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Exploitation of Compartmentalization in RAFT Miniemulsion Polymerization to Increase the Degree of Livingness

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ABSTRACT

It is demonstrated that the degree of livingness (chain-end fidelity) in RAFT polymerization for a given degree of polymerization can be markedly increased in miniemulsion polymerization relative to the corresponding homogeneous bulk system. Polymerization of styrene was conducted using a poly(methyl methacrylate) benzodithioate as macroRAFT agent in both miniemulsion and bulk. The substantially higher polymerization rate in miniemulsion, which is attributed to the segregation effect (compartmentalization) causing a reduction in the rate of bimolecular termination, makes it possible to reach a given degree of polymerization in a significantly shorter time than in the corresponding bulk system. As a consequence, fewer initiating radicals are required throughout the polymerization, leading to higher livingness in the more rapid miniemulsion system. It is demonstrated how this approach facilitates synthesis of high molecular weight block copolymers comprising slowly propagating monomers such as styrene and methacrylates.

KEYWORDS: livingness; RAFT; segregation; block copolymer; miniemulsion

INTRODUCTION

Reversible deactivation radical polymerization (RDRP)¹ is a powerful technique for synthesis of a wide range of well-defined polymer architectures. RDRP retains the versatility of radical polymerization along with much of the control of anionic polymerization - the most well-known variants of RDRP are reversible addition-fragmentation chain transfer (RAFT) polymerization,²⁻⁶ atom transfer radical polymerization (ATRP),⁷⁻⁹ and nitroxide-mediated polymerization (NMP).¹⁰⁻¹² RDRP was initially developed in homogeneous systems

(solution/bulk), but it is now possible to conduct RDRP in a wide variety of heterogeneous systems (emulsion polymerization etc).¹³⁻¹⁵ Heterogeneous systems have several advantages over homogeneous systems such as no use of organic solvents (in case of aqueous emulsion polymerization for example), improved heat transfer characteristics, lower viscosity of the final product, and the product (latex) can often be used directly without further treatment (e.g. coatings/paints, floor polishes and finishes).

RDRPs conducted in heterogeneous systems such as emulsion and miniemulsion polymerizations are inherently more complex than their homogeneous counterparts. One of the added complexities of a heterogeneous system is that of compartmentalization. Compartmentalization effects refer to how chemical reactions are influenced by physical confinement of reactants to small spaces, *e.g.* submicron-size monomer droplets and polymer particles.^{13,16-21} Such effects are fairly well understood theoretically both for RDRP systems based on the persistent radical effect such as NMP and ATRP, as well as degenerative transfer systems such as RAFT. RAFT emulsion polymerization was first reported in 1998, and has since been studied extensively.^{2,13,15,22} In the case of RAFT, the polymerization rate (R_p) is generally higher in a compartmentalized system such as a miniemulsion polymerization than in the corresponding homogeneous (bulk/solution) system due to segregation of propagating radicals leading to a reduced termination rate.²³⁻³⁰ Based on theoretical work by Tobita,²¹ a threshold particle diameter can be derived below which RAFT polymerization proceeds faster than its corresponding bulk polymerization. The polymerization rate in the presence of a RAFT agent (mainly dithiobenzoate-based systems) is however typically lower than in its absence – the origin of this observation has been debated extensively.³¹ The two main explanations proposed are (i) slow fragmentation of the intermediate radicals,³² and (ii) cross-termination between propagating radicals and intermediate radicals.³³⁻³⁵ It has however relatively recently been concluded that there is overwhelming evidence in favour of explanation (ii).³¹ It is usually observed that the extent of such retardation in the presence of a RAFT agent is greater in miniemulsion than in bulk.^{13,25} This has been proposed to have mainly two reasons:¹³ (i) In a zero-one system, the time a radical in a particle is able to propagate is reduced since the radical is in the form of a RAFT intermediate radical that does not propagate for part of the time;²⁵ (ii) Increased

rate of radical exit in case of a low MW RAFT agent with relatively hydrophilic R-group. However, the RAFT polymerization rate in miniemulsion is typically still higher than the corresponding bulk system.

