Scheme 3. Reactions that May Occur from the Reaction of Bis(dithiobenzoyl) Disulfide with AIBN Initiator



Results and Discussion

An important factor in the performance of this system involves the in situ generation of RAFT chains. Scheme 3 shows that the production of growing RAFT chains by the in situ generation process does not result in loss of radical activity due to the reaction of the initiating radicals with the bis(dithiobenzoyl) disulfide. The species generated during the reaction of the initiator fragment with the bis(dithiobenzoyl) disulfide include radical species (A). This species is probably quite stable and has previously been suggested to be unreactive.[27] However, it is possible that this species may undergo side reactions other than directly producing RAFT-end-capped chains. This is consistent with the MALDI–TOF observations discussed later. The species produced by these side reactions may have greater chain lengths than the "typical" growing chain produced by normal RAFT initiation. It should also be noted that the formation of radical species (A) allows the formation of chains containing two RAFT agents. Thus, chains with architecture other than that typical of RAFT polymerization reactions are possible. Also, induced decomposition of the bis(dithiobenzoyl) disulfide may occur, due to a propagating radical reaction with the bis(dithiobenzoyl) disulfide, and thus it is possible that the RAFT agent is "released" into the polymerization reaction faster than may be predicted on the basis of initiator decomposition alone.

MALDI–TOF Characterization of Oligomers. The effect of oligomer length on the performance of the resulting dispersions was determined using the 60 and 80 min polystyrene RAFT end-capped oligomers.

Obtaining useful MALDI–TOF spectra of the oligomers was difficult, and resolution was poor. Both 60 and 80 min oligomers were analyzed using MALDI–TOF MS. The spectrum obtained for the 60 min oligomers is shown in Figure 1. MALDI spectra can be used to determine whether the dormant polystyrene oligomers are dithiobenzoate-end-capped.[28]

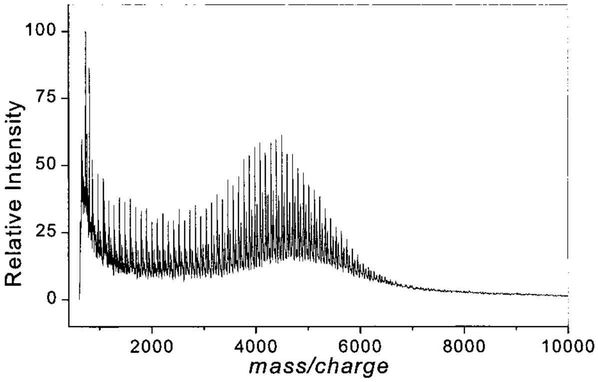


Figure 1. MALDI–TOF MS spectrum of the styrene oligomers synthesized by the in situ RAFT bulk reaction of AIBN (0.162 g), bis(dithiobenzoyl) disulfide (0.201 g), and styrene (26.25 g) at 80 °C for 60 min.

To prove the presence of a dithiobenzoate end group, any mass peak in the MALDI–TOF spectrum should fit the following expression:

$$M_{\text{peak}} = M_{\text{initiator}} + nM_{\text{monomer}} + M_{\text{end group}} + M_{\text{counterion}} \quad (1)$$

where M_{peak} is the molar mass value of the selected peak, $M_{\text{initiator}}$ the molar mass of the initiating group, M_{monomer} the molar mass of the monomer, n the number of monomer repeat units, $M_{\text{end group}}$ the molar mass of

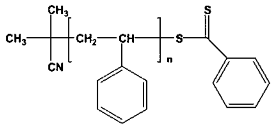


Figure 2. General expected structure of the oligomers synthesized by in situ RAFT bulk polymerization.

chain end group, and $M_{\text{counterion}}$ the molar mass of counterion used for ionization. The calculated value for n should be very close to a positive integer. The expected general structure of the oligomers is shown in Figure 2. The corresponding masses for the major products are $M_{\text{initiator}} = 68.09$ g mol^{-1}, $M_{\text{dithiobenzoate end group}} = 153.25$ g mol^{-1}, and $M_{\text{counterion}}(\text{Ag}^{+}) = 107.86$ g mol^{-1}. Figure 2 shows the expected structure of the oligomers that contain an AIBN initiating group and a dithiobenzoate end-cap.

