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TEMPO-mediated radical polymerization of styrene in aqueous miniemulsion: Macroinitiator concentration effects

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ABSTRACT

The control/livingness in nitroxide-mediated polymerization of styrene (S) in aqueous miniemulsion at 125 °C employing a poly(S)-2,2,6,6-tetramethylpiperidinyl-1-oxy (PS-TEMPO) macroinitiator and the surfactant sodium dodecylbenzenesulfonate has been shown to depend strongly on the macroinitiator concentration for particles of approximate number-average diameter 65 nm. The control/livingness was relatively poor at $[\text{PS-TEMPO}]_0 \leq 0.02$ M due to the combined effect of enhanced spontaneous initiation and the interface effect (whereby deactivation is suppressed due to interfacial activity of TEMPO). Satisfactory control/livingness was obtained at higher $[\text{PS-TEMPO}]_0$ as a result of the interface effect and enhanced spontaneous initiation exerting less pronounced influence per chain than at lower $[\text{PS-TEMPO}]_0$. Polymerizations using the sulfonate surfactant DOWFAX 8390 gave similar results, indicating that the present macroinitiator concentration effects are not specific to SDBS-based systems. The results also demonstrate that TEMPO-mediated polymerization of S in miniemulsion can proceed at a higher rate than in bulk with good control/livingness.

1. Introduction

Precise control over macromolecular structure is not possible in conventional radical polymerization due to the overall polymerization time being much longer than the very short time that passes as each chain grows to its final molecular weight (MW). The development of controlled/living radical polymerization (CLRP), which is based on the concept of a dynamic equilibrium between propagating radicals and their corresponding dormant species, allows precise macromolecular engineering as a result of extending the time that a chain grows to last over the entire polymerization [1]. The CLRP methods that have received the most attention are nitroxide-mediated polymerization (NMP) [2,3], atom transfer radical polymerization (ATRP) [4,5], and reversible addition-fragmentation chain transfer (RAFT) polymerization [6,7].

One of the present challenges is the implementation of CLRP in aqueous dispersed systems [8–13]. In particular, *ab initio* emulsion NMP initially proved problematic. However, Charleux and coworkers recently carried out *ab initio* emulsion NMP by utilizing self-assembly of an *in situ* formed poly(sodium acrylate)-based amphiphilic diblock copolymer using *N-tert*-butyl-*N*-[1-diethylphosphono(2,2-dimethylpropyl)] (SG1) [14,15]. Cunningham and coworkers [16] reported successful *ab initio* emulsion NMP of styrene (S) employing two nitroxides, 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) and the extremely hydrophobic 4-stearoyl-TEMPO, where the purpose of the latter is to prevent monomer droplet nucleation. Implementation of NMP in miniemulsion [17–27] and microemulsion [28] has been fraught with much less difficulty. In a miniemulsion, monomer droplets are directly converted to polymer particles, and the complex nucleation step in *ab initio* emulsion polymerization is thereby avoided.

Miniemulsion NMP is characterized by several intrinsic features that are absent in the corresponding homogeneous systems. The extent of nitroxide partitioning to the aqueous phase may influence the polymerization [19,29,30], leading to higher polymerization rate (R_p) and lower control/livingness in the pre-stationary state [29]. For sufficiently small particles, compartmentalization may also affect the polymerization [31–36], manifesting itself as the confined space effect (leading to an increase in deactivation rate) and the segregation effect (leading to a decrease in termination rate). Moreover, the particle/water interface can influence the deactivation reaction in TEMPO-mediated aqueous miniemulsion polymerization of S at 125 °C employing the surfactant sodium dodecylbenzenesulfonate (SDBS) [25,27,37]. For sufficiently small particles (particle diameter < 110 nm), control/livingness was gradually lost with decreasing particle size, accompanied by a very marked increase in R_p [25,27]. This interface effect has its origin in interfacial activity of TEMPO [27,38], resulting in some fraction of TEMPO being located at/in the vicinity of the interface, causing a decrease in the effective TEMPO concentration available to

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participate in deactivation. An additional feature of these systems is enhanced spontaneous (thermal) initiation. The spontaneous initiation rates ($R_{i,th}$) of S during conventional, non-living polymerization in aqueous miniemulsion using SDBS or polyvinyl alcohol (PVA) as surfactants at 110 and 125 °C are markedly higher than in bulk [39], experimental data being consistent with the enhanced radical generation having its origin at the oil–water interface (spontaneous radical generation according to the bulk mechanism would also occur within the polymer particles). Cunningham and coworkers have suggested that SDBS itself participates in radical generation according to an unknown mechanism based on the observation that R_p in the TEMPO-mediated miniemulsion polymerization of S at 135 °C increased with an increase in the SDBS concentration, whereas no significant such effect was observed for DOWFAX 8390 (disulfonated alkyl diphenyloxide sodium salt) [40]. El-Aasser et al. [41] found that $R_{i,th}$ in the presence of excess TEMPO of S in bulk was the same as in aqueous miniemulsion using DOWFAX 8390. Adding to the complexity of the picture, the presence of TEMPO influences the rate of spontaneous radical generation in bulk S [41–44]. However, the TEMPO concentration during NMP under normal conditions is very low (5×10^{-5} M [45]), and the effect of TEMPO on $R_{i,th}$ during actual polymerization conditions is negligible, as evidenced by the fact that R_p in the S/TEMPO/125 °C system can be predicted based on $R_{i,th}$ in bulk without consideration of the effect of TEMPO [45].

The present study focuses on the interface effect and the influence of enhanced spontaneous initiation on aqueous miniemulsion NMP of S employing a polystyrene (PS)-TEMPO macroinitiator and SDBS at 125 °C. It is shown that the macroinitiator concentration, *i.e.* the targeted MW, is a crucial experimental parameter that exerts major influence on both R_p and the control/livingness in these systems.

2. Experimental

2.1. Materials

S was purified by distillation under reduced pressure in a nitrogen atmosphere. Benzoyl peroxide (BPO) was purified by recrystallization using chloroform/methanol. TEMPO (Aldrich), SDBS (Nacalai Tesque Inc., Kyoto, Japan), DOWFAX 8390 (Dow Chemical, USA, 35.7% aqueous solution), PS (degree of polymerization (DP) = 2000; Wako Pure Chemical Industries, Ltd., Japan), special-grade hexadecane (HD) (Nacalai Tesque Inc., Kyoto, Japan) and methanol were used as-received.