In RAFT polymerization, the number of dead chains originating from bimolecular termination of propagating radicals ideally corresponds directly to the cumulative number of radicals generated from the initiator (depending on the mode of termination, *i.e.* combination vs. disproportionation).³⁶⁻³⁹ This follows from the simple fact that all radicals eventually terminate. In regards to maximization of the polymerization rate by increasing the initiation rate, there is consequently a trade-off between polymerization rate and livingness for a given degree of polymerization. However, if the rate of consumption of monomer per number of radicals generated (*i.e.* the kinetic chain length) can be increased, then the livingness can be increased without one having to pay the price of a low polymerization rate. This concept has been exploited to prepare high order multiblock copolymers via RAFT polymerization of monomers with a high propagation rate coefficient (k_p).³⁶⁻³⁹ Since the rate of polymerization is typically higher in miniemulsion than in the corresponding homogeneous system at the same initiation rate (R_i), less initiator is required to achieve the same degree of polymerization (and conversion) over the same polymerization time. As a result, miniemulsion polymerization can in theory be exploited to achieve higher degrees of livingness than the corresponding homogeneous system. Segregation of propagating radicals in emulsion polymerization can also be exploited in the same way to maintain high livingness for high degrees of polymerization in RAFT, thereby enabling synthesis of high MW polymers.^{40,41}

In the present work, we have quantified to what extent the polymerization rate can be increased in RAFT miniemulsion polymerization relative to the corresponding bulk system for a range of

different concentrations of a dithiobenzoate-based macroRAFT agent (*i.e.* different target degrees of polymerizations). It is demonstrated that this increase in polymerization rate can be exploited to achieve markedly higher degrees of livingness in miniemulsion than in bulk. The concept is illustrated by synthesis of high molecular weight triblock copolymer comprising the slowly propagating monomers styrene (S) and methyl methacrylate (MMA), which is not possible in the corresponding bulk system under the present conditions.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA, Sigma-Aldrich) and styrene (S, Sigma-Aldrich) were passed through a column of basic alumina (Ajax Chemical, AR) to remove inhibitor. Azobisisobutyronitrile (AIBN, Sigma-Aldrich) was purified by recrystallization from methanol. Toluene (Chem-Supply), sodium dodecyl sulfate (SDS, Ajax Chemical), hexadecane (HD, Sigma-Aldrich), dichloromethane (DCM, Ajax Chemical), potassium persulfate (KPS, Sigma-Aldrich), and tetrahydrofuran (THF, Chem-Supply) were used as received. The RAFT agent 2-cyano-2-propyl benzodithioate (CPDB, Sigma-Aldrich) was used as received. Distilled de-ionized (DDI) water was obtained from a Milli-Q water purification system.

Characterization

Monomer conversions were determined by gravimetry by drying the latex in a vacuum oven for 24 h and subsequently drying for 6 h in high vacuum oven at 45 °C. Number-average molar mass (M_n) and molar mass distribution (\mathcal{D}) were measured using a size exclusion chromatography (SEC) instrument with THF (HPLC grade stabilized with 2,6-dibutyl-4-methylphenol (BHT), 0.05% w/v) as the eluent at 40 °C and 1 mL/min⁻¹ equipped with an auto-injector Shimadzu SIL-10AD, 5.0 μ m bead-size guard column from Polymer Laboratories (50x7.5 mm²), 4 linear PL (Styragel) columns

(105, 104, 103 and 500 Å) and RID-10A differential refractive index (RI) and UV-Vis detectors. The theoretical molar mass ($M_{n,th}$) was calculated using equation 1:

$$M_{n,th} = \frac{[M]_0 \times M_M \times X}{[RAFT]_0} + M_{RAFT} \quad (1)$$

where $[M]_0$ and $[RAFT]_0$ are the initial monomer and RAFT concentrations, respectively, M_M is the molar mass of the monomer, X is the fractional conversion of monomer and M_{RAFT} is the molar mass of the macroRAFT agent. Droplet/particle diameters (d_z) and droplet/particle size distributions (PDI) were measured by Dynamic Light Scattering (DLS) using a Malvern Zetasizer Nano with DTS software. The instrument was equipped with a 4 mW He-Ne laser at a wavelength of 633 nm and an avalanche photodiode (APD) detector with the angle set at 173°.