The MALDI−TOF spectrum of the oligomers synthesized in bulk for 60 min (Figure 1) shows that there is a regular spacing of peaks, corresponding to the styrene repeat unit (104.13 g mol^{-1}), and the peak molar mass lies at 4185.84 g mol^{-1}. The peak molar mass corresponds to a value of 37.04 for the number of styrene repeat units (n) and is consistent with the expected structure of the oligomers in Figure 2. When the same is done for the oligomers synthesized in bulk for 80 min, a value of 76.97 (with corresponding peak molar mass 8344.09 g mol^{-1}) is obtained for n. The scatter about an integral value of n is observed throughout the spectrum, is within the uncertainties in peak positions in the spectrum, and is due to poor resolution.

This confirmed that the polystyrene oligomers contain dithiobenzoate end-caps, which were capable of being reactivated for further propagation.

Other distributions with spacings corresponding to the styrene repeat unit were also evident. All of these distributions were assignable to species formed by the RAFT process. Some of these are due to different initiator end groups, such as the termination products corresponding to chains initially formed by monomer initiation (effectively with no initiator end group). A significant secondary distribution corresponds to species containing two RAFT groups, four initiator end groups, styrene repeat units, and the Ag^{+} counterion. This species is presumably due to peculiarities associated with the in situ generation of the RAFT agent, which allows multiple RAFT agents per chain (see Scheme 3), each of which may be terminated by another chain containing an initiator end group. These peaks could thus correspond to the case of two midchain RAFT groups being terminated by short-chain groups containing initiator end groups. Artifacts resulting from the ionization process in MALDI−TOF have also been reported in the literature.[29] The most important of these is the possibility of dimer formation and detection during time-of-flight experiments. Such an effect could also give rise to the second observed distribution, although the second (artifact) distribution would then be expected at twice the masses of the main distribution. Thus, it is unlikely that this effect is the source of the second observed distribution, although tests to eliminate this possibility were inconclusive, due to the difficulties in reliably obtaining useful spectra. Further investigations of higher resolution MALDI−TOF spectra are in progress.

Table 2. SEC Results for the Polymerization at 80 °C of Two Different Oligomers Synthesized by the in Situ RAFT Bulk Reaction of AIBN (0.162 g), Bis(dithiobenzoyl) Disulfide (0.201 g), and Styrene (26.25 g) at 80 °C for 60 and 80 min and Emulsified in Water (150 g) Employing a SLS (0.433 g)/*n*-HD (1.359 g) Emulsifier Combination

conv[a] (%)	$\bar{M}_{\text{n}}$	$\bar{M}_{\text{w}}$	PDI
Run A: SLS/*n*-Hexadecane + 60 min Oligomers			
33	10 700	13 100	1.22
40	13 100	16 900	1.30
51	16 200	22 200	1.37
62	17 200	24 100	1.41
67	19 000	27 700	1.46
Run B: SLS/*n*-Hexadecane + 80 min Oligomers			
31	8400	10 000	1.20
35	12 200	15 900	1.31
43	13 500	17 800	1.31
51	16 600	23 100	1.39
63	19 700	30 300	1.53
71	21 500	33 900	1.58

[a] Conversion is with respect to the initial amount of monomer used in the initial bulk reaction.

Table 3. SEC Results for the Polymerization at 80 °C of Two Different Oligomers Synthesized by the in Situ RAFT Bulk Reaction of AIBN (0.162 g), Bis(dithiobenzoyl) Disulfide (0.201 g), and Styrene (26.25 g) at 80 °C for 60 and 80 min and Emulsified Employing a SLS (0.433 g)/1-HD (1.455 g) Emulsifier Combination

conv[a] (%)	$\bar{M}_{\text{n}}$	$\bar{M}_{\text{w}}$	PDI
Run C: SLS/1-Hexadecanol + 80 min Oligomers			
31	9 100	12 100	1.33
40	11 300	16 100	1.42
44	13 900	22 000	1.59
51	15 600	26 900	1.73
63	17 800	33 000	1.83
69	19 600	39 300	2.01
Run D: SLS/1-Hexadecanol+ 60 min Oligomers			
31	8 600	17 700	2.06
36	10 300	19 800	1.94
43	12 100	24 600	2.03
50	15 500	33 600	2.17
65	19 000	44 200	2.32

[a] Conversion is with respect to the initial amount of monomer used in the initial bulk reaction.

