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Reversible addition fragmentation transfer (RAFT) polymerization of styrene in a miniemulsion: A mechanistic investigation[☆]

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Abstract

The RAFT polymerization of styrene in miniemulsion using 1-phenylethyl phenyl-dithioacetate (PEPDTA) as a RAFT agent was investigated, in attempt to reveal the mechanism for the often observed inferior performance such as low polymerization rate, broad molecular weight distribution and particle size distribution in the RAFT miniemulsion polymerization with regular levels of surfactant and co-stabilizer (1 wt% sodium dodecyl sulfate and 2 wt% hexadecane). It is strongly evident that a few of large oligomer particles consisting of oligomer, RAFT agent (RAFT agent refers to the original RAFT agent), and monomer would be formed in the early stage of the polymerization due to the superswelling of the first nucleated droplets. With the regular levels of surfactant and co-stabilizer, the observed low polymerization rate, broadened molecular weight distribution, slow conversion of the RAFT agent, lower N_p, and broadened particle size distribution could be well explained by the formation of these large oligomer particles and their prolonged existence. When the formation of the oligomer particles was suppressed by increasing surfactant and co-stabilizer levels and wise selection of types of RAFT agent, the molecular weight distribution could be narrowed to around 1.3 and particle size distribution could be close to that of the conventional non-living miniemulsion polymerization.

Keywords: RAFT polymerization; Miniemulsion polymerization; Polymerization kinetics

1. Introduction

Reversible addition–fragmentation chain transfer (RAFT) polymerization has been well established in homogeneous polymerization systems, such as bulk or solution polymerization. As a novel technique for controlled/living polymerization, the mechanism for RAFT living polymerization, as illustrated in Scheme 1, has been well accepted [1–3]. The role of intermediate radicals (species (2) or (5)), however, remains controversial [4–6].

More recently, RAFT polymerization in emulsion has been of particular interest as it is desirable for commercial applications [4,7,8]. The RAFT emulsion polymerization has been quite unsuccessful. Loss of molecular weight control, high levels of coagulum, thick red layers (phase separation) forming during the course of polymerization, and very slow polymerization rates have been reported [4,7,8]. These phenomena have been ascribed to the transport of RAFT agent from monomer droplets to particles [7]. To circumvent this problem, researchers turned to RAFT miniemulsion polymerization [9–19]. Miniemulsion polymerization is a modified emulsion polymerization process. In this process, monomer is pre-emulsified into 30–500 nm monomer droplets by high shear and then stabilized by the combination of surfactant and co-stabilizer [20,21]. For a well-controlled miniemulsion polymerization system, radical entry into the monomer droplets is believed to be the dominant particle nucleation mechanism [20]. Ideally, the final polymer latex might be a copy of the initial miniemulsion in terms of particle size and distribution [21]. Thus, the need for RAFT agent transport can be eliminated (the RAFT agent will be at the reaction loci from the beginning of the polymerization) and RAFT miniemulsion polymerization has been thought to be an ideal alternative for RAFT emulsion polymerization. However, it was proved that the situation is considerably more complicated than researchers anticipated. Increasing reports showed evidence that RAFT polymerization in miniemulsion gained only limited success [9,10,13,14,16]. De Brouwer et al.

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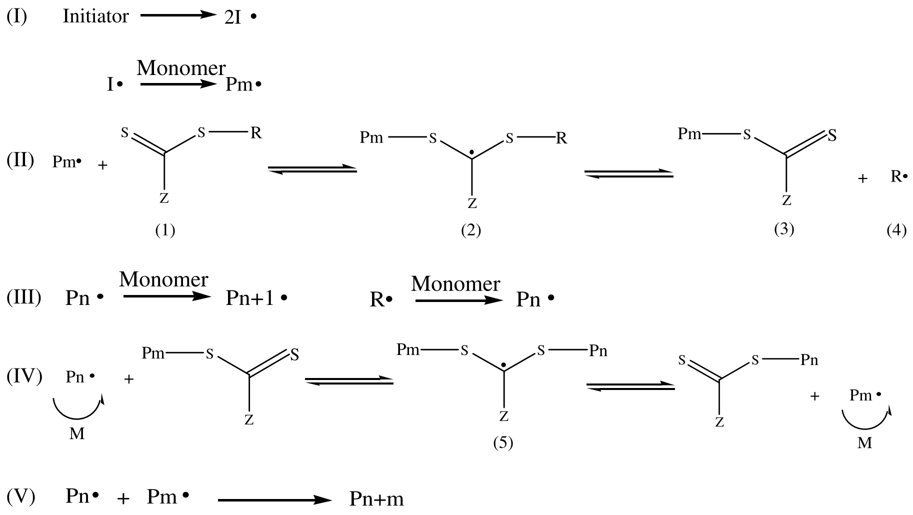
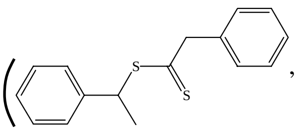
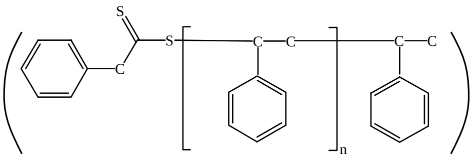


Scheme 1. The mechanism for RAFT polymerization.

[9,10] reported stability problems in RAFT miniemulsion polymerization when an ionic surfactant was used. When non-ionic surfactant was used, however, the polymerization became well controlled in molecular weight and colloidal stability, but retardation in polymerization rate was observed. Retardation in polymerization rate and high molecular weight polydispersity index (PDI) was reported by Butte et al. [13] and Heuts et al. [14] with sodium dodecyl sulfate (SDS) as a surfactant, though no colloidal stability was reported. In the paper by Heuts' group [14], it was reported that by replacing 1-phenylethyl phenyldithioacetate



PEPDTA, RAFT agent) with oligomeric PEPDTA



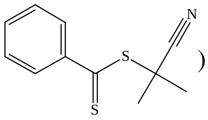
the polymerization rate increased to resemble the corresponding non-living miniemulsion polymerization but the high PDI was still observed. The retardation effect was conceivably related to the exit of the $R^{\cdot}$ radical resulting from the first transfer reaction with the RAFT agent [14]. It was assumed that the exit of the $R^{\cdot}$ radical would lead to low nucleation efficiency, resulting in a decreased polymerization rate. As to the high PDI of the polymer, irreversible termination was considered to be the cause by Heuts et al. [14], though uneven RAFT agent distribution was argued by Butte et al. [13]. Tonge et al. [11] and Mcleary et al. [12] reported that miniemulsion polymerization with 4-cyano-4-(thiobenzoyl) pentanoic acid as a RAFT agent gave good control only at high ionic surfactant concentrations (10 wt% with respect to monomer) and high hexadecane concentration (4 wt% with respect to monomer) while the polymerization proceeded very slowly. More recently, amphipathic RAFT agents were used in both emulsion [17] and miniemulsion [16] polymerization. Control of the polymerizations was found to be rather good but the PDI was still high, especially for low RAFT agent concentrations. In our previous communication [19], we demonstrated that the fast RAFT polymerization of styrene with low PDI and dead chain percentage could be achieved by using a carefully designed miniemulsion polymerization system.