2.2. Preparation of macroinitiator (PS-TEMPO)

S (13.5 g; 0.13 mol), BPO (371 mg; 1.53 mmol) and TEMPO (285 mg; 1.83 mmol) were charged in a glass tube, degassed with several N_2 cycles, sealed off under vacuum and heated at 125 °C for 4 h in an oil bath. The polymer was recovered by precipitation in excess methanol, and subsequently purified by reprecipitation four times using toluene/methanol and dried in a high vacuum oven. S conversion = 18%, $M_n = 2650$, $M_w/M_n = 1.12$.

2.3. Polymerization procedures

Miniemulsion polymerizations (5.0 wt% solids' content based on 100% S conversion): A solution of S (0.75 g), PS-TEMPO (0, 11, 22, 44, 132 mg; 0, 5, 10, 20, 60 mM), HD (26.5 mg) and PS (0.75 mg; DP = 2000) was mixed with an aqueous solution of SDBS (45 mg; 6 wt% rel. to S). PS was added to improve the colloidal stability (no PS was added in the polymerizations with the three highest PS-TEMPO concentrations). Miniemulsion polymerizations using DOWFAX 8390 were carried out in the same way, replacing SDBS with DOWFAX 8390 (60 mg; 8 wt% rel. to S). Miniemulsion polymerizations at 135 °C were carried out using SDBS (9 mM rel. aqueous phase) and DOWFAX 8390 (7 mM rel. aqueous phase) with PS-TEMPO (19.1 mM) and HD (26.5 mg). Miniemulsion polymerizations with DOWFAX 8390 (40 mM rel. aqueous phase) at 135 °C were also performed using both 5 and 20% solids contents in the absence of HD.

Emulsification was carried out using ultrasonication (Ultrasonic Homogenizer, Nissei, US-600T) for 12 min at 0 °C. The resulting emulsions were transferred to glass ampules (each ampule contained ca. 4 mL), degassed using several N_2/vacuum cycles and sealed off under vacuum. The polymerizations were carried out at 125 °C shaking the ampules horizontally at 110 cycles $\min^{-1}$.

The bulk polymerizations at 135 °C were performed in glass ampules (ca. 1.5 g S per ampule) using the recipe of the organic phase of the miniemulsion polymerizations (no HD).

2.4. Measurements

S conversions were determined by gas chromatography (Shimadzu Corporation, GC-18A) with helium as carrier gas, employing *N*,*N*-dimethylformamide as solvent and *p*-xylene as internal standard.

Molecular weight distributions (MWDs) were obtained by gel permeation chromatography (GPC) employing a Tosoh GPC system equipped with two TSK gel columns (GMHHR-H, 7.8 mm i.d. × 30 cm) using tetrahydrofuran (THF) as eluent at 40 °C at a flow rate of 1.0 mL $\min^{-1}$, and a refractive index detector (RI-8020). The column was calibrated against five standard PS samples (1.05×10^3–5.48×10^6 g/mol).

Particle size distributions were measured using dynamic light scattering (FPAR-1000, Otsuka Electronics, Osaka, Japan) at the light scattering angle of 160° at room temperature. Number-average (d_n) and weight-average (d_w) droplet diameters (given in figure captions) were obtained using the Marquadt analysis routine.

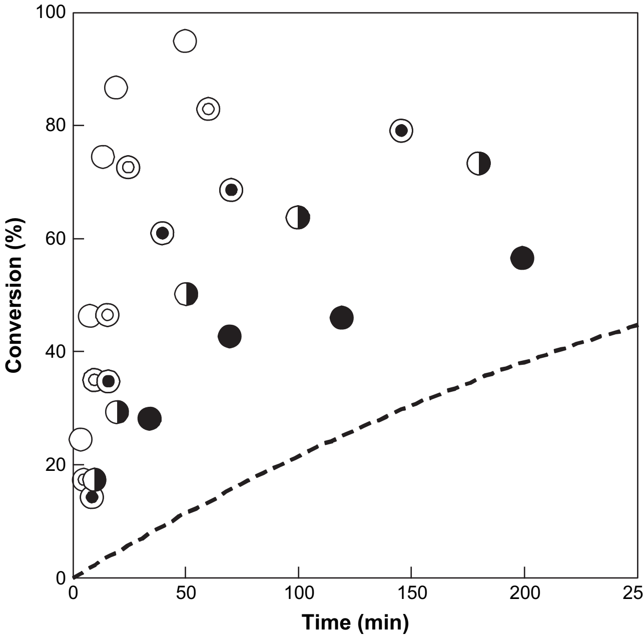

Fig. 1. Conversion–time plots for TEMPO-mediated miniemulsion polymerization of S at 125 °C using SDBS as surfactant at various PS-TEMPO macroinitiator concentrations: $[\text{PS-TEMPO}]_0 = 0$ M (○; $d_n \approx 64$ nm; $d_w \approx 72$ nm), 5 mM (◎; $d_n \approx 65$ nm; $d_w \approx 86$ nm), 10 mM (⦿; $d_n \approx 65$ nm; $d_w \approx 85$ nm), 20 mM (◑; $d_n \approx 62$ nm; $d_w \approx 74$ nm), 60 mM (●; $d_n \approx 56$ nm; $d_w \approx 68$ nm). The broken line is TEMPO-mediated polymerization of S in bulk at 125 °C with $[\text{alkoxyamine}]_0 = 20$ mM from Ref. [45].

The values given are average values over the course of the polymerizations.

3. Results and discussion

3.1. Rate of polymerization

Fig. 1 shows conversion vs. time data for TEMPO-mediated radical polymerizations of S in miniemulsion ($d_n \approx 65$ nm) at 125 °C using SDBS as colloidal stabilizer at different PS-TEMPO macroinitiator concentrations, as well as literature data for the corresponding bulk polymerization [45]. The particle size distributions were similar for all macroinitiator concentrations (Fig. 2).