Recommencing of Polymerization in Dispersion. After the initial bulk step, *n*-hexadecane and 1-hexadecanol were used as cosurfactants in a 4:1 ratio with the anionic surfactant, SLS, in the emulsification step. For each of the two SLS/cosurfactant emulsifier combinations the effect of changing the molar mass of the emulsified oligomers was also investigated. The results of each emulsifier combination employed with each of the two different oligomers are shown in Tables 2 and 3 and in Figures 3 and 4 (conversions given are with respect to the initial amount of monomer used in the bulk step). Final particle sizes for these systems were much larger than for a typical miniemulsion (approximately 600−700 nm diameter as measured using dynamic light scattering). This is presumably due to the relatively low shear used in the preparation of the dispersions but is also likely to be due to stability issues due to swelling of droplets with the RAFT oligomers, since the particle size for dispersions prepared without the oligomers (150−200 nm) is much smaller.

The following discussions of the results of these polymerizations will be compared what might be expected for miniemulsion polymerizations. This comparison is useful because of the basic similarities between miniemulsions and the systems studied here, such as

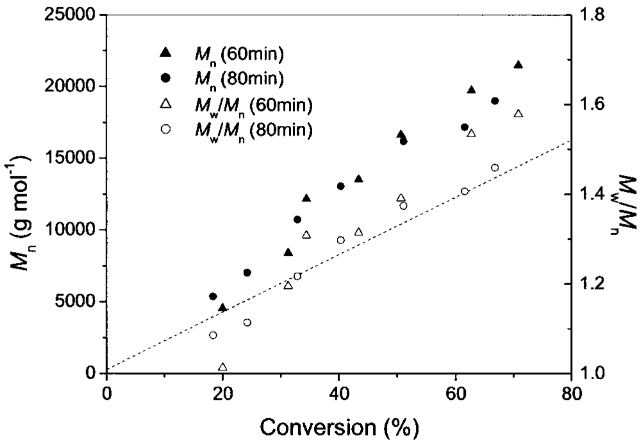


Figure 3. Number-average molar mass and polydispersity vs conversion at 80 °C for the polymerization of two different oligomers synthesized by the in situ RAFT bulk reaction of AIBN (0.162 g), bis(dithiobenzoyl) disulfide (0.201 g), and styrene (26.25 g) at 80 °C for 60 and 80 min and emulsified in water (150 g) employing a SLS (0.433 g)/*n*-HD (1.359 g) emulsifier combination. The dotted line indicates predicted molar masses.

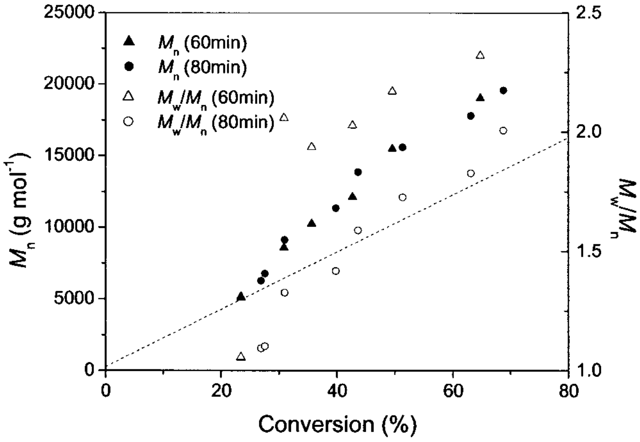


Figure 4. Number-average molar mass and polydispersity vs conversion at 80 °C for the polymerization of two different oligomers synthesized by the in situ RAFT bulk reaction of AIBN (0.162 g), bis(dithiobenzoyl) disulfide (0.201 g), and styrene (26.25 g) at 80 °C for 60 and 80 min and emulsified employing a SLS (0.433 g)/1-HD (1.455 g) emulsifier combination. The dotted line indicates predicted molar masses.

the use of the hydrophobic cosurfactant, and the initial droplet/particle formation by the application of shear.