Theoretically, Luo et al. [22] simulated the swelling behavior of oligomer chains formed at the very beginning of living free radical miniemulsion polymerization. It was shown that the super-swelling could be used to explain colloid instability, broadened particle size distribution, low nucleation efficiency, and high PDI in RAFT miniemulsion polymerization [22]. Although Luo et al.'s simulations can explain some experimental observations [10–12,14], a detailed physical mechanism describing RAFT miniemulsion polymerization process has not been developed yet. In particular, the knowledge about how the heterogeneous nature of miniemulsion polymerization interplays with RAFT chemistry and how that interplay influences the performance of the system is lacking. In this paper, we investigate the influence of reaction parameters on the performance of RAFT miniemulsion polymerization to reveal the mechanism of RAFT miniemulsion polymerization and to elucidate the reasons for those identified problems.

2. The experimental

2.1. Materials

De-ionized water (conductivity < 4 μS/cm) was used as received. Styrene (St) was purified by distillation. 2,2′-Azobis(isobutyronitrile) (AIBN, 98%) was re-crystallized twice from methanol. Potassium persulfate (KPS, > 99%), SDS (surfactant), hexadecane (HD, co-stabilizer, from Aldrich) were used without further purification.

PEPDTA and 2-cyanoprop-2-yl dithiobenzoate (CPDB, ) were synthesized and purified according to the literature [23,24].

2.2. Bulk polymerization

The mixture of St, AIBN, and PEPDTA was transferred to glass tubes and deoxygenated by degasifying and replacing with nitrogen for five times. The tubes, sealed with septa, were then bathed in 70 °C water, and a tube was removed at the preset time. The reactions were quenched by cooling the solutions in an ice bath and adding hydroquinone tetrahydrofuran (THF) solution. The polymer was isolated by evaporating off the solvent and residual monomer.

2.3. Miniemulsion polymerization

The initial miniemulsion was prepared according to the following procedure. Styrene was first mixed with hexadecane and the RAFT agent. This organic mixture was then added to the aqueous phase (water and SDS) under stirring. After 10 min, the coarse emulsion mixture was ultrasonified by using a KS-600 Sonifier (amplitude 70%, 600 W) for a time period of 15 min. The obtained miniemulsion was then transferred to a 250 ml five-neck flask, equipped with a condenser, a thermometer, a nitrogen inlet, and a mechanical stirrer. The miniemulsion was stirred at room temperature for 10 min, then immersed in a thermostated water bath at 75 °C. The reactor (deoxygenated for 60 min before the miniemulsion was charged) was deoxygenated by purging with nitrogen for 20 min, while the temperature of the water bath remained constant. Finally, the addition of KPS dissolved in 5 g water gave the zero time of the polymerization. The regular withdrawal of samples was separated into two parts (one for measuring conversion, the other for determining particle size), quenched with hydroquinone. This allowed us to follow the conversion of monomer as a function of time and the evolution of molar masses, molar mass distributions, and N_p as a function of monomer conversion.

2.4. Sample characterization

Monomer conversion was followed gravimetrically. Each part of the latex samples was diluted with 50 parts of SDS-saturated water and kept at 50 °C under 10 mmHg for 15 h to drive off the residue monomer, then the particle size was measured by dynamic light scattering (Malvern 3000HSA) after a sonification treatment. In some cases, the particle size of the latexes was further examined by transmission electron microscopy (TEM, JEOL JEM-200CX). The samples were prepared as follows: 0.03 g final latex was diluted by 20 g deionized water. For Exps 8 and 9, the diluted latex was driven off the residue monomer at 50 °C under 10 mmHg for 15 h. One drop of the dilution was dripped onto the carbon coated copper mesh and dried at room temperature. The particle size distribution was derived from the TEM image statistic (800–1000 particles for each sample were counted with TCI Image Analyzing Software 2.1, Nanjing Gongyun Science and Technology Co. Ltd).

The number of particles was calculated by Eq. (1):

$$N_p = \frac{6M_T x}{\pi \bar{d}_w^3 \rho_p} \tag{1}$$

where M_T is the initial monomer concentration in $g_{styrene}/ml_{water}$; x is the monomer conversion; ρ_p is the density of polystyrene, which is 1.06 g/ml; and $\bar{d}_w$ is the volume average diameter determined by DLS.

Molar masses and molar mass distributions of the polymers were determined at 298 K by GPC (Waters 150C) with three PL columns (10^4, 10^3, 500 Å) and a RI and UV (at 254 nm) dual-detector. The eluent was THF with a flow rate of 1 ml/min. The measurement was calibrated using polystyrene standard samples with molecular weight ranging from 580 to 355,000 g mol^{-1}.

3. Results and discussion

3.1. Experimental results

A series of styrene RAFT miniemulsion polymerizations were carried out at high concentrations of SDS (surfactant) and HD (co-stabilizer) in attempt to make the polymerization systems more stable. As a comparison, styrene bulk RAFT polymerization (Exp 1), conventional (non-‘living’) miniemulsion polymerization (Exp 2), and a typical RAFT miniemulsion polymerization with regular levels of SDS and HD (Exp 9) were also performed. Table 1 summarizes the recipes for each experiment. In order to systematically investigate the effect of the reaction parameters on the performance of RAFT miniemulsion polymerization, the experiments were designed as follows. Exps 3 and 4 were used to investigate the influence of co-stabilizer concentration (HD) while Exps 5 and 6 were designed to study the effect of surfactant concentration (SDS). Finally, the influence of RAFT agent concentrations were studied by Exps 5 and 7 while the influence of RAFT agent type was studied by Exps 3 and 8. No bulk phase separation was observed in all miniemulsion polymerization.

3.1.1. Polymerization rates and the number of particles

All the kinetic curves are presented in Fig. 1 and the number of particles in the final latex is listed in Table 1. Just as predicted by Butte [13], the rate of the RAFT miniemulsion polymerization is indeed much higher than that of the bulk RAFT polymerization, which demonstrates the compartmentalization effect of miniemulsion polymerization systems (note: decomposition rate constants are close for AIBN and KPS at the current conditions). On the other hand, it is obvious that the polymerization rate of the conventional miniemulsion polymerization (Exp 2) is the

Table 1
Recipes and the particle number in the final latex for all experimental runs

Exp	Monomer (g)	Water (g)	Initiator (g)	RAFT agent (g)	$[I]_0$/$[\mathrm{RAFT}]_0$ (molar ratio)	SDS (wt%)	HD (wt%)	$\bar{d}_w$[a] (nm)	N_p (/ml water)
1	30	–	0.11[b]	0.27[c]	0.67	–	–	–	–
2	20	80	0.08[d]	–	–	5	5	77	9.9×10^{14}
3	20	80	0.12[d]	0.18[c]	0.67	5	5	115	3.0×10^{14}
4	20	80	0.12[d]	0.18[c]	0.67	5	15	106	3.8×10^{14}
5	20	80	0.08[d]	0.30[c]	0.26	5	5	110	3.4×10^{14}
6	20	80	0.08[d]	0.30[c]	0.26	9	5	94	5.4×10^{14}
7	20	80	0.08[d]	0.25[c]	0.31	5	5	106	3.9×10^{14}
8	20	80	0.12[d]	0.14[e]	0.67	5	5	134	1.4×10^{14}
9	20	80	0.08[d]	0.25[c]	0.31	1	2	215	3.4×10^{13}