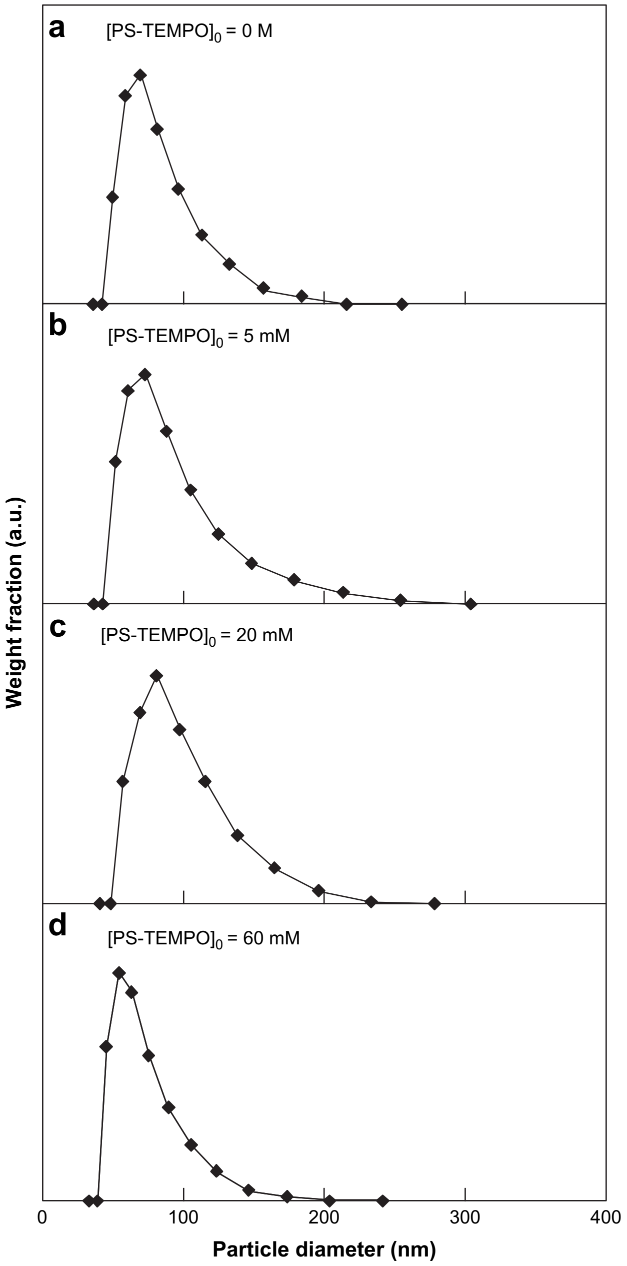

Fig. 2. Particle size (weight) distributions of TEMPO-mediated miniemulsion polymerization of S at 125 °C using SDBS as surfactant at various PS-TEMPO macroinitiator concentrations: (a) $[\text{PS-TEMPO}]_0 = 0$ M ($d_n \approx 64$ nm; $d_w \approx 72$ nm); (b) $[\text{PS-TEMPO}]_0 = 5$ mM ($d_n \approx 65$ nm; $d_w \approx 86$ nm); (c) $[\text{PS-TEMPO}]_0 = 20$ mM ($d_n \approx 62$ nm; $d_w \approx 74$ nm); (d) $[\text{PS-TEMPO}]_0 = 60$ mM ($d_n \approx 56$ nm; $d_w \approx 68$ nm).

The polymerization rate (R_p) increased significantly with decreasing initial PS-TEMPO concentration ($[\text{PS-TEMPO}]_0$) (0–60 mM). The initial R_p in the absence of PS-TEMPO was approximately 12 times greater than for $[\text{PS-TEMPO}]_0 = 60$ mM. The value of R_p in the non-living system ($[\text{PS-TEMPO}]_0 = 0$) has been discussed previously [39].

In TEMPO-based NMP of S at 125 °C in bulk/solution, R_p is independent of the alkoxyamine concentration [46]. In NMP in homogeneous systems, R_p is independent of [alkoxyamine] in the stationary state, whereas in the pre-stationary state, R_p increases with increasing [alkoxyamine]. The homogeneous system S/TEMPO/125 °C reaches the stationary state in a few minutes, and thus proceeds in the stationary state for all but a negligible part of the conversion range (unlike S/SG1, which mainly proceeds in the pre-stationary state) [46]. The strong dependence of R_p on $[\text{PS-TEMPO}]_0$ in the present miniemulsion polymerization can thus be attributed to the heterogeneous nature of the system – the polymerization proceeds fundamentally differently compared to in bulk/solution.

3.2. Molecular weight distributions

Fig. 3 shows the MWDs corresponding to the data in Fig. 1. The MWDs in the absence of PS-TEMPO were essentially independent of conversion. This behaviour, as well as the high $M_n \approx 2.3 \times 10^5$ g/mol, is consistent with chain transfer to monomer being the main end-forming event (as normally seen in conventional emulsion polymerization of S [47]) as discussed previously [39].

The MWDs obtained in the presence of PS-TEMPO exhibited a marked dependence on $[\text{PS-TEMPO}]_0$. At the highest $[\text{PS-TEMPO}]_0$ of 60 mM, good control/livingness was obtained as evidenced by narrow MWDs shifting to higher MW with increasing conversion. The control/livingness over the MWDs was gradually lost with decreasing $[\text{PS-TEMPO}]_0$. The bimodal nature of the polymerization with $[\text{PS-TEMPO}]_0 = 5$ mM is caused by the original PS-TEMPO macroinitiator remaining unreacted at relatively high conversion due to the high R_p, *i.e.* it is not dead macroinitiator [25,27]. In bulk/solution, control/livingness is (partially) lost when $[\text{PS-TEMPO}]_0$ is too low (*i.e.* the target $M_{n,th}$ is too high), because the probability of an individual chain undergoing termination or side reactions such as transfer increases with increasing degree of polymerization [46,48]. For S/TEMPO in bulk/solution, such difficulties are encountered at intermediate/high conversion when $M_n >$ approx. 100,000 g mol^{-1} is targeted [46], *i.e.* much higher MWs than in the present system at $[\text{PS-TEMPO}]_0 = 20$ mM ($M_{n,th} \approx 40{,}000$ g mol^{-1} at 100% conversion). In other words, this cannot explain why control/livingness was severely compromised even at low conversion with $[\text{PS-TEMPO}]_0 = 5$ mM (Fig. 3b).

It is of interest that R_p in the miniemulsion polymerization with $[\text{PS-TEMPO}]_0 = 60$ mM was markedly higher than in bulk while the control/livingness still remained satisfactory, demonstrating how the performance of NMP in a dispersed system can in some cases be superior to that in the corresponding bulk system. We previously reported similar results in terms of R_p and control/livingness by the exploitation of the interface effect on the nitroxide and enhanced $R_{i,th}$ in the presence of extra free TEMPO [27]. Cunningham and coworkers [49] have reported that it is possible to obtain both higher R_p and control/livingness in these systems by the use of the water-soluble additive ascorbic acid (which consumes free TEMPO).