In the SLS/*n*-hexadecane systems (Table 2, Figure 3) the molar mass increased in a linear and predictable fashion with increasing conversion, which is consistent with the behavior of a living system. Furthermore, the molar mass distribution remained relatively narrow, with polydispersity gradually increasing with conversion. Throughout the reaction, the observed molar masses were larger than those predicted (shown as a dotted line in Figure 3), with the deviation slowly increasing with conversion. This deviation may be in part attributed to incomplete conversion of the bis(dithiobenzoyl) disulfide to RAFT chains. This is certainly possible, since the purity of the bis(dithiobenzoyl) disulfide was between 90 and 100%. The increasing polydispersity and deviation of molar mass from predictions indicates gradual loss of control; i.e., the system is not ideal. The molar mass evolution is considered in further detail later.

Results of the dispersions employing 1-hexadecanol (Table 3, Figure 4) were not good, especially with regard to molar mass distributions. Fatty alcohols have been reported not to stabilize droplets in miniemulsions as efficiently against Ostwald ripening as do the corresponding alkanes.[24]

If this is the case, nucleation sites outside of the preformed droplets will therefore be better supplied with free monomer in a dispersion employing 1-hexadecanol than one using *n*-hexadecane as a cosurfactant. This may lead to uncontrolled, conventional emulsion polymerization sites that will cause a broadening of the molar mass distribution. This broadening was indeed observed in our systems employing 1-hexadecanol as cosurfactant, although the source was not directly verified. More importantly, the molar mass distributions in the 1-hexadecanol systems appeared to be bimodal, with a new component of (approximately constant) much higher molar mass than the original chains. This is strongly suggestive of extensive polymerization in the absence of the RAFT agent for the component corresponding to the new distribution, which in turn suggests polymerization outside the original dispersion droplets/particles. This will be addressed further in the discussion of the molar mass distributions below.

None of the emulsifier systems exhibited any colloidal destabilization as the polymerization reaction proceeded, and no phase-separated red layer was observed. This observation is different from some in previous studies of systems containing oligomeric RAFT agents,[18,19,30] where the latexes were destabilized when such RAFT agents were used. In those systems, the monomer type or degree of polymerization of the oligomers was different, and the miniemulsions were prepared differently, also resulting in different (usually smaller) particle sizes. An important difference here is that the entire bulk phase was dispersed after the period when a significant number of very short oligomers were present in the system, which is a speculated source of destabilization. Note also that in the current case the oligomers were preswollen with monomer in the bulk step, and there was no new batch of initiator added, as is typically the case when oligomeric or polymeric RAFT agents are used in miniemulsions. Presumably one or more of these factors is responsible for the observed differences. Many of the comparable systems consisted of much smaller particles, which were predicted to undergo superswelling by Luo et al.[31] The stability of the dispersions in this study is consistent with the predictions of Luo et al.,[31] who predict no superswelling-based destabilization for larger droplets and for high hydrophobe concentrations, such as is the case here.

The rates of reaction are similar to those observed in miniemulsion systems studied in this laboratory[32] starting with a normal RAFT agent. This suggests, but does not prove, that loss processes due to inefficiencies in the in situ generation of the RAFT agent are small, as may be expected by examination of Scheme 3, which suggests that most initiator-derived radicals result eventually in growing chains, with some termination events. Complete conversions seem to be unattainable in these systems, as shown in Figure 5.

One of the characteristics of the RAFT process (Scheme 1) is that the reversible deactivation reaction is much faster than the propagation reaction of the growing polymer chain ($k_{\mathrm{add}} \gg k_{\mathrm{p}}$). The deactivation

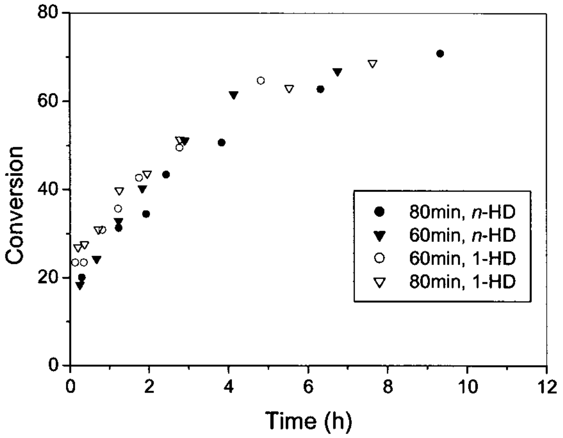


Figure 5. Conversion vs time at 80 °C for the polymerization of two different oligomers synthesized by the in situ RAFT bulk reaction of AIBN (0.162 g), bis(dithiobenzoyl) disulfide (0.201 g), and styrene (26.25 g) at 80 °C for 60 and 80 min and emulsified in water (150 g) employing a SLS (0.433 g)/*n*-HD (1.359 g) and a SLS (0.433 g)/1-HD (1.455 g) emulsifier combination.