[a] Determined by DLS.
[b] AIBN.
[c] PEPDTA.
[d] KPS.
[e] CPDB.

highest, even though a higher SDS or KPS concentration was used in some cases of RAFT miniemulsion polymerization. This polymerization retardation has also been reported by other groups [9,10,14]. In comparison of Exp 2 with Exps 3, 7, and 8, which have a similar recipe, it is clear from Table 1 that the number of particles in those cases of RAFT miniemulsion polymerization is much less than that of the corresponding RAFT agent-free miniemulsion polymerization (Exp 2), though it is reasonable to assume that the number of the initial droplets of these systems should be similar due to the very similar recipe and the same miniemulsification procedure. In comparison among RAFT polymerizations in miniemulsion with various recipes, it is found that the higher SDS or KPS concentration is, the higher polymerization rate is, just as in conventional miniemulsion polymerizations. However, it is interesting to find that the concentration of HD also has a great influence on the polymerization rate. In Exp 4, the level of HD was increased from 5 wt% in Exp 3 to 15 wt%. The polymerization of Exp 4 proceeds faster than that of Exp 3, as shown in Fig. 1. From Table 1, it can be found that the number of particles of Exp 4 is higher than that of Exp 3, which is in good agreement with the change in the polymerization rate. Moreover, the retardation in polymerization appears to be RAFT-agent-type dependent (Exp 3 (PEPDTA) vs Exp 8(CPDB)), as shown in Fig. 1. In comparison of Exp 8 with Exp 3, it is found that the number of particles of Exp 8 is much fewer than that of Exp 3.

3.1.2. Particle nucleation

The evolution of particle size was monitored during the polymerizations in Exps 2–7. Combining the kinetic curves shown in Fig. 1, the evolutions of N_p as a function of monomer conversion were calculated and shown in Fig. 2.

From Fig. 2, the nucleation process of RAFT miniemulsion polymerization with respect to monomer conversion seems similar to that of non-RAFT miniemulsion polymerization (Exp 2), though those RAFT systems end with the much lower number of particles.

3.1.3. Number average molecular weight and molecular weight distribution

3.1.3.1. $\bar{M}_n$ and PDI evolution with monomer conversion.

RAFT ‘living’ polymerization is actually not a true living polymerization since the irreversible termination is still unavoidable during the polymerization, as shown in Scheme 1. Thus, the number average molecular weight of RAFT polymerization can be predicted by [9,10,14]

$$\bar{M}_\mathrm{n} = M_\mathrm{RAFT} + \frac{x[M]_0 M_\mathrm{M}}{[\mathrm{RAFT}]_0 + f[I]_0(1-\mathrm{e}^{-k_\mathrm{d}t})} \tag{2}$$

where $[I]_0$, $[\mathrm{RAFT}]_0$, k_d, and f are the initial molar concentration of initiator and RAFT agent, the dissociation rate constant of initiator, and the initiation efficiency, respectively. M_RAFT, M_M, $[M]_0$, x, and t are molecular weight of the RAFT agent, molecular weight of monomer, initial monomer concentration, monomer conversion, and polymerization time, respectively. In Eq. (2), the contribution of irreversible termination is expressed in term of $f[I]_0(1-\mathrm{e}^{-k_\mathrm{d}t})$. For RAFT polymerization in miniemulsion,

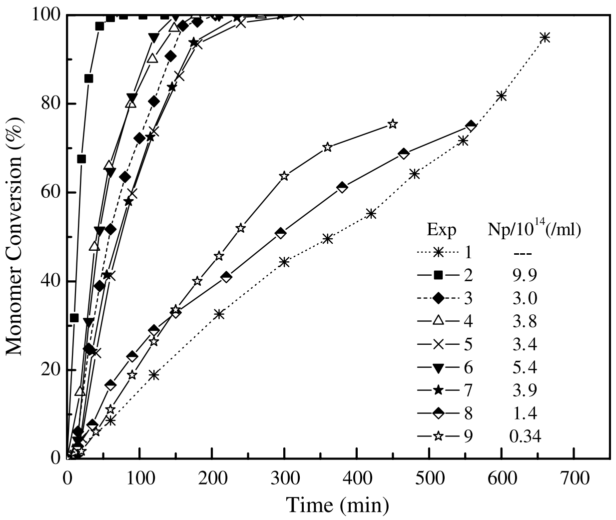


Fig. 1. Evolution of monomer conversion as a function of time.

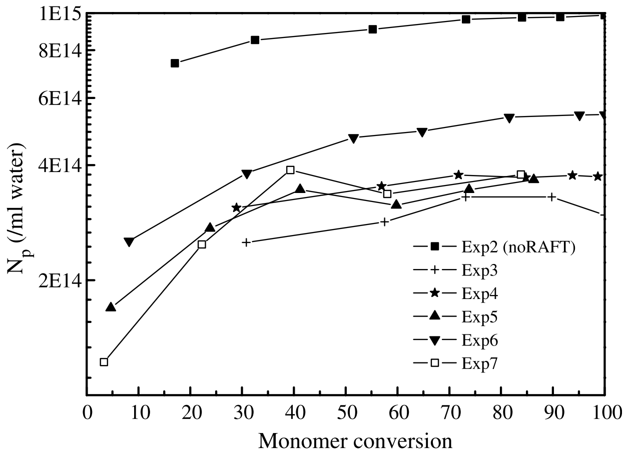


Fig. 2. Evolutions of N_p as a function of monomer conversion in Exps 2–7.

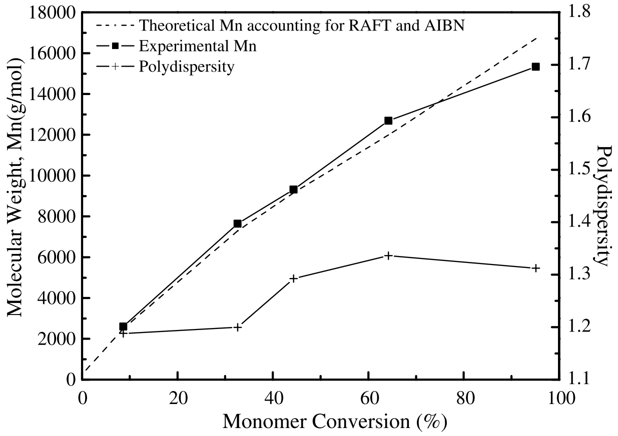


Fig. 3. $\bar{M}_n$ and PDI evolution with monomer conversion for the bulk polymerization (Exp 1).

the theoretical $\bar{M}_n$ can also be described by Eq. (2) but f should be expressed by [25]:

$$f = \left\{ \frac{\sqrt{k_d[I]_0 k_{t,aq}}}{k_{p,aq} C_{w,mon}} + 1 \right\}^{1-Z} \tag{3}$$

where $C_{w,mon}$ is the monomer concentration in the aqueous phase, $k_{t,aq}$ the termination rate coefficient in the aqueous phase, $k_{p,aq}$ the propagation rate coefficient in the aqueous phase, and Z the number of monomer units required such that the oligomer radical becomes surface active. Eqs. (2) and (3) were proved to fit well with the evolution of $\bar{M}_n$ in RAFT miniemulsion polymerization with the parameters listed in Table 2 [14].