There are at least three inherent features of TEMPO-mediated polymerization of S in miniemulsion that set the system apart from the corresponding bulk/solution polymerization: (i) compartmentalization, (ii) enhanced spontaneous radical generation, and (iii) the interface effect. These will now be discussed in turn with regards to the observed loss of control/livingness and increase in R_p with decreasing $[\text{PS-TEMPO}]_0$.

3.3. Compartmentalization

Theoretical work has revealed that for sufficiently small particles, compartmentalization effects in NMP [33,34,50] (and ATRP [51]) are manifested as the segregation effect on termination, and the confined space effect on both the deactivation reaction and geminate termination of thermal radicals generated in pairs (spontaneous initiation of S [52]). Simulations have shown that compartmentalization effects in dispersed systems of S/TEMPO at 125 °C with $[\text{PS-TEMPO}]_0 = 20$ mM are insignificant if the particle diameter (d) > approx. 100 nm [33,34]. However, the extent of compartmentalization depends on $[\text{PS-TEMPO}]_0$ – the lower $[\text{PS-TEMPO}]_0$, the higher is the critical d at which compartmentalization effects begin to influence the polymerization [34]. Therefore, based on these simulations, compartmentalization would be anticipated to exert some influence on all of the TEMPO-mediated polymerizations in Fig. 1, with the possible exception of $[\text{PS-TEMPO}]_0 = 60$ mM. The effect of compartmentalization would be a reduction in R_p due to the confined space effect causing both the deactivation rate and the rate of geminate termination of spontaneously generated radicals to increase. Moreover, if compartmentalization were significant, R_p would increase with increasing $[\text{PS-TEMPO}]_0$ [33]. The facts that (i) R_p was significantly higher in miniemulsion than in bulk, and (ii) R_p decreased with increasing $[\text{PS-TEMPO}]_0$ thus indicate that another factor(s) exerts a stronger influence on the polymerization than compartmentalization. It should here be noted that Tobita [35] has recently showed that a fluctuation effect (referring to different particles containing different numbers of nitroxide molecules) can cause an increase in R_p as a compartmentalization effect (in addition to the confined space effect and the segregation effect). Such an effect may to some extent influence the present results. However, also in the presence of such fluctuation effects, R_p would increase with $[\text{PS-TEMPO}]_0$, contrary to what was observed.

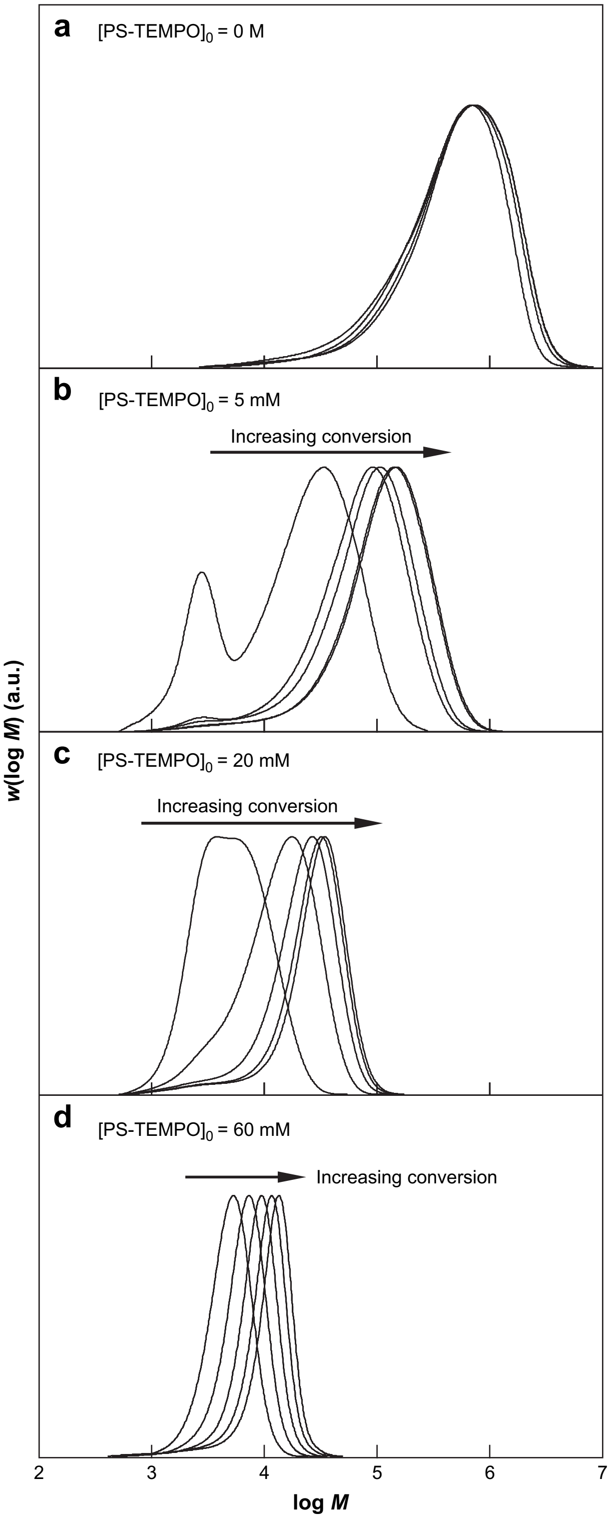

Fig. 3. Molecular weight distributions normalized to peak height for TEMPO-mediated miniemulsion polymerization of S at 125 °C using SDBS as surfactant at various PS-TEMPO macroinitiator concentrations: (a) $[\text{PS-TEMPO}]_0 = 0$ M ($d_n \approx 64$ nm; $d_w \approx 72$ nm; conversions: 24, 46, 74, 86, 95%); (b) $[\text{PS-TEMPO}]_0 = 5$ mM ($d_n \approx 65$ nm; $d_w \approx 86$ nm; conversions: 17, 35, 46, 73, 83%); (c) $[\text{PS-TEMPO}]_0 = 20$ mM ($d_n \approx 62$ nm; $d_w \approx 74$ nm; conversions: 17, 29, 50, 64, 73%); (d) $[\text{PS-TEMPO}]_0 = 60$ mM ($d_n \approx 56$ nm; $d_w \approx 68$ nm; conversions: 28, 42, 46, 56, 63%).

El-Aasser et al. [18] reported that R_p decreased somewhat on increasing $[\text{PS-TEMPO}]_0$ by a factor of four in aqueous miniemulsion of S at 125 °C using DOWFAX 8390, but that there was no significant effect on the MW control. However, although $d_n < 100$ nm, the particle size distributions were broad with numerous much larger particles. The vast majority of polymer (by weight) would form in the larger particles, thus explaining the absence of significant compartmentalization, enhanced initiation and interface effects (see related discussion below).