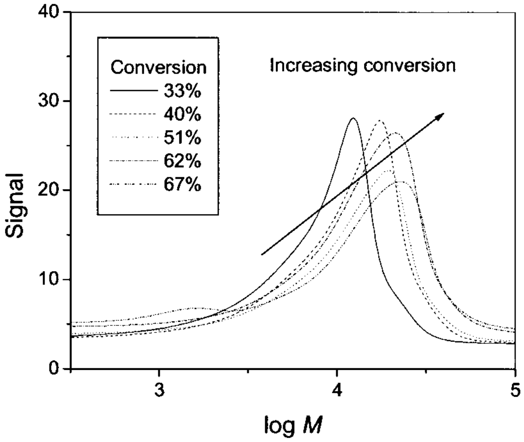


Figure 6. Molar mass distributions for the polymer produced by the reaction at 80 °C of oligomers synthesized by the in situ RAFT bulk reaction of AIBN (0.162 g), bis(dithiobenzoyl) disulfide (0.201 g), and styrene (26.25 g) at 80 °C for 60 min and emulsified in water (150 g) employing a SLS (0.433 g)/*n*-HD (1.359 g) emulsifier combination.

reaction is also faster than the reactivation of the dormant chain ($k_{\mathrm{add}} > k_{-\mathrm{add}}$). As conversion increases, higher internal viscosities of the droplets may cause the deactivation reaction of the RAFT process to become diffusion-controlled and to become slower (since this reaction is between long chains and the chemically controlled rate for deactivation is very rapid). This happens before the reactivation reaction becomes diffusion-controlled, causing the ratio of the rate coefficients of the deactivation and reactivation reactions ($k_{\mathrm{add}}/k_{-\mathrm{add}}$) to decrease. The relative concentration of the active species will then increase. Propagation will therefore not necessarily be faster, just more likely to take place (relatively) than before. The increase in the concentration of the active species may increase the probability of irreversible termination through bimolecular coupling. The change in the ratio of rate coefficients will probably also lead to broadening of the molar mass distributions. This is proposed as a possible explanation for the loss of control in the later stages of the reactions and is currently under investigation.

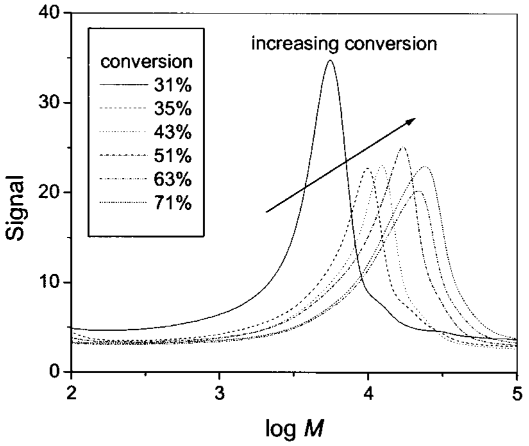


Figure 7. Molar mass distributions for the polymer produced by the reaction at 80 °C of oligomers synthesized by the in situ RAFT bulk reaction of AIBN (0.162 g), bis(dithiobenzoyl) disulfide (0.201 g), and styrene (26.25 g) at 80 °C for 80 min and emulsified in water (150 g) employing a SLS (0.433 g)/*n*-HD (1.359 g) emulsifier combination.