The $\bar{M}_n$ and polydispersity index (PDI) evolutions against monomer conversion of the RAFT bulk polymerization (Exp 1) are presented in Fig. 3. From Fig. 3, it is clear that the experimental $\bar{M}_n$ steadily increases with polymerization and agrees well with theoretical $\bar{M}_n$ as described by Eq. (2) with $k_d = (4.72 \times 10^{-5}\ s^{-1})$ [26] and $f = 0.62$. In the meanwhile, the PDI steadily rises from 1.2 to 1.35 then levels off after 60% monomer conversion. The increase in PDI could be ascribed to the irreversible termination of free radicals. The leveling-off in PDI in the late stage of the polymerization might be due to the suppression of the irreversible termination, as evident by the gel effect shown in Fig. 1.

However, for RAFT polymerization in miniemulsion, the scenarios are different and complex. Firstly, for those cases using PEPDTA and higher SDS and HD concentrations (Exps 3–7), the $\bar{M}_n$ and PDI evolution against monomer conversion curves were similar. The representative $\bar{M}_n$ evolution against monomer conversion curve is illustrated in Fig. 4. In the early and middle stage of the polymerizations (monomer conversion < 40%), the $\bar{M}_n$s were positively deviate from the theoretical predictions. However, as seen in Table 3, the experimental $\bar{M}_n$ data in the late stage of the polymerizations are in good agreement with the theoretical predictions with exceptions of the CPDB system (Exp 8) and Exp 9 (with regular concentrations of SDS and HD: 1 wt% SDS and 2 wt% HD). This observation indicates that some of the RAFT agent does not play a role in the polymerization until monomer conversion is sufficiently high. Actually, the deviation was also found by Butte et al. [13] in a different system, as shown in Fig. 3 of Ref. [12], but was considered an experimental error without any comments. This observation will be further analyzed in Section 3.1.4.

Table 2
Kinetic parameters for calculation of molar mass in RAFT miniemulsion polymerization [14]

Parameter	Value at 75 °C
k_d	$4.35 \times 10^{-5}\ s^{-1}$
$k_{t,aq}$	$5.0 \times 10^8\ L\ mol^{-1}\ s^{-1}$
$k_{p,aq}$	$1.7 \times 10^3\ L\ mol^{-1}\ s^{-1}$
Z	2
$C_{W,mon}$	$0.006\ mol\ L^{-1}$

As seen in Fig. 5, the PDI with 1% SDS and 2% HD (Exp 9) increases steadily from 1.3 to 2.0 during the entire polymerization course. This was similarly reported by Heuts group [14]. However, in the cases of Exps 3–7, where the higher concentration of SDS and HD were used, the PDI values are much lower than that of Exp 9 but sensitive to the recipe variations. With the increase in monomer conversion, the PDI increases firstly before reaching a maximum value at some point between 40 and 75% monomer conversion and then

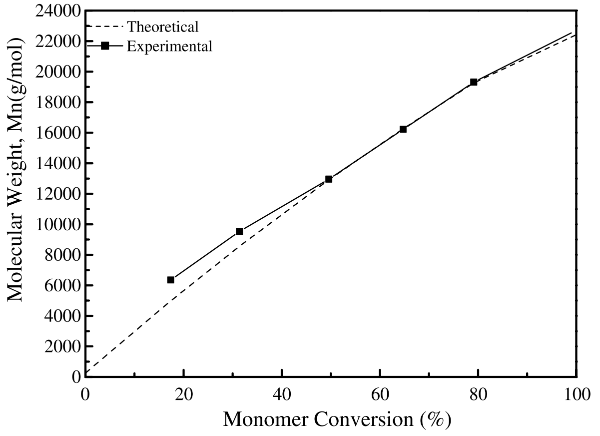


Fig. 4. $\bar{M}_n$ vs monomer conversion for Exp 3 (5 wt% SDS, 5 wt% HD).

Table 3
Experimental and theoretical $\bar{M}_n$s at full conversion

Exp	3	4	5	6	7	8[a]	9[b]
Theoretical (g/mol)	22,704	23,934	15,319	16,127	18,568	27,068	13,568
Experimental (g/mol)	22,417	23,569	15,285	15,817	18,151	20,498	14,259

[a] Monomer conversion: 75%. $\bar{M}_n$ randomly deviates from the theoretical predictions during the polymerization course. It is felt that the system was not as stable as that of PEPDTA under the same recipe conditions and thus a representative sample was difficult to take.

[b] Monomer conversion: 78%.

decreases. In the case of Exp 8, where CPDB replaced PEPDTA as the RAFT agent, the PDI rises steadily from 1.23 to 1.9 even at 5 wt% SDS and 5 wt% HD, similar to the case of Exp 9, where PEPDTA was used but with 1 wt% SDS and 2 wt% HD.

3.1.3.2. GPC curve evolution with monomer conversion. To find what determines PDI evolution with monomer conversion and the final PDI value, GPC curve evolution with monomer conversions of Exps 3, 4, and 9, as shown in Fig. 6, was analyzed carefully (the evolution trends of GPC curves of Exps 5, 6 and 7 are very similar to Exps 3 and 4. For conciseness, those curves do not show there). In the case of Exp 9, where typical levels of surfactant and co-stabilizer for miniemulsion polymerization was used, two peaks are shown in the GPC curves during the entire studied polymerization process. Butte et al. [13] reported similar results in a different RAFT system. The molecular weight of both peaks grows during the polymerization but the lower molecular weight portion (oligomer) is found to grow slower than that of the higher molecular weight portion (polymer). By increasing the levels of SDS and HD, the oligomer peak diminishes (Exps 3 and 4). More interestingly, the oligomer peak can shrink or even disappear in the late stage of the polymerization. Combining the corresponding evolution of GPC curves and PDI with monomer conversion, as shown in Figs. 5 and 6 (Exps 3, 4 and 9), it is found that the PDI evolution with monomer conversion is closely related to the oligomer peak evolution. During the period of PDI increasing, the oligomer peak or tailing in GPC spectra changes little with monomer conversion. However, in the late stage of the polymerization of Exps 3 and 4, the oligomer tailing shrinks considerably, leading to PDI decrease.