Cunningham and coworkers [26] recently reported data for the miniemulsion system S/TEMPO/Dowfax 8390/135 °C. As the particle size decreased in the range $d_n = 47–163$ nm with increasing surfactant concentration, R_p decreased and the livingness increased, but M_w/M_n remained relatively unaffected (R_p in miniemulsion was lower than in bulk). These results are qualitatively consistent with the confined space effect and the segregation effect. However, theory predicts that $d <$ approx. 50 nm is required for the confined space effect to manifest itself in this system [33,34], and it is thus puzzling that a pronounced decrease in R_p relative to bulk was observed for particles as large as 163 nm. This apparent discrepancy between our results and those of Cunningham and coworkers is addressed further in the next section.

3.4. Enhanced spontaneous radical generation

The spontaneous (thermal) initiation rates ($R_{i,th}$) of S in aqueous miniemulsion using SDBS or PVA as surfactants at 110 and 125 °C (conventional, non-living polymerization) are markedly higher than in bulk [39]. As mentioned in Section 1, data reported by Cunningham and coworkers suggest that the enhanced $R_{i,th}$ is related to the presence of SDBS [40]. In order to investigate to what extent, if at all, the present results (increase in R_p and gradual loss of livingness with decreasing [PS-TEMPO]; Figs. 1 and 2) are specific to SDBS, polymerizations were carried out using the surfactant DOWFAX 8390.

Fig. 4 shows conversion vs. time data for TEMPO-mediated radical polymerizations of S at 125 °C in miniemulsion with DOWFAX ($d_n \approx 80$ nm) and SDBS ($d_n \approx 62$ nm) with $[\text{PS-TEMPO}]_0 = 20$ mM. R_p was much higher in miniemulsion than bulk also when using DOWFAX. R_p was slightly higher for SDBS than DOWFAX. However, rather than being a direct result of the surfactant type, this difference most likely has its origin in the slightly smaller particle size in the SDBS polymerization (SDBS, $d_n \approx 60$ nm; DOWFAX, $d_n \approx 80$ nm). In the case of SDBS-based systems, it has been shown that R_p increases with decreasing particle size in this particle size region, postulated to be caused by (i) an interface effect on the nitroxide [25,27,37] and (ii) $R_{i,th}$ increasing with decreasing particle size (the enhanced $R_{i,th}$ is believed to originate at the oil–water interface, and the total interfacial area increases with decreasing particle size) [39].

Fig. 5 shows the MWDs corresponding to the data in Fig. 4 for DOWFAX and SDBS at close to 65% conversion, revealing how the MWDs were very similar. It can thus be concluded that the very pronounced effects of $[\text{PS-TEMPO}]_0$ in Figs. 1 and 2 are not specifically related to the surfactant SDBS.

The above findings with regards to SDBS and DOWFAX may appear inconsistent with data reported by Cunningham and coworkers [26,40]. They observed that R_p in the TEMPO-mediated miniemulsion polymerization of S at 135 °C increased with increasing SDBS concentration, whereas no major change and much lower R_p (than with SDBS) was observed when increasing the DOWFAX concentration [40]. In their study, "DOWFAX 8390 and SDBS gave similar mean particle sizes of approximately 120 ± 10 nm at both 20 and 100 mM" (corresponding to 3–15 wt% SDBS and 5–26 wt% DOWFAX rel. to monomer). In a subsequent paper [26], they reported that R_p was lower than that in bulk, and decreased with decreasing particle size ($d_n = 47$–163 nm) in the DOWFAX system (see Section 3.3). The inconsistency is thus that we observed an increase in R_p in miniemulsion ($d_n \approx 80$ nm) relative to bulk when using DOWFAX, whereas Cunningham and coworkers did not ($d_n = 47$–163 nm). In order to eliminate effects of temperature (125 vs. 135 °C), HD, solids' content and $[\text{PS-TEMPO}]_0$, various polymerizations were carried out at 135 °C, including using the recipe of Cunningham and coworkers [26]. The results in Fig. 6 show that none of the above experimental parameters is the source of the apparent discrepancy between our results at 125 °C and the results of Cunningham and coworkers at 135 °C. All miniemulsion polymerizations in Fig. 6 (135 °C) had higher R_p than the corresponding bulk polymerization. However, the increase in R_p relative to bulk was smaller than at 125 °C (Fig. 1). The main factor causing differences in R_p in the miniemulsion polymerizations in Fig. 6 is most likely the particle size; R_p increased with decreasing particle size in the range $d \approx 65$–150 nm, consistent with previous data on the S/TEMPO/SDBS/125 °C miniemulsion system [25,27].

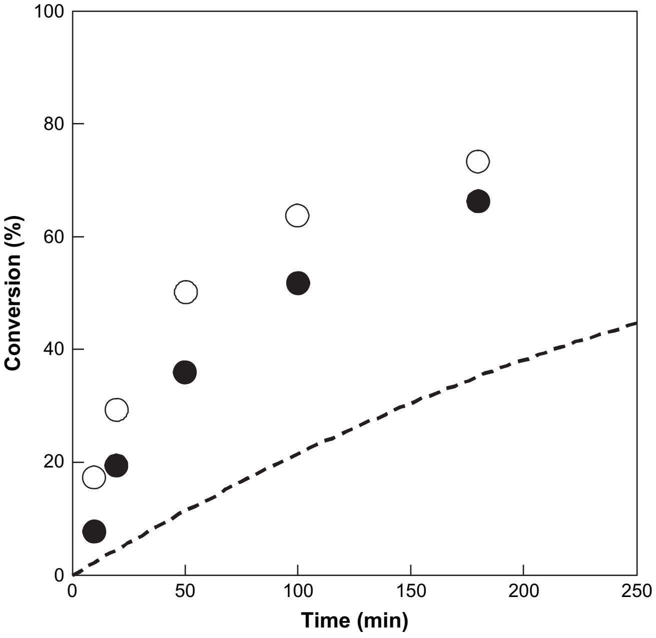

Fig. 4. Conversion–time plots for TEMPO-mediated miniemulsion polymerizations of S at 125 °C ($[\text{PS-TEMPO}]_0 = 0.02$ M) using SDBS (○; $d_n \approx 62$ nm; $d_w \approx 74$ nm) and DOWFAX 8390 (●; $d_n \approx 80$ nm; $d_w \approx 99$ nm). The broken line is TEMPO-mediated polymerization of S in bulk at 125 °C with $[\text{alkoxyamine}]_0 = 20$ mM from Ref. [45].