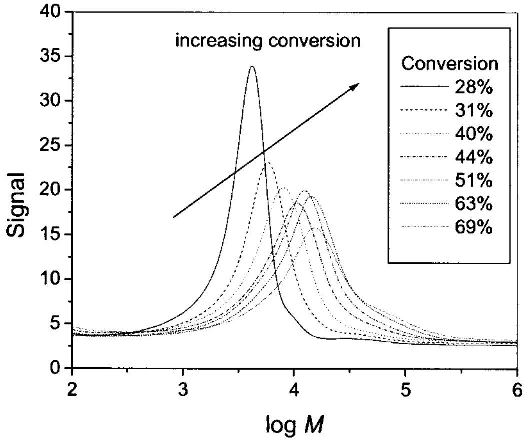


Figure 8. Molar mass distributions for the polymer produced by the reaction at 80 °C of oligomers synthesized by the in situ RAFT bulk reaction of AIBN (0.162 g), bis(dithiobenzoyl) disulfide (0.201 g), and styrene (26.25 g) at 80 °C for 80 min and emulsified in water (150 g) employing a SLS (0.433 g)/1-HD (1.455 g) emulsifier combination.

The molar mass distributions for the two different emulsifier systems are shown in Figures 6−9. In an ideal system where the free radical polymerization process is conducted in a controlled manner, the molar mass distribution should become narrower as the polymerization reaction progresses, and molar mass as a function of conversion should be predictable. The curves shown in Figures 6−9 show the signal obtained from the SEC instrument vs the logarithm of the molar mass of the two different emulsifier systems containing the different oligomers. The different reactions are referred to as follows:

Reaction A: SLS/*n*-hexadecane (*n*-HD) system containing oligomers synthesized in bulk for 60 min.

Reaction B: SLS/*n*-HD system containing oligomers synthesized in bulk for 80 min.

Reaction C: SLS/1-hexadecanol (1-HD) system containing oligomers synthesized in bulk for 80 min.

Reaction D: SLS/1-HD system containing oligomers synthesized in bulk for 60 min.

In Figure 6 all curves show tailing toward the lower molar mass region. This could be indicative of some fraction of the oligomers not being reinitiated in the

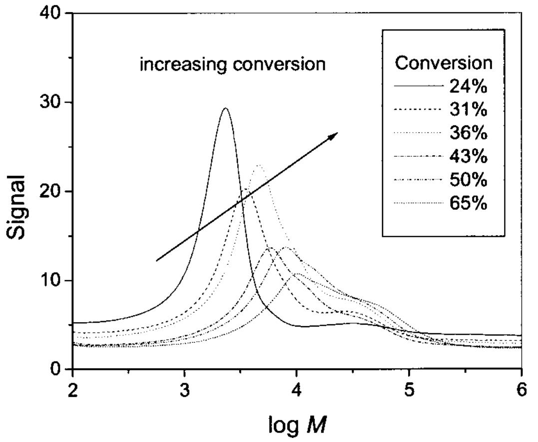


Figure 9. Molar mass distributions for the polymer produced by the reaction at 80 °C of oligomers synthesized by the in situ RAFT bulk reaction of AIBN (0.162 g), bis(dithiobenzoyl) disulfide (0.201 g), and styrene (26.25 g) at 80 °C for 60 min and emulsified in water (150 g) employing a SLS (0.433 g)/1-HD (1.455 g) emulsifier combination.

miniemulsion polymerization step. This tailing could be due to a large fraction of termination products during the polymerization, leaving a tail of shorter chains. The tailing may also be due to delayed release of RAFT agents (of lower molar mass, due to shorter growth periods), due to the nature of their in situ formation, which may occur until significant conversions are reached. Another important factor that may be a peculiarity of the in situ RAFT formation process is the nature of some of the chains that may be formed by this process (see Scheme 3). Some of these species can have multiple growth sites when more than one RAFT agent exists per chain and thus gives chains of higher molar mass. If termination of the intermediate radical is possible, the terminated product may have significantly higher molar mass than the living chains. Some of these terminated chains may cease growing (the situation being complicated by the possibility of more than one growth site per chain), leading to broadening of the molar mass distribution with conversion. Moreover, such termination reactions reduce the amount of RAFT agent per chain, thus increasing the average molar mass of the chains later formed, since there is now more monomer per growing chain. Thus, deviation above the predicted molar mass by this mechanism, while still retaining much of the living character, is a strong possibility. This is consistent with the observations. A further factor that is consistent with such a mechanism is the high molar mass peak beyond the main peak at the lowest conversions. This peak is presumably due to a termination process (giving a molar mass 2 or more times the average, as observed). A similar peak is not evident in later samples, which may be because the formation and termination of these species only occurs early in the polymerization, while a considerable amount of unreacted bis(dithiobenzoyl) disulfide is present. This would also cause a visible tailing toward low molar mass at intermediate conversions, as observed. The formation of significant amounts of polymer outside the droplets appears unlikely, since throughout the reaction there is no fraction of significantly different molar mass from the main distribution.