3.1.3.3. Dependence of the final PDI on reaction parameters. From Fig. 5, it seems that all of the following factors such as the level of co-stabilizer, surfactant, initiator, and RAFT agent and type of RAFT agent have an influence on the PDI of the final polymer. The influence of HD was investigated by Exp 3 (5 wt% HD) and 4 (15 wt% HD). By comparison, it is evident that increasing the level of HD leads to a decrease in the final PDI, though the initial PDI is little influenced by the level of HD. As to the level of surfactant, it is shown from Fig. 5 (Exp 5 (5 wt% SDS) vs Exp 6 (9 wt% SDS)) that the higher concentration of SDS gives a lower final PDI. Comparing Exp 3 ($[I]_0/[\mathrm{RAFT}]_0=0.67$) with Exp 5 ($[I]_0/[\mathrm{RAFT}]_0=0.26$), it is found that the higher initiator level leads to the higher initial and final PDIs due to a larger number of irreversible terminations. Comparing Exp 5 (0.3 g RAFT agent) with Exp 7 (0.25 g RAFT agent), it is interesting to find that a decrease in the level of RAFT agent leads to a decrease in PDI. When CPDB (Exp 8) replaced PEPDTA (Exp 3) as a RAFT agent, it turned out that the final PDI dramatically increases, despite that the initial PDI is rather low, as shown in Fig. 5. The possible reason will be discussed in Section 3.2.

3.1.4. RAFT agent conversion

By using Eq. (2), one can derive the conversion of the RAFT agent at different monomer conversions. After simple algebraic rearrangement for Eq. (2), one can easily calculate a $[\mathrm{RAFT}]_0$ value by using a $\bar{M}_n$ value measured by GPC, which is designated as $[\mathrm{RAFT}]_{0,\mathrm{GPC}}$. The physical meaning of $[\mathrm{RAFT}]_{0,\mathrm{GPC}}$ is the molar concentration of the consumed RAFT agent. So, the conversion of RAFT agent can be calculated by [26]

$$C_{\mathrm{RAFT}} = \frac{[\mathrm{RAFT}]_{0,\mathrm{GPC}}}{[\mathrm{RAFT}]_0} \tag{4}$$

where $[\mathrm{RAFT}]_0$ is the molar concentration of the RAFT agent in a recipe.

The plot of C_{RAFT} vs monomer conversion is shown in Fig. 7 for various experiments. As seen in Fig. 7, the RAFT agent conversion in the bulk RAFT polymerization remains constant around 95% after monomer conversion over 10%. Considering the error in $\bar{M}_n$ measurement, it is believed the RAFT agent should be completely consumed at 10% monomer

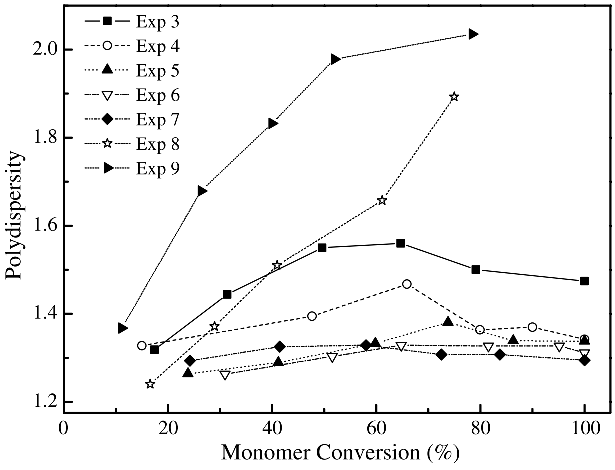


Fig. 5. Polydispersity index for all RAFT miniemulsion polymerization runs.

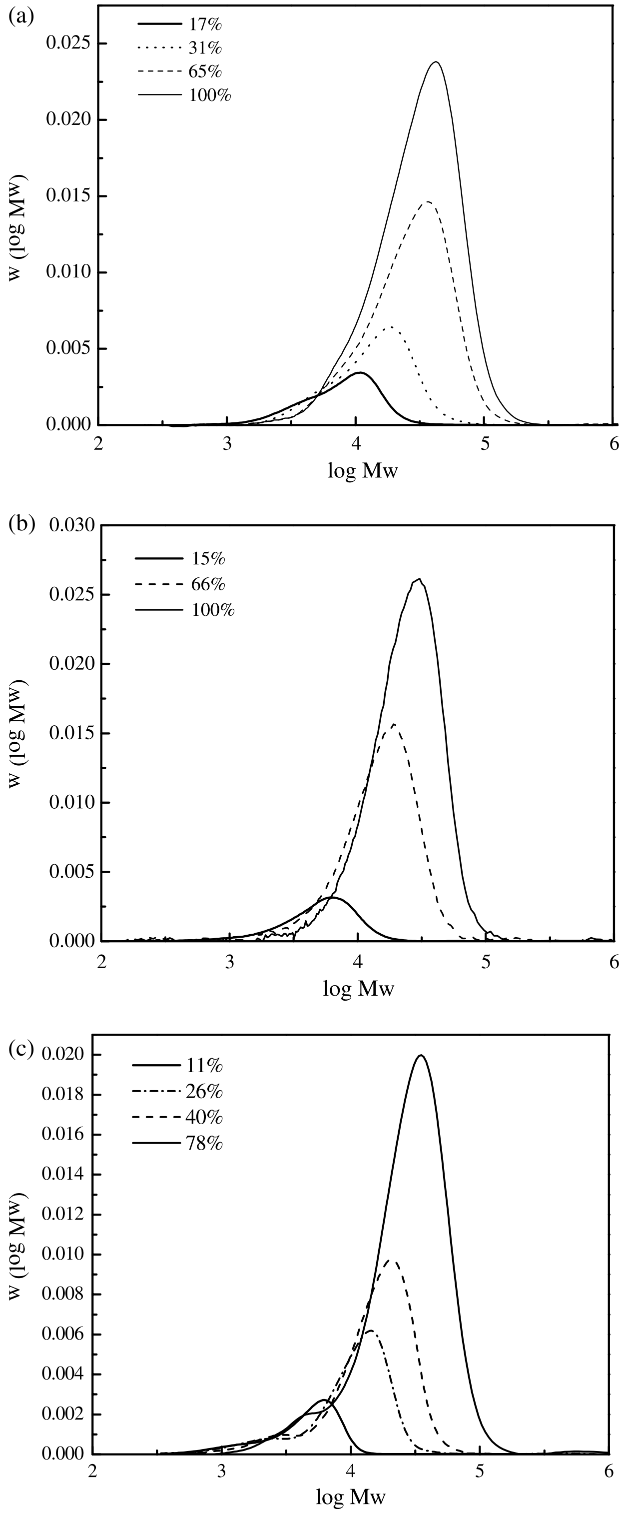


Fig. 6. GPC curves at different monomer conversions for Exps 3, 4, and 9 (note: GPC spectra have been scaled with their respective conversions). (a) Exp 3 (5 wt% SDS and 5 wt% HD), (b) Exp 4 (5 wt% SDS and 15 wt%), (c) Exp 9 (1 wt% SDS and 2 wt% HD).

conversion, in good agreement with theoretical predictions [27]. In contrast with this, it is seen that although the majority of the RAFT agent is indeed consumed in the early stage of polymerization, the full conversion of the RAFT agent is only reached at much higher monomer conversion in the RAFT miniemulsion polymerization. Additionally, the conversion curves of the RAFT agent seem to be quite dependent on polymerization conditions. For Exp 9, where 1 wt% SDS and 2% HD were used, around 15% of the RAFT agent molecules were left un-reacted even when the polymerization was finished at around 80% monomer conversion. By contrast, for Exps 3–7, where higher SDS and HD were used, much higher conversion of the RAFT agent was obtained in the early stage of the polymerizations and the full RAFT agent conversion was found to be achieved at 45–65% monomer conversion, dependent on the specific recipe. Specifically, it can be found from Fig. 7 that before the RAFT agent is fully consumed, the fraction of the un-reacted RAFT agent decreases with the increase of HD concentrations (Exp 3, 5 wt% vs Exp 4, 15 wt%), with the increase of SDS concentration (Exp 5, 5 wt% vs Exp 6, 9 wt%), or with the decrease of the RAFT agent concentration (Exp 5, 0.30 g vs Exp 7, 0.25 g) at the same monomer conversion.