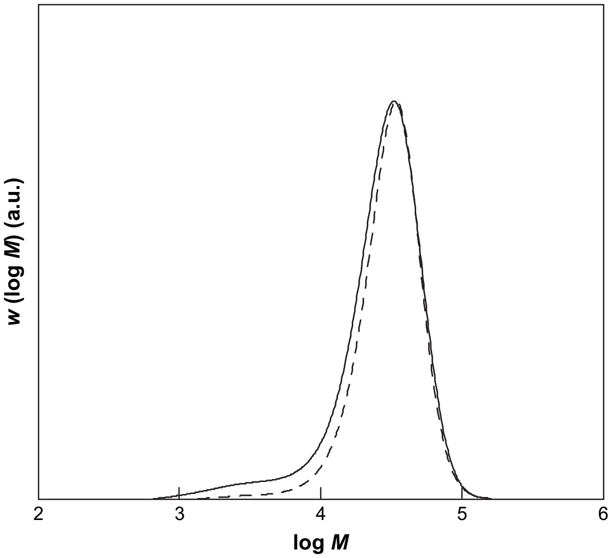

Fig. 5. Molecular weight distributions normalized to peak height for TEMPO-mediated miniemulsion polymerizations of S ($[\text{PS-TEMPO}]_0 = 0.02$ M) at 125 °C using SDBS (full line; 64% S conversion; $d_n \approx 62$ nm) and DOWFAX 8390 (broken line; 66% conversion; $d_n \approx 80$ nm).

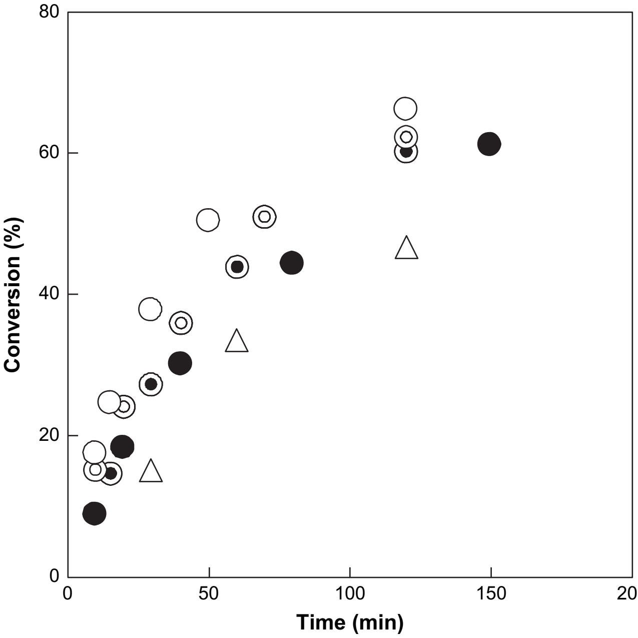

Fig. 6. Conversion–time plots for TEMPO-mediated polymerizations of S ($[\text{PS-TEMPO}]_0 = 0.0191$ M) at 135 °C under various conditions: miniemulsion 5 wt% solids/SDBS/HD (○; $d_n \approx 65$ nm; $d_w \approx 74$ nm); miniemulsion 5 wt% solids/DOWFAX 8390/HD (◎; $d_n \approx 85$ nm; $d_w \approx 108$ nm); miniemulsion 5 wt% solids/DOWFAX 8390 (◉; $d_n \approx 85$ nm; $d_w \approx 108$ nm); miniemulsion 20 wt% solids/DOWFAX 8390 (●; $d_n \approx 150$ nm; $d_w \approx 164$ nm); bulk (△).

The origin(s) of the apparent discrepancy between the present DOWFAX data and the corresponding results reported by Cunningham and coworkers remains unclear. It is noted that the emulsification procedures employed were different: ultrasonication (the present work) vs. microfluidization (Cunningham and coworkers), and it can be speculated that the different results are (partly) related to this. Differences in particle size distributions as well as uncertainty in particle size measurements may also be contributing factors.

Spontaneous radical generation plays an important role in NMP of S. In the presence of spontaneous initiation, a stationary state is reached, where the propagating radical concentration ([P•]) is governed by the rates of spontaneous initiation and bimolecular termination according to $[P\bullet] = (R_{i,th}/k_t)^{0.5}$ (*i.e.* the same as in a non-living system), where k_t is the termination rate coefficient [46]. Spontaneous initiation is thus not a problem with regards to control/livingness unless $R_{i,th}$ is too high, as evidenced by the fact that it is possible to increase R_p by the addition of a slowly decomposing radical initiator while still maintaining reasonable control/livingness [53–55].

We previously showed by modeling and simulations [27] that the enhanced $R_{i,th}$, as estimated independently by experiment [39], cannot alone explain the increase in R_p and decrease in control/livingness for small particles in the TEMPO-mediated miniemulsion polymerization of S at 125 °C using SDBS as stabilizer at $[\text{PS-TEMPO}]_0 = 20$ mM. The overall picture that emerges is thus that for sufficiently small (~65 nm) particles and/or sufficiently low $[\text{PS-TEMPO}]_0$, R_p increases and control/livingness is reduced as a combined effect of enhanced $R_{i,th}$ and the interface effect. Under such conditions, compartmentalization effects [33,34] are too weak to significantly influence R_p and control/livingness.

The water solubility of TEMPO is low, and it has been shown that TEMPO partitioning between the aqueous and particle phases exerts only a negligible influence in these systems [27,29,56,57].

3.5. Interface effect

We have previously reported that R_p increased with decreasing particle size ($70 \leq d_n \leq 170$ nm) in the TEMPO-mediated miniemulsion polymerization of S at 125 °C using SDBS as stabilizer at $[\text{PS-TEMPO}]_0 = 20$ mM as a result of an interface effect [25,27,37]. Due to the interfacial activity of TEMPO [27,38], some fraction of TEMPO in the particles reside at or near the interface, thus being unable/less able to participate in deactivation reactions with propagating radicals [25,27,37].