Synthesis of PMMA macroRAFT

MMA was polymerized in the presence of CPDB RAFT agent (Scheme 1) to synthesize PMMA-based macroRAFT (PMMA-DTB). MMA (4.20 g), CPDB (0.186 g), AIBN (7×10^{-3} g) and 1.5 mL toluene were mixed in a 25 mL vial and degassed by purging nitrogen for 30 min in an ice bath. The oil bath was preheated at 70 °C and the vial was immersed for 12 h. The polymerization was stopped by cooling and the polymer was subsequently dissolved in dichloromethane and precipitated in cold methanol (repeated three times). Monomer conversion was determined by ¹H NMR, integrating the vinyl peaks of monomer (6.05 and 5.5 ppm) relative to that of the methoxy peak of the polymer backbone (3.6 ppm). Conversion 92 %, $L = 94.9$ % (Eq. 3), $M_{n,SEC} = 5350$ g mol⁻¹ ($M_{n,th} = 4900$ g mol⁻¹), $\mathcal{D} = 1.12$. (¹H NMR spectra for pure macroRAFT shown in Figure SI1)

Chain extension of PMMA macroRAFT (PMMA-DTB) in miniemulsion

PMMA-DTB ($M_{n,SEC} = 5350$ g mol⁻¹; $\mathcal{D} = 1.12$) was chain extended with styrene in miniemulsion

(Scheme 1 and Table 1). In a typical experiment, the organic and the aqueous phases were prepared separately. The organic phase was prepared by mixing styrene (2.5 g), PMMA-DTB (0.080–0.240 g) and hexadecane (0.125 g), and the aqueous phase was prepared by mixing SDS (0.125 g) and DDI water (9.5 g). A stock solution of KPS was prepared separately by dissolving KPS (0.0144 g) in DDI water (5 g). The organic phase was added to the aqueous solution of SDS, and subsequently ultrasonicated using a Branson 450 probe (maximum output power of 500 W) at an amplitude of 50% for 10 min. KPS stock solution (0.5 g) was then added and the vial was degassed by purging nitrogen for 30 min in an ice bath. The oil bath was preheated at 60 °C and the vial was immersed for the prescribed polymerization time. Samples were periodically withdrawn to monitor conversion by gravimetry, particle size by DLS, M_n and \bar{D} by SEC as functions of time. The polymerization was stopped by cooling using an ice bath.

Scheme 1. Synthesis of PMMA-*b*-PS diblock copolymer in miniemulsion and bulk. (Should be displayed in two columns)

Chain extension of PMMA macroRAFT (PMMA-DTB) in bulk

The concentration of AIBN (1.0×10^{-3} mol L⁻¹) was adjusted so that the rate of radical generation would be close to that of the corresponding miniemulsion polymerization (KPS = 1.9×10^{-3} mol L⁻¹, decomposition profile plot and cumulated concentration of generated radicals for AIBN and KPS in Figure S2). In a typical experiment styrene, PMMA-DTB, AIBN, hexadecane, and trioxane (internal standard) were added to a 25 mL vial, which was subsequently sealed and degassed by purging nitrogen for 30 min in an ice bath. The vial was immersed into an oil bath preheated at 60 °C for 24 h. Samples were periodically withdrawn to monitor conversion, M_n and \bar{D} by SEC as functions of time. Monomer conversion was calculated by ¹H NMR, integrating the vinyl

peaks of monomer (5.20 and 5.76 ppm) at t_0 and given time t against the trioxane peak (5.10 ppm).

Synthesis of triblock copolymer PMMA-*b*-PS-*b*-PS-DTB

PMMA block: PMMA-DTB was synthesized in bulk according to the procedure described in section “Synthesis of PMMA macroRAFT”. PMMA-*b*-PS-DTB was subsequently synthesized in miniemulsion following the procedure described in Section “Chain extension of PMMA macroRAFT (PMMA-DTB) in miniemulsion”. The temperature was 75 °C and the amount of PMMA-DTB (0.240 g) was adjusted to target 500 repeating units of styrene at full conversion. PMMA-*b*-PS-*b*-PS-DTB triblock copolymer: The latex (3 g) of PMMA-*b*-PS-DTB, water (2 g), styrene (0.573 g) and KPS (3.3×10^{-4} g) were charged into a 25 mL vial. The vial was sealed and degassed by purging nitrogen for 30 min. After 24 h of polymerization at 75 °C, polymerization was stopped by cooling and the conversion was measured by gravimetry.

RESULTS AND DISCUSSION

The overall objectives of the present work has been to (i) establish to what extent one can exploit the rate enhancement in RAFT miniemulsion polymerization vs. the corresponding RAFT solution/bulk polymerization to improve the degree of livingness, and (ii) to exploit this phenomenon for efficient synthesis of block copolymers of low k_p monomers. Two sets of experiments were conducted: In Exp 1–8 (Table 1), the polymerization rates in miniemulsion and the corresponding bulk systems were compared and various factors affecting the polymerization rates were investigated. In Exp 9–10 (Table 2), high DP triblock copolymers of the low k_p monomers styrene and MMA were synthesized.