The un-reacted RAFT agent molecules could be directly monitored by UV detector installed in our GPC system. Fig. 8 presents the evolution of GPC UV spectra with monomer conversion for Exps 5, 6, and 9. By calibrating with the pure RAFT agent, the peak appeared at 31.55 min was assigned to the RAFT agent molecules. It is clear that in Exp 9 (with 1 wt% SDS and 2% HD), the peak of the RAFT agent appears during the entire studied polymerization course. In Exp 5 (with 5 wt% SDS and 5 wt% HD), the peak disappears after 62.9% monomer conversion. In Exp 6 (with 9 wt% SDS and 5 wt% HD), the peak disappears after 30.9% monomer conversion. These direct observations are qualitatively in good agreement with those data presented in Fig. 7.

3.1.5. Particle size and particle size distribution

The particle size and particle size distribution of the final latexes of Exps 2–9 were investigated by TEM. Particles size distributions are shown in Fig. 9. Fig. 9(a) is the particle size distribution of the RAFT agent-free miniemulsion polymerization (Exp 2). It is found that the particle size distribution is rather narrow. However, for the cases of Exps 3–5, 7, and 8 using similar recipes but with RAFT agent, the particle size distribution is apparently broader. Statistical data about particle size and particle size distributions are listed in Table 4.

$$\bar{D}_\mathrm{n} = \frac{\sum_{i=1}^{k} n_i D_i}{\sum_{i=1}^{k} n_i} \tag{5}$$

$$\bar{D}_\mathrm{v} = \left(\frac{\sum_{i=1}^{k} n_i D_i^3}{\sum_{i=1}^{k} n_i} \right)^{1/3} \tag{6}$$

In Table 4, it is clearly shown that increasing HD level (Exp 3, 5 wt% HD vs Exp 4, 9 wt% HD) causes much narrower

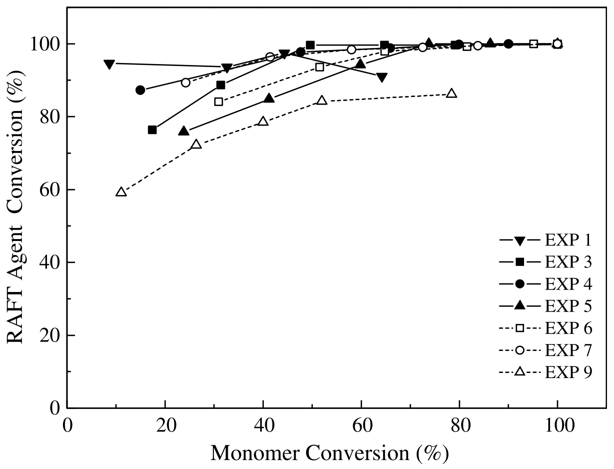


Fig. 7. RAFT agent conversion evolution with monomer conversion.

particle size distribution. Comparing Exp 5 with Exp 6, it is seen in Table 4 that increasing SDS from 5 wt% (Exp 5) to 9 wt% (Exp 6) also results in much narrower particle size distribution. In Exp 8, where CPDB was used as the RAFT agent, and in Exp 9, where a typical level of SDS and HD were used, particle size distributions are very broad.

3.2. Discussion

Schork et al. has shown that the conventional miniemulsion polymerization is a robust process in terms of N_p [28]. More recently, Landfester et al. [29] summarized all reported research results of particles size distribution in the miniemulsion polymerization. They concluded that the PSD obtained in the conventional miniemulsion polymerization is less than 1.10 (measured by dynamic light scattering) and independent of surfactant and co-stabilizer (hexadecane) concentration. In the current study, the particle size distribution of Exp 2 (control experiment) is rather narrow, in good agreement with literature reports. However, in the cases of RAFT miniemulsion polymerization of Exps 3, 4, 5, 7, 8, and 9, we found that the particle size distributions are broadened and much more sensitive to the polymerization recipe than those of conventional miniemulsion polymerization. Beside Exp 6 (5 wt% SDS, 9 wt% HD), the other RAFT polymerization systems have more or less bimodal particle size distributions.

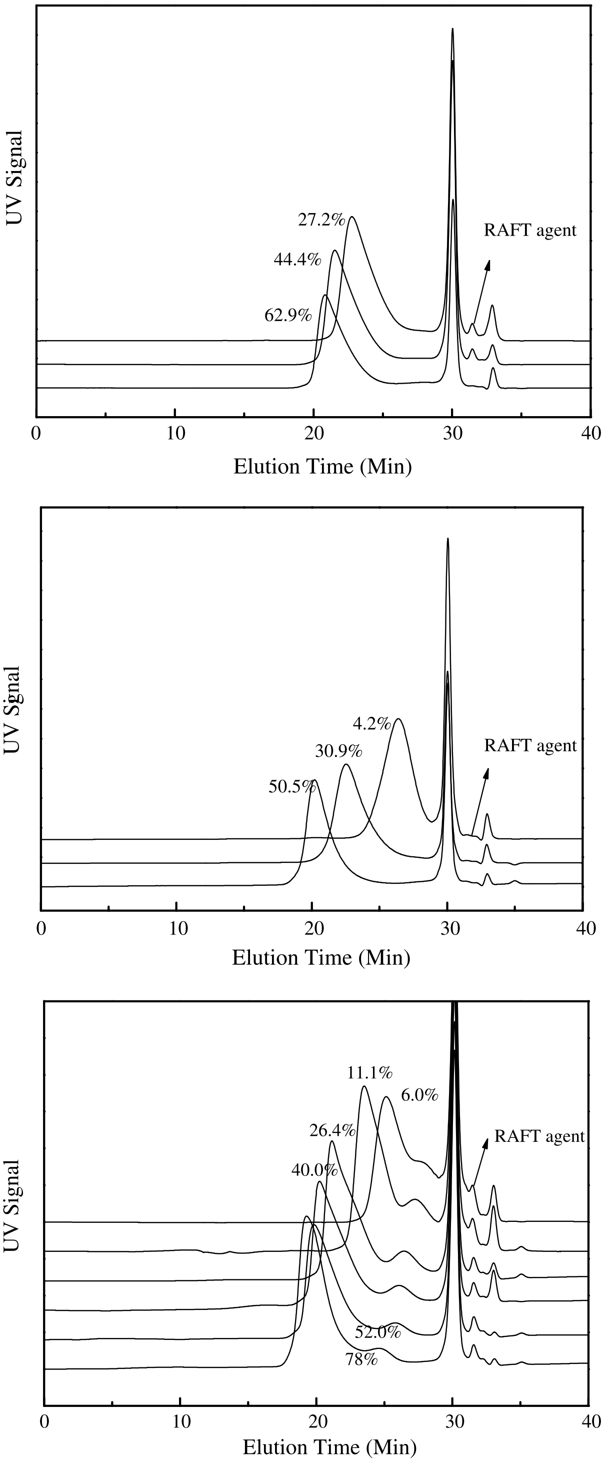


Fig. 8. GPC spectrum evolution with monomer conversion in Exps 5, 6, and 9. Exp 5 (5 wt% SDS and 5 wt%). Exp 6 (9 wt% SDS and 5 wt% HD), Exp 9 (1 wt% SDS and 2% HD).