The rate of diffusion of low MW species like TEMPO within polymer particles that are not in the glassy state is very high [47,56], and it is thus reasonable to assume that the rate of diffusion of TEMPO from the particle interior to the interface does not play a significant role with regards to whether the interface influences the polymerization. Consequently, the significance of the interface effect would be dictated by the interfacial area available per TEMPO molecule, *i.e.* the occurrence or not of the interface effect can be correlated with the ratio n_T/A, where n_T denotes the number of TEMPO molecules per particle and A denotes the interfacial area per particle. If n_T/A is greater than some critical value, the interface effect would not be significant. It is more convenient to express this ratio in terms of n_{PT}/A (where n_{PT} is the number of PS-TEMPO per particle; in homogeneous systems, [TEMPO] is approximately proportional to [PS-TEMPO] [46]). In our previous work [25] on TEMPO-mediated miniemulsion polymerization at 125 °C with $[\text{PS-TEMPO}]_0 = 20$ mM, the interface effect was operative at $d_n \approx 70$ nm but not at $d_n \approx 170$ nm, corresponding to $n_{PT}/A = 1.41 \times 10^{17}$ (70 nm) and 3.41×10^{17} molecules/m^2 (170 nm). One would thus not expect any significant interface effect if $n_{PT}/A \geq 3.41 \times 10^{17}$ molecules/m^2. Thus, at approximately the same particle size ($d_n \approx 70$ nm), the interface effect would be expected to be markedly reduced if $[\text{PS-TEMPO}]_0$ was increased by a factor of 2.4 (=3.41/1.41). In the present study, the polymerization with $[\text{PS-TEMPO}]_0 = 60$ mM corresponds to $n_{PT}/A = 3.37 \times 10^{17}$ ($\approx 3.41 \times 10^{17}$) molecules/m^2. In agreement with expectation, R_p was much lower at this high $[\text{PS-TEMPO}]_0$. The absence of any major interface effect is also supported by the system behaving in a controlled/living manner as evidenced by the MWDs remaining narrow ($M_w/M_n < 1.34$) and shifting to high MW with increasing conversion (Fig. 3d).

3.6. Number of chains

Fig. 7 shows the number-average MW (M_n) and polydispersity (M_w/M_n) as functions of conversion. At the highest $[\text{PS-TEMPO}]_0$ of 60 mM, there was good agreement between M_n and the theoretical M_n ($M_{n,th}$) and $M_w/M_n < 1.34$. $M_{n,th}$ was calculated using Eq. (1):

$$M_{n,th} = \alpha[S]_0 M_S/[\text{PS-TEMPO}]_0 + M_{n,\text{PS-TEMPO}} \quad (1)$$

where α denotes fractional conversion, $[S]_0$ is the initial S concentration, M_S is the molar mass of S, and $M_{n,\text{PS-TEMPO}}$ is M_n of the PS-TEMPO macroinitiator. The control/livingness was gradually lost as $[\text{PS-TEMPO}]_0$ was decreased, as evidenced by broader MWDs and

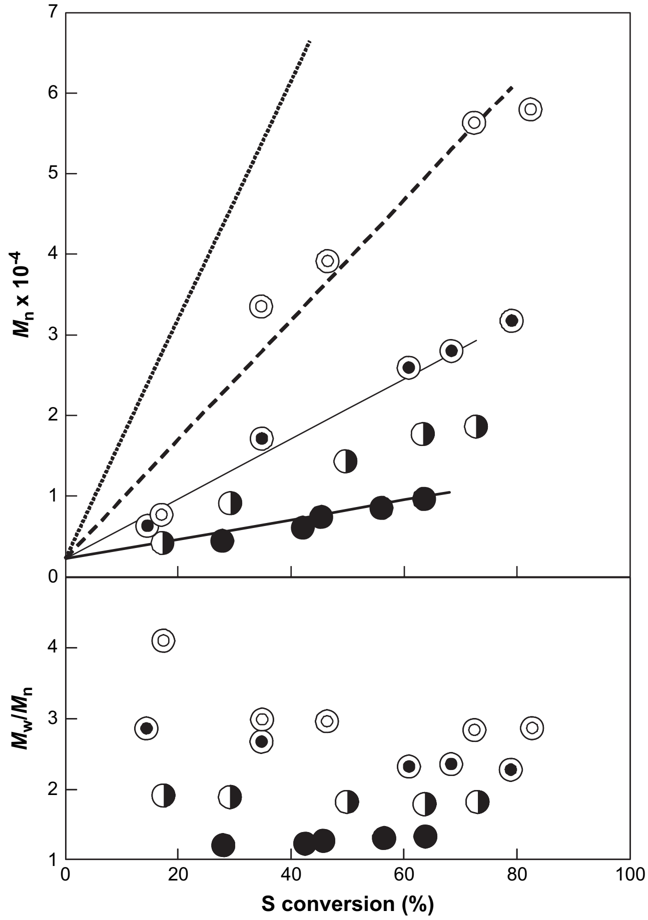

Fig. 7. Number-average molecular weights (M_n) and polydispersities (M_w/M_n) vs. conversion for TEMPO-mediated miniemulsion polymerization of S at 125 °C using SDBS as surfactant at various PS-TEMPO macroinitiator concentrations: $[\text{PS-TEMPO}]_0 = 5$ mM (◎, ···; $d_n \approx 65$ nm; $d_w \approx 86$ nm), 10 mM (◉, - - -; $d_n \approx 65$ nm; $d_w \approx 85$ nm), 20 mM (◑, —; $d_n \approx 62$ nm; $d_w \approx 74$ nm), 60 mM (●, ——; $d_n \approx 56$ nm; $d_w \approx 68$ nm). The straight lines represent the respective theoretical M_n according to Eq. (1).

a less pronounced shift to high MW with increasing conversion. The loss of control, evident in Fig. 3b and c, is largely caused by the interface effect [25,27] causing a reduction in deactivation rate, which leads to a lower number of activation–deactivation cycles experienced per chain during its growth (thus higher M_w/M_n) as well as an increased rate of termination (thus poorer livingness and higher M_w/M_n). However, enhanced $R_{i,th}$ would also contribute loss in control/livingness.

The plots of M_n vs. conversion also showed a strong dependence on $[\text{PS-TEMPO}]_0$ – the lower $[\text{PS-TEMPO}]_0$, the greater was the deviation between M_n and $M_{n,th}$ such that $M_n < M_{n,th}$. For $[\text{PS-TEMPO}]_0 = 60$ mM, M_n vs. conversion was linear, but for lower $[\text{PS-TEMPO}]_0$, downward curvature occurred, the extent of which increased with decreasing $[\text{PS-TEMPO}]_0$. Significant low MW tailing can be seen in the MWDs at the lower $[\text{PS-TEMPO}]_0$. These observations are consistent with continuous generation of new chains throughout the polymerization. Assuming that the rate of generation of new chains is independent of $[\text{PS-TEMPO}]_0$, the number fraction of new chains would decrease with increasing $[\text{PS-TEMPO}]_0$. Chain transfer to monomer would be responsible for some fraction of the new chains [58]. The interface effect [25,27] results in an increase in the extent of termination (predominantly by combination for S), and thus a reduction in the number of chains and an increase in M_n. However, it appears plausible that the most significant factor in causing the downward curvature in M_n vs. conversion and $M_n < M_{n,th}$ is the enhanced $R_{i,th}$ in miniemulsion [39].