Broadening of the molar mass distribution in miniemulsion systems has been discussed by Butté et al.[30] The two factors suggested for the broadening in that study were a broad spread of droplet nucleation times, leading to uneven distribution of RAFT agents between particles, and the potential loss of living character of the polymeric RAFT agents before the reaction starts (leading to a low molar mass tail of unactivated chains). A large spread of nucleation times is unlikely in this system, because of the large particle sizes. The large particle sizes lead to a large average number of propagating radicals per particle for most of the reaction (estimated to be about 40 from early in the reaction) and a very low particle number. The low particle number means that the probability of not nucleating a droplet quite early in the reaction is extremely low, since the rate of reaction is high, and thus the average number of propagating species per particle is high. The second of the events described above may occur in the current study and may lead to some broadening of the molar mass distribution. However, such an explanation seems unable to account for the significant increase in polydispersity with conversion, since the number of dead chains required would have to be very high.

The sample at 67% conversion in run A shows a significant fraction of its distribution in the lower molar mass region. This may also be an indication that at higher conversions shorter chains form by transfer and then terminate, since deactivation might have become diffusion-controlled at this stage. In Figure 7 the tailing toward the lower molar mass region is not as pronounced as in Figure 6, although it is still evident. The earlier samples (31–51% conversion) also show a significant high molar mass shoulder, which is not apparent for the later samples. This is qualitatively consistent with the behavior of run A.

There is very pronounced tailing (later characterized as secondary peak formation) toward the high molar mass region through the sample set in Figures 8 and 9 (much more distinct in Figure 9). Moreover, the polymer in the higher molar mass region is often of significantly higher molar mass than the main, “controlled” peak and does not change significantly with respect to the peak region with conversion. The relative amount of this polymer increases with conversion. The peak molar masses of the main peak are also much lower as a function of conversion than in Figures 6 and 7. These results strongly suggest that a large fraction of polymerization is occurring in an uncontrolled manner, in the presence of much less RAFT agent than for the controlled fraction.

This is consistent with polymerization reactions leading to high molar mass compounds at aqueous phase nucleation sites outside of the original emulsified droplets. Such polymerization sites probably contain little RAFT agent, especially if formed after the initial emulsification step, due to the likely poor transport of the water-insoluble RAFT agent through the aqueous phase. This will be more probable in the systems employing 1-hexadecanol as cosurfactant and SLS as surfactant than in the systems using SLS and *n*-hexadecane, due to poorer droplet stability. The tailing to high molar mass in Figures 8 and 9 may also be an indication of loss of control in the droplets themselves at high conversions, although Figure 9 is strongly suggestive of two environments: one where there is good molar mass control and another where there is very little.

Clearly, the control is much poorer for the 60 min oligomers than for the 80 min oligomers in the poor

1-HD system, suggesting that oligomer length is very important for systems that are not particularly stable. In the case of the better-performing *n*-HD systems, the 60 min oligomers appear to give better results (although not significantly better), and neither case shows evidence of growth outside the main locus of polymerization.

Conclusions

A simple, novel two-step approach has been taken to face the challenges of conducting RAFT polymerization in an aqueous medium. The objective of restricting all polymerization reactions to within dispersion droplets, to avoid red layer formation, was attempted using a preceding bulk step in which dithiobenzoate-end-capped oligomers were synthesized, followed by conducting the second part of the polymerization reaction after emulsification of the resultant oligomers. No destabilization of the latex, neither initially nor through the course of the reaction, was observed. The relative stability of the dispersions is consistent with the predictions of Luo et al.[31] The choice of cosurfactant (hydrophobe) proved to be an important variable in the performance of the dispersion, with alkanes proving to be more efficient than the corresponding fatty alcohols. The molar mass of the end-capped oligomers synthesized in bulk beforehand also played a role in the overall results. Lower molar mass oligomers gave better results, which is indicative of a larger portion of the droplet population being preserved against monomer diffusion[23−25] (since shorter chains will allow the preservation of smaller particles due to the oligomers' smaller radii of gyration).

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