It is believed that the final polymer latex might be a copy of the initial miniemulsion in terms of particle size and distribution in a well-controlled conventional miniemulsion polymerization [20]. As an approximation, Fig. 9(a) is considered to be the initial mini-droplet size distribution prior to the polymerization. The droplet size and its distribution prior to polymerization are determined by the breakup and coalescence process during the sonification. The main controlling factors for droplet size and its distribution are the emulsified equipment, emulsification procedure, monomer phase viscosity, and interfacial tension [30]. In comparison with the recipe of Exp 2, what is different for Exps 3, 4, 5, 7, and 8 is the concentrations of the RAFT agent, hexadecane, and initiator. The initiator was added after the miniemulsion had formed, so the mild change in the concentration of the initiator could little affect the droplet size and droplet size distribution. Due to the changed amount of RAFT agent and hexadecane is small relative to the amount of the whole oil phase, the viscosity of the oil phase and interfacial tension should be little changed. Based on the two point considerations mentioned above, it is reasonable to assume that the droplet sizes and their

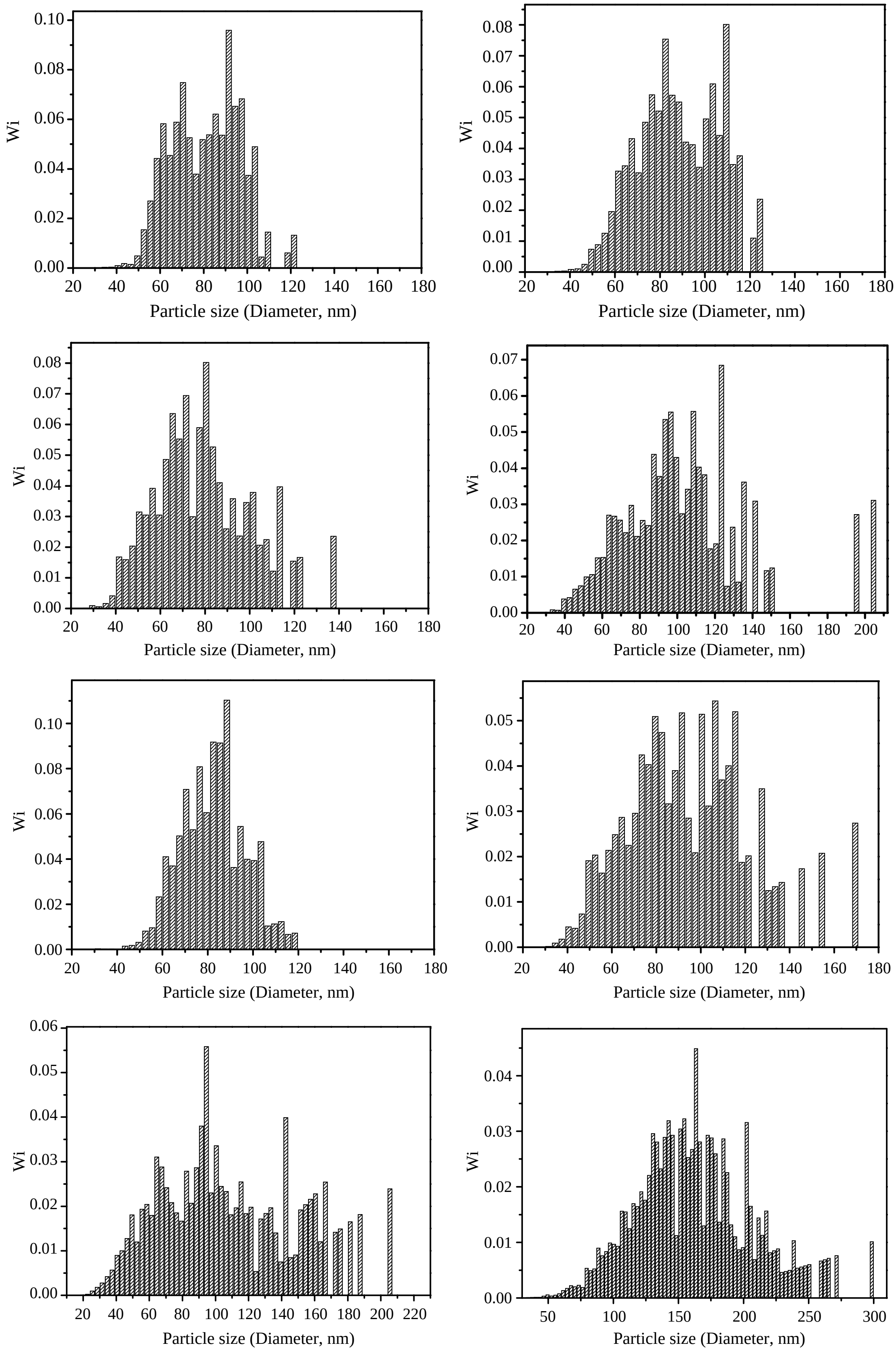


Fig. 9. Comparison of particle size distributions of the final latexes obtained by TEM between the non-RAFT control experiment. (a) Exp 2 and RAFT miniemulsion polymerization; (b) Exp 3; (c) Exp 4; (d) Exp 5; (e) Exp 6; (f) Exp 7; (g) Exp 8; and (h) Exp 9.

Table 4
Particle size and particle size distribution of Exps 2–9 statistically calculated from TEM images

Exp	2	3	4	5	6	7	8	9
D_n[a]	71.45	76.32	79.4	75.30	74.76	71.61	63.32	121.6
D_v[b]	81.28	105.16	97.8	105.88	82.61	95.27	121.11	173.2
D_v/D_n	1.14	1.38	1.23	1.41	1.10	1.33	1.80	1.42

[a] Calculated by Eq. (5).
[b] Calculated by Eq. (6).

distributions of Exps 3, 4, 5, 7, and 8 should be similar with those of Exp 2. However, a careful comparison between Exp 2 and Exps 3, 4, 5, 7, and 8 shows that the fractions of both the smallest and biggest particles of Exps 3, 4, 5, 7, and 8 are higher than those of Exp 2 (as seen in Fig. 9). This observation suggests that the RAFT polymerization dramatically changes the particle sizes and their distributions. Additionally, from Fig. 2, it is indicated that a large number of droplets (or particles) disappear in the beginning stage of the RAFT polymerization. These observations suggest that the colloidal systems are unstable more or less in the beginning of the RAFT miniemulsion polymerization, even though there were no observations of bulk phase separations.