Bulk and miniemulsion polymerization

PMMA-DTB mediated miniemulsion and bulk polymerizations of styrene (Exp 2–4 and 6–8,

respectively) were conducted at the same reaction conditions using the same recipes except that the miniemulsion systems contained water and surfactant. The amount of AIBN (bulk polymerizations) and KPS (miniemulsion polymerizations) were adjusted such that the rates of radical generation were similar for bulk vs miniemulsion (Figure S2). Three different degrees of polymerization (DP) of styrene were targeted at full conversion, *i.e.* 500, 1000 and 1500, and compared with the corresponding non-living systems (absence of macroRAFT agent, Exp 1 and 3).

Table 1 summarizes the experimental conditions and results for PMMA-DTB macroRAFT polymerization of styrene in bulk and miniemulsion. There are two important observations (Figures 1 and 2): (i) The polymerization rates were higher in miniemulsion than bulk for each target DP, and (ii) In the miniemulsion polymerizations, the polymerization rate increased markedly with increasing target DP, *i.e.* with decreasing amount of macroRAFT agent, but this trend was absent in bulk (Figure S3). Note that all polymerizations were stopped at 24h, reaching only 12% conversion in bulk, and hence the experimental DPs are lower in bulk than in miniemulsion (Table 1). Linear increases in M_n with conversion were observed for both systems with $M_n \approx M_{n,th}$ as expected for RAFT polymerization (Figure 3 and Figure S4). The droplet/particle size as determined by DLS (Figure 4) remained approximately constant with increasing conversion in all cases, consistent with droplet nucleation being the predominant nucleation mechanism. These general trends are consistent with previous experimental observations²³⁻³⁰ and theoretical work.^{21,27-30,42} The enhanced polymerization rate in miniemulsion is caused by segregation (compartmentalization) of propagating radicals leading to a reduced bimolecular termination rate. Luo *et al.*²⁵ studied the effect of PS-DTB macroRAFT concentration on styrene polymerization in miniemulsion using KPS at 75 °C. The results revealed that the rate of styrene

polymerization decreased with increasing macroRAFT concentration. However, in bulk polymerization the effect of macroRAFT concentration was negligible. Suzuki *et al.*^{29,30} observed that the PS-DTB mediated styrene polymerization in miniemulsion was much faster than corresponding bulk at 60 °C - a significant enhancement in rate was observed with miniemulsion droplets of approximately 107 nm in diameter due to reduced termination reactions.

Table 1. Experimental conditions and results for chain extensions of PMMA-DTB macroRAFT in miniemulsion and bulk. **(should be displayed in two columns)**

Figure 1. Conversion-time data for polymerization of styrene at 60 °C using various concentrations of PMMA-DTB macroRAFT (degree of polymerization of styrene at full conversion indicated by DPs in legend) in miniemulsion (filled symbols) and bulk (empty symbols) (see Table 1).

Figure 2. Initial polymerization rate plotted vs initial concentration of macroRAFT agent for polymerization of styrene at 60 °C using PMMA-DTB macroRAFT (degree of polymerization of styrene at full conversion indicated by DPs in legend) in miniemulsion (filled symbols) and bulk (empty symbols) (see Table 1).

Figure 3 Evolution of M_n and \bar{D} with conversion for polymerization of styrene at 60 °C using PMMA-DTB macroRAFT (degree of polymerization of styrene at full conversion indicated by DPs in legend) in miniemulsion (filled symbols) and bulk (empty symbols) (see Table 1). **(should be displayed in two columns)**

As outlined in the Introduction, the presence of a RAFT agent (especially for dithiobenzoates) is accompanied by a reduction in polymerization rate.³¹ The two main theories are (i) slow fragmentation of the intermediate radicals,³² and (ii) cross-termination between propagating radicals and intermediate radicals,^{33–35} although recently there is strong evidence in favour of the latter.³¹ In compartmentalized zero-one systems, *i.e.* dispersed systems where each droplet only contains zero or one radical for any kinetically significant time period (termination occurs instantaneously if two propagating radicals are present in one droplet/particle), an additional cause of retardation has been proposed to be the fact that some fraction of the time a droplet/particle is a “one” is “wasted” when the radical is present in the form of an intermediate radical (which does not propagate) as opposed to a propagating radical.²⁵ It is not trivial to unequivocally prove that a system is zero-one. Experimentally, it is required to demonstrate that even if the initiation rate is increased, the average number of propagating radicals per particle (\bar{n}) reaches a maximum value at 0.5. The value of \bar{n} was calculated for the miniemulsion polymerizations in the present study using eqn 2:

$$\bar{n} = \frac{\text{slope} \times V_p \times N_A}{k_p} \quad (2)$$

where “slope” (product of k_p and $[P\bullet]$) corresponds to that of the first-order plot of the monomer conversion vs time, V_p is the particle volume based on d_z , N_A is Avogadro’s Number and k_p is the propagation rate coefficient for styrene ($341 \text{ L mole}^{-1} \text{ s}^{-1}$ at 60°C).⁴³ The values of \bar{n} are below 0.5 in all cases (Figure 5), thus consistent with (but not proving) that these are zero-one systems. The extent of retardation increased with increasing RAFT concentration (lower targeted DP) as shown in Figure 2. Consistent with this observation, the value of \bar{n} decreased with increasing RAFT concentration (Figure 5).

Figure 4. Plots of particle diameter and PDI vs conversion for polymerization of styrene at

60°C using PMMA-DTB macroRAFT (degree of polymerization of styrene at full conversion indicated by DPs in legend) in miniemulsion (filled symbols) and bulk (empty symbols) (see Table 1).

Figure 5 Average-number of propagating radicals per particle plotted vs conversion for polymerization of styrene at 60°C using PMMA-DTB macroRAFT (degree of polymerization of styrene at full conversion indicated by DPs in legend) in miniemulsion (filled symbols) and bulk (empty symbols) (see Table 1).

The livingness represents the number fraction of living chains, *i.e.* chains possessing a RAFT end group at the ω -end. The number of dead chains corresponds to half the number of initiator radicals generated that initiate a chain if termination occurs by combination exclusively.³⁶ In order to improve the degree of livingness, the total number of radicals generated over the polymerization time should thus be minimized. This can be accomplished by (i) reducing the initiation rate (lower initiator concentration or use of an initiator that decomposes more slowly) or (ii) reducing the polymerization time (or both). However, both (i) and (ii) would lead to lower conversion (lower DP), all else being constant. It follows that, if we identify conditions where the polymerization rate is sufficiently high even at a lower initiation rate, we can increase the livingness.^{36–38} It is important to note that this reasoning does not apply to iniferter systems using RAFT agents⁴⁴ (incl. PET-RAFT,⁴⁵ where no exogenous radical source exists) or RDRP systems based on the persistent radical effect such as NMP and ATRP, where each termination event leads to the loss of a living chain. In RAFT polymerization the concentration of living chains ideally remains constant (in absence of RAFT end group degradation or other side reactions) throughout the polymerization, and the livingness can thus be predicted from eqn 3:⁴⁶

$$L = \frac{[CTA]_0}{[CTA]_0 + 2 \times f \times [I]_0 \times (1 - e^{-k_d t}) \times (1 - \frac{f_c}{2})} \quad (3)$$

$[CTA]_0$, $[I]_0$ are the initial concentrations of the RAFT agent and initiator, respectively and f_c is the fraction of propagating radicals that terminate via coupling. The term $2 \times f \times [I]_0 \times (1 - e^{-k_d t})$ corresponds to the total number of radicals generated from the initiator where f is the initiator efficiency (assumed to be 0.6 in the present work) and k_d is the rate constant of decomposition for KPS ($k_d = 5.1 \times 10^{16} e^{-140.2/RT}$)⁴⁷ and AIBN ($k_d = 4.47 \times 10^{15} e^{-131.7/RT}$).⁴⁸

Based on the significantly higher polymerization rates in miniemulsion than bulk, it follows that the livingness would, based on theory, be higher in miniemulsion for a given degree of polymerization. In order to quantify this effect, the theoretical livingness was plotted vs the experimental DP (Figure 6) for the miniemulsion and bulk polymerizations in Figure 1. The time taken to reach a given DP (conversion) allows one to calculate the theoretical livingness based on eqn 3 for each data point of Exp 2-4 and 6-8 (Table 1). The obtained livingness values were subsequently plotted vs. the corresponding experimental DP as obtained by M_n SEC. The resulting Figure 6 enables us to compare quantitatively the livingness for miniemulsion vs bulk as a function of DP. The thought behind this plot is to provide a roadmap indicating how a compartmentalized system can be exploited to access high DP with elevated polymerization rate relative to the corresponding homogeneous system. All the data series have an initial value of 94.9% at DP = 0, which corresponds to the livingness of the initial macroRAFT agent (eqn 3).