It is of interest to estimate whether the deviations between M_n and $M_{n,th}$ are quantitatively consistent with our previously experimentally estimated value of $R_{i,th} = 1.82 \times 10^{-6}\ \text{M s}^{-1}$ for the spontaneously initiated conventional (non-living) radical polymerization of S in miniemulsion with SDBS ($d_n \approx 65$ nm) at 125 °C [39]. Tentatively assuming that the presence of PS-TEMPO and TEMPO does not influence $R_{i,th}$ (the presence of TEMPO may influence $R_{i,th}$ [42–44]) and that $R_{i,th}$ remains approximately constant with conversion (based on our data in Ref. [39], it appears that $R_{i,th}$ decreases somewhat with conversion), the approximate concentration of new chains derived from spontaneous initiation can be calculated from Eq. (2):

$$[\text{chain}]_{\text{th,calc}} = R_{i,th}t \qquad (2)$$

where t denotes the polymerization time. An experimental estimate of the concentration of new chains can be obtained from Eq. (3):

$$[\text{chain}]_{\text{new,exp}} = (M_{n,th}/M_n - 1)[\text{PS-TEMPO}]_0 \qquad (3)$$

The value of $[\text{chain}]_{\text{new,exp}}$ is affected not only by $R_{i,th}$, but also by any mechanism that alters the number of chains, such as termination and chain transfer to monomer or other low MW species. In other words, perfect agreement between $[\text{chain}]_{\text{th,calc}}$ and $[\text{chain}]_{\text{new,exp}}$ is not to be anticipated – this approach merely serves to test whether it appears quantitatively reasonable that $R_{i,th}$ is a main factor in causing the observed deviations of M_n from $M_{n,th}$. The values of $[\text{chain}]_{\text{th,calc}}$ and $[\text{chain}]_{\text{new,exp}}$ thus obtained are listed in Table 1, revealing that in most cases, the values are indeed relatively similar. The values of both $[\text{chain}]_{\text{th,calc}}$ and $[\text{chain}]_{\text{new,exp}}$ increase with increasing conversion, as expected, except for $[\text{chain}]_{\text{new,exp}}$ in the case of the highest macroinitiator concentration of $[\text{PS-TEMPO}]_0 = 60$ mM. In the latter case, $M_n \approx M_{n,th}$ (Fig. 7) and scatter in the M_n values render the resulting values of $[\text{chain}]_{\text{new,exp}}$ less reliable. The data in Table 1 thus constitute strong evidence that the enhanced $R_{i,th}$ in miniemulsion is a main factor causing $M_n < M_{n,th}$, the effect of which increases with decreasing $[\text{PS-TEMPO}]_0$. Moreover, these results strongly support our previously experimentally estimated value of $R_{i,th}$, which was obtained using a completely independent approach based on conventional (non-living) radical polymerization of S in miniemulsion at 125 °C [39].

Table 1
Calculated ($[\text{Chain}]_{\text{th,calc}}$; Eq. (2)) and experimentally estimated ($[\text{Chain}]_{\text{new,exp}}$; Eq. (3)) concentrations of new chains generated throughout the TEMPO-mediated miniemulsion polymerizations of S at 125 °C using SDBS as surfactant at various initial PS-TEMPO macroinitiator concentrations

$[\text{PS-TEMPO}]_0$ (mM)	Conversion (%)	$[\text{Chain}]_{\text{th,calc}} \times 10^3$ (M)	$[\text{Chain}]_{\text{new,exp}} \times 10^3$ (M)	$[\text{Chain}]_{\text{th,calc}}/[\text{chain}]_{\text{new,exp}}$
5	34.7	1.09	3.60	0.30
	46.5	1.75	4.83	0.36
	72.6	2.73	5.63	0.48
	82.8	6.55	6.79	0.96
10	34.8	1.75	7.44	0.24
	60.9	4.37	9.72	0.45
	68.5	7.64	10.60	0.72
	79.1	15.83	10.71	1.48
20	29.2	2.18	10.96	0.20
	49.9	5.46	10.85	0.50
	63.6	10.92	11.20	0.98
	73.0	19.66	13.69	1.44
60	27.9	3.82	21.23	0.18
	42.3	7.64	18.70	0.41
	45.6	13.10	6.32	2.07
	56.3	21.84	6.18	3.53
	63.7	32.76	4.50	7.28

4. Conclusions

TEMPO-mediated radical polymerization of S in aqueous miniemulsion using SDBS ($d_n \approx 65$ nm) as surfactant at 125 °C has been investigated with regards to effects of $[\text{PS-TEMPO}]_0$ (*i.e.* the effect of the targeted molecular weight). In agreement with previous work, the control/livingness was relatively poor at $[\text{PS-TEMPO}]_0 \leq 20$ mM due to the combined effect of enhanced spontaneous initiation [39] (relative to bulk) and the interface effect [25,27,37]. However, good control/livingness was obtained with a higher $[\text{PS-TEMPO}]_0$ of 60 mM, as a result of both the interface effect and enhanced spontaneous initiation exerting a less pronounced effect per chain than at lower $[\text{PS-TEMPO}]_0$. Similar results were obtained using the surfactant DOWFAX 8390, indicating that the above effects are not specific to SDBS.

The interface effect is mainly manifested as loss of control over the MWDs (significant broadening), whereas enhanced spontaneous initiation causes M_n to deviate downwards from the theoretical trend with conversion due to the continuous generation of new chains. This deviation was found to be quantitatively consistent with our previously estimated value of $R_{i,th}$ in the corresponding non-living miniemulsion system at the same temperature by a completely independent approach.

Implementation of NMP in aqueous dispersed systems is vital in order to be able to develop commercially viable processes. In addition to the above mechanistic/kinetic insights, the present work has also shown that it is in some cases possible to achieve higher polymerization rates in miniemulsion NMP compared to the corresponding homogeneous system, without compromising the control/livingness.

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