Traditionally, coalescence and Ostwald ripening are considered to be two mechanisms to cause colloidal instability [31,32] However, these two mechanisms obviously fail to explain the observations that when introduced a small amount of RAFT agent, the latex particle size and particle size distribution become very sensitive to the system parameters like SDS and HD levels. The observations that the narrow particle size distribution of the controlled experiment without RAFT agent (Exp 2) and the dependence of the particle size and particle size distribution on the types of RAFT agent clearly (Exp 3 vs 8) strongly support that the nature of the RAFT polymerization is related to the observed colloidal instability. In the RAFT polymerization, the polymerization product in the early stage is oligomer. By theoretical simulations [22], it has been found that the first nucleated particles, which consist of considerable oligomer chains, could attract a great deal of monomer from un-nucleated droplets, driven by the differences in chemical potential. By attracting monomers from un-nucleated droplets, the nucleated particles with many oligomer chains can grow by a factor of a hundred in volume in some specific cases (‘super-swelling’ of particles). The super-swelling results in the formation of the super-swollen particles (designated as oligomer particles), which are much lager in size, and a large number of un-nucleated droplets reduce in size or even disappear, which is consistent with the TEM observations shown in Fig. 9.

The direct consequence of the superswelling is the disappearance of a large number of droplets and the formation of a few of the super-swollen particles. These special super-swollen particles, which consist of many oligomer chains and RAFT agent molecules, designated as oligomer particles, are much larger in size. Due to less pronounced compartmentalization effect ($R_p \propto 1/v_p$ where v_p is the oligomer particle volume swollen by monomer), the polymerization rate in these oligomer particles is much lower than that in the normal particles. This kinetic difference between two kinds of particles plays a key role to understand many aspects of the RAFT miniemulsion polymerization: (1) During the ensuing polymerization, monomer and the original RAFT agent (PEPDTA) molecules would gradually transport from the oligomer particles, across water, to the normal particles. The oligomer particles play a role of monomer and PEPDTA reservoir for the normal particles. Because part of PEPDTA molecules is stored in the oligomer particles, the apparent consumption rate of PEPDTA for the whole miniemulsion polymerization is much slower than that of the corresponding bulk polymerization. PEPDTA molecules were still observed even at high monomer conversion in the systems of RAFT polymerization in miniemulsion, as shown in Figs. 7 and 8. (2) PDI evolution curves with monomer conversion might actually reflect the relative polymerization rates within the oligomer and polymer particles. In the early stage of the polymerization, the polymerization within the oligomer particles proceeds very slowly due to a weak compartmentalization effect (note: the oligomer particles are much larger in size and $R_p \propto 1/v_p$). The oligomer chains in the oligomer particles grow slower while the polymer chains in polymer particles grow much faster, leading to the increase in PDI with monomer conversion. As the polymerization proceeds, the monomer and RAFT agent steadily transfer from the oligomer particles across water to the polymer particles. As a result, the concentration of RAFT agent in the oligomer particles is gradually decreased, as indicated in Figs. 7 and 8. In the meanwhile, the oligomer particles shrink, leading to the polymerization rate in the oligomer particles is much enhanced. After 60–70% monomer conversion, the monomer concentration in the polymer particles should be rather low while the monomer concentration in the oligomer particles could still be much higher since the mixing free energy is lower for an oligomer/monomer mixture than that of a polymer/monomer mixture [22]. As a result, the polymerization rate in the oligomer particles becomes higher than that in the polymer particles, diminishing the gap in molecular weight between oligomer and polymer, leading to a sharp decrease in PDI. In extreme cases such as Exps 8 and 9 where the colloids are less stable, the amount of RAFT agent in the oligomer particles was too large to be consumed before the polymerization was complete. So, PDIs rise in the whole studied range. The above growth mode of oligomer chains within the oligomer particles is in good agreement with the GPC curve observations, as shown in Fig. 6.

The degree of super-swelling of particles has theoretically been shown very sensitive to the system parameters [22]. It has been found by simulations [22] that low interfacial tension (high SDS) and high level of co-stabilizer (high HD) can help to suppress the super-swelling. The order of the degree of super-swelling predicted by the theoretical simulations is in good agreement with the order of particle size distribution observed (Exp 6 > Exp 4 > Exp 7 > Exp 3 > Exp 5 > Exp 9 > Exp 8). The inferior performance of miniemulsion polymerization using CPDB as a RAFT agent (Exp 8) could be ascribed to the much higher chain transfer constant (for PEPDTA $C_{tr}=130$ [14] at 60 °C, whereas for CPDB it is too large to be measured accurately [33]. In the case of CPDB, phenyl group provides the much higher stability of the intermediate radical than benzyl group of PEPDTA does.), which has been shown to aggravate the super-swelling by a more recent simulation [34].

From the above discussion, it is concluded that the formation of the oligomer particles plays a key role in deteriorating the performance of RAFT miniemulsion polymerization. With increased levels of SDS and HD, the formation of the oligomer particles was suppressed. As a result, the particle size distribution and molecular weight distribution became narrower.

4. Conclusion

RAFT miniemulsion polymerization of styrene was studied with various levels of surfactant, co-stabilizer, and RAFT agent and two kinds of RAFT agent with different transfer constants. The polymerization kinetics, molecular weight and its distribution, and the particle number evolution against the monomer conversion were recorded. Using PEPDTA as a RAFT agent, it was found that:

- N_p is much lower than that of the non-RAFT miniemulsion polymerization counterpart.
- PSDs are much more broader than that of non-RAFT miniemulsion polymerization. Specifically, a number of the smaller particles and a few of the much larger particles than the particles produced in the non-RAFT counterpart were observed.
- Polymerization retardation was observed. And the polymerization rate increased with increase of the levels of surfactant and co-stabilizers.
- RAFT agent consumes much more slowly than that of the bulk RAFT polymerization and M_ns show positive deviations more or less from theoretical prediction from the beginning to middle stage of the polymerization.
- With the regular levels of surfactant and co-stabilizer (1 wt% SDS, 2 wt% HD), PDIs rise steadily during the whole polymerization process. With much higher levels of SDS and HD, PDIs rise first and then decrease to a rather low value with monomer conversion.
- With the regular levels of surfactant and co-stabilizer, two peaks in GPC spectrum were observed. The molecular weights of two peaks were found to grow simultaneously but at different growth rates during the polymerization.

The particle sizes and their distributions of the final latex were carefully analyzed with comparison with the blank experiment. It was strongly evident that a few of large oligomer particles consisting of oligomer, RAFT agent, and monomer would be formed in the early stage of the polymerization, resulting from the superswelling of those first nucleated particles. The poor performance of RAFT miniemulsion polymerization with regular surfactant and co-stabilizer levels could be well explained by the formation of these large oligomer particles and their prolonged existence. When the formation of the oligomer particles was suppressed by using higher surfactant and co-stabilizer levels than the conventional miniemulsion polymerization, the molecular weight distribution (PDI) could be narrowed to around 1.3 and particle size distribution could be close to that of the convention non-living miniemulsion polymerization.

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