Figure 6. Livingness (from eqn 3) plotted as a function of experimental degree of polymerization for polymerization of styrene at 60 °C using PMMA-DTB macroRAFT (degree of polymerization of styrene at full conversion indicated by DP_s in legend) in miniemulsion (filled symbols) and bulk (empty symbols) (see Table 1).

As DP increases, there is a decrease in livingness as dead chains are progressively generated. The decrease in livingness to reach a given value of DP is more pronounced when the polymerization rate is low (*i.e.* in bulk vs miniemulsion) – this is a consequence of the fact that the two systems (bulk vs miniemulsion with the same target DP) have the same initiation rates, and therefore a higher number of radicals, and thus a higher number of dead chains, are generated in the slower bulk system. The results demonstrate that it is possible to achieve a higher value of DP with higher livingness in a miniemulsion system than in the corresponding bulk system.

Synthesis of triblock copolymer

High-order multiblock copolymers have been synthesized by RAFT polymerization but are typically limited to high k_p monomers such as acrylates and acrylamides.^{36-38,49-51} Methacrylate-based multiblock copolymers have recently been prepared by use of methacrylate macromonomers as “sulfur-free” RAFT agents in emulsion polymerization using a continuous monomer feed process via syringe

pump to keep the monomer concentration low (a requirement to render the methacrylate macromonomer approach “living”).^{22,52-55} As demonstrated above, polymer of a given DP can be prepared with higher livingness in the miniemulsion system than in the corresponding bulk system. Next, it is illustrated how this feature can be exploited to synthesize triblock copolymer involving low k_p monomers. PMMA-DTB was chain extended with styrene in miniemulsion to yield PMMA-*b*-PS-DTB (Exp 9), which was further extended by addition of a second batch of styrene monomer (no intermediate purification of PMMA-*b*-PS-DTB) to produce PMMA-*b*-PS-*b*-PS-DTB (Exp 10). High DPs of 500 were targeted for each PS block (Scheme 2 and Table 2). Successive MWDs are displayed in Figure 7 along with M_n and \bar{D} data in Figure 8, demonstrating good control/livingness with $M_n \approx M_{n,th}$ and $\bar{D} < 1.5$.

The theoretical livingness (Table 2; eqn 3) was 84.2 and 74.4% after the second and third blocks, respectively. Synthesis of such a triblock copolymer under the corresponding homogeneous conditions (bulk/solution) would invariably be next to impossible and leading to substantially lower livingness due to the low rate of polymerization.

Scheme 2. Synthesis of PMMA-*b*-PS-*b*-PS-DTB triblock copolymer. (should be displayed in two columns)

Table 2. Characteristics of PMMA-*b*-PS-*b*-PS-DTB triblock copolymer. (should be displayed in two columns)

Figure 7. Molecular weight distributions for the synthesis of PMMA-*b*-PS-*b*-PS-DTB (Exp 9, 10 in Table 2) triblock copolymer (the percentages in the legend indicate the individual styrene conversions for the 2nd and 3rd blocks).

Figure 8. Evolution of M_n and \bar{D} for PMMA-*b*-PS-DTB (red; Exp 9) PMMA-*b*-PS-*b*-PS-DTB (blue; Exp 10).

CONCLUSIONS

Synthesis of block copolymers, especially multiblock copolymers, by iterative RAFT polymerizations requires high livingness (end-group fidelity) to be attained at each polymerization step. The livingness achievable is closely related to the polymerization rate – the higher the value of k_p and the lower the value of k_t (termination rate coefficient), the lower initiation rate is required. The livingness is directly related to the initiation rate, given that each radical species eventually terminates, giving rise to dead chains. In the present work, it is demonstrated that due to the enhanced polymerization rate when conducting RAFT in a miniemulsion system comprising sufficiently small particles, the livingness can be improved relative to the corresponding bulk system. The rate enhancement in miniemulsion is due to the compartmentalization effect on the apparent k_t ,

causing a reduction in the termination rate. Polymerization of styrene was performed employing a dithiobenzoate-based poly(methyl methacrylate) macroRAFT agent in both miniemulsion and bulk. Based on the experimental polymerization rates coupled with theoretical calculations of the degree of livingness as a function of the degree of polymerization, it is clarified to what extent the livingness can be improved relative to bulk in a miniemulsion system. It is demonstrated that the present miniemulsion technique facilitates synthesis of high molecular weight block copolymers of low k_p monomers such as styrene and methacrylates.

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