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Comparison of RAFT polymerization of methyl methacrylate in conventional emulsion and miniemulsion systems

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Abstract

In this study, we have conducted the reversible addition–fragmentation chain transfer (RAFT) polymerization of methyl methacrylate (MMA) in two heterogeneous systems, i.e. conventional emulsion and miniemulsion, with identical reaction conditions. The main objective is to compare the living character in both systems according to the nucleation mechanism, the latex stability, the particle sizes and particle size distributions of latexes, the molecular weights and molecular weight distributions (or polydispersity index, PDI) of PMMA, and the kinetics of the RAFT polymerization. The RAFT agent used in both systems was 2-cyanoprop-2-yl dithiobenzoate (CPDB). The effects of an oil-soluble initiator 2,2′-azobisisobutyronitrile (AIBN) and a water-soluble initiator kalium persulfate (KPS) on the RAFT/emulsion and RAFT/miniemulsion polymerizations were investigated. Methyl-β-cyclodextrin (Me-β-CD) was used as a solubilizer. The average molecular weights and molecular weight distributions (PDIs) of dried PMMA samples were characterized by gel permeation chromatography (GPC). The experimental results showed that the RAFT/miniemulsion polymerization of MMA exhibited better living character than that of RAFT/emulsion polymerization under the conditions of our experiment. The PDI of PMMA in RAFT/miniemulsion polymerization was decreased with the addition of Me-β-CD. However, Me-β-CD did not have influence on the PDI of PMMA prepared in RAFT/emulsion polymerization.

Keywords: RAFT polymerization; Emulsion; Miniemulsion

1. Introduction

Researches in controlled/living free radical polymerizations have increased significantly during the past two decades [1–4]. The reversible addition–fragmentation chain transfer (RAFT) polymerization is one of the most versatile methods of controlled/living free radical polymerization [5]. The mild conditions required for the RAFT process and wide range of monomers make this method more proficient in designing molecular architectures. So far, most of the RAFT polymerizations have focused on the homogeneous systems, for example, bulk or solution [6–8]. The mechanism and rules have been well established.

Recently some researchers turned to apply the RAFT process in emulsion and miniemulsion systems [9–13], as controlled radical polymerization in water-dispersed media is industrially preferred. If RAFT polymerization can be successfully performed in these systems, the application will be greatly enhanced. However, colloidal instability is a major problem when implementing RAFT polymerization in emulsion. The rate retardation, the phase separation and the loss of control of molecular weight distribution are always observed [12,14–16]. These can be attributed to the poor transport of the hydrophobic RAFT agent from the monomer droplets to the particles. For a similar system, a RAFT polymerization in miniemulsion seems more promising. In an ideal case, the final particles are just the copy of the initial droplets. Thus, the RAFT agents can be equally distributed in the droplets at the beginning of the polymerization, and the transport of the RAFT agents is eliminated during the whole

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polymerization process. In fact, RAFT polymerization in miniemulsion at first was not so successful. The colloidal instability was still observed with ionic surfactants [10,11,17]. Several strategies were used to enhance the stability of the latex by improving the living properties of the RAFT polymerization and decreasing the particle size distribution and molecular weight distribution [10,18–22]. Luo et al. proposed a superswelling theory [23] to explain the reason why the latex would lose stability during the living free radical miniemulsion polymerization. More recently, a derivation based on Lifshitz–Slyozov–Wagner (LSW) theory [24] was also proposed by Qi and Schork. They tried to evaluate the effect of a RAFT agent on the diffusion stability of the miniemulsions before the onset of polymerization.

Fig. 1 shows two representative schemes of the nucleation mechanisms for RAFT/emulsion polymerization and RAFT/miniemulsion polymerization. In conventional emulsion system, the free radicals enter into the micelles or particles, and the micelles swollen by monomers are considered as the main loci of nucleation and polymerization (Fig. 1(a)). Monomer droplets in conventional emulsion serve only as the monomer reservoirs. With the polymerization marching on, the monomer would diffuse from those monomer droplets to the micelles or particles through the aqueous phase. In RAFT/emulsion polymerization, for the control of the molecular weight of polymers, a water-insoluble RAFT agent (CPDB) was added to the emulsion polymerization system. The RAFT agent dissolved in the monomer droplet should also transfer to the polymerization loci. However, its hydrophobicity made it difficult to transfer through the aqueous phase to particles. A partial reaction took place inside the monomer droplets. As a result, the control of the molecular weight and molecular weight distribution was always failing [9,14,15,25]. The RAFT agents and RAFT-capped chains floated on the surface of the emulsion and even coagulated during the course of the polymerization [9,14].

As early as 1973, Ugelstad et al. presented a conception of miniemulsion [26]. The difference between the miniemulsion polymerization and conventional emulsion polymerization is that the initial larger monomer droplets can be divided into smaller submicrometer ones with the diameter ranging from 50 to 500 nm by a strong shear or ultrasonication. These submicrometer droplets could stably exist with the combination of surfactant and co-stabilizer. With the decrease of droplets' size and the increase of the specific surface area, nearly all of the surfactants are adsorbed onto the surface of the droplets. Therefore, there are no enough surfactants to form micelles in the aqueous phase [27]. As a result, droplet nucleation is considered as the predominant particle nucleation mechanism in miniemulsion polymerization. This nucleation mechanism is also favorable for RAFT/miniemulsion polymerization of MMA because the RAFT agent has already been present in the polymerization loci (monomer droplets). It eliminates the transfer of the RAFT agent from the monomer droplets through water phase into the polymerization loci, as shown in Fig. 1(b).

Although RAFT polymerizations in emulsion and miniemulsion have been reported [13], the direct comparison of these two systems has never been done in the previous literature. Here we conduct the polymerization of methyl methacrylate in both emulsion and miniemulsion with an identical recipe to discover the intrinsic rules which make different at the kinetics and living character of RAFT polymerization in these two systems.

In our former work, adding a small amount of β-cyclodextrin (β-CD) to the RAFT/miniemulsion polymerization of butyl methacrylate and methyl methacrylate was proved to be able to facilitate the transportation of water-insoluble low-molecular-weight RAFT agent, and to ensure that RAFT

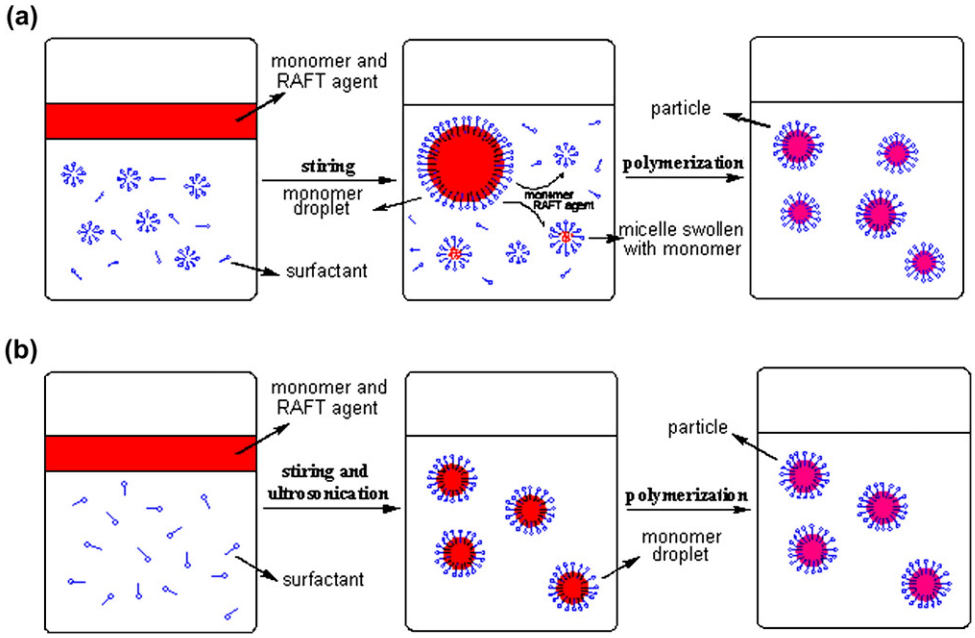

Fig. 1. Representative schemes for the nucleation mechanisms of the RAFT polymerizations of MMA in (a) conventional emulsion and (b) miniemulsion.

agent was homogeneously distributed in the polymerization loci [19,28]. Thus, the molecular weight distributions of the produced polymers were decreased. In this paper, a small amount of methyl-β-cyclodextrin (Me-β-CD) was also added to the RAFT polymerization of MMA in both emulsion and miniemulsion media to investigate its effect on the latex stability and living polymerization.

2. Experimental section

2.1. Materials

Methyl methacrylate (MMA; Shanghai Chemical Reagent Co., China) was washed with 5% NaOH to remove the inhibitor and then distilled under reduced pressure prior to use. 2,2′-Azobisisobutyronitrile (AIBN; Shanghai Chemical Reagent Co., 98%) was recrystallized from ethanol. Kalium persulfate (KPS) was recrystallized from cold water and then kept in a refrigerator under 4 °C. 2-Cyanoprop-2-yl dithiobenzoate (CPDB) was prepared according to the previous literatures reported by Mitsukami et al. [29] and Thang et al. [30]. The chemical structure of CPDB is shown in Fig. 2. Methyl-β-cyclodextrin (Me-β-CD) was purified by recrystallization from deionized water. Hexadecane (HD; Merck), sodium dodecyl sulfate (SDS; Farco Chemical Supplies, 99%), tetrahydrofuran (THF) and hydroquinone were of reagent grade and used as received.

2.2. RAFT/emulsion polymerization

Methyl methacrylate (MMA, 20 g) was first mixed with AIBN and RAFT agent. This oil phase was thoroughly mixed by magnetic stirring until homogeneous. Then the oil phase was slowly added into an aqueous solution which dissolved an ionic surfactant (SDS) and Me-β-CD (if used). After agitation, the emulsion was added into a 250 mL four-necked, round-bottomed flask equipped with a reflux cooler, a thermometer, a mechanical stirrer and a nitrogen inlet. The solution was deoxygenated via purging with N_2 gas. After bubbling for 30 min, the emulsion was heated to 70 °C to start the polymerization. Samples were taken at regular time intervals throughout the reaction for analysis.

2.3. RAFT/miniemulsion polymerization

Miniemulsion was prepared by dissolving water-soluble components in deionized water and a separate solution of oil-soluble components in monomer. The separate solutions were combined and stirred to homogeneous, and then the crude emulsion was ultrasonicated by a probe (JYD-650, Shanghai Zhixin Instrument Co., China) for 40 times with the lifetime of 2 s and an interval of 1 s. The obtained miniemulsion was transferred to a 250 mL four-necked, round-bottomed flask. After bubbling N_2 for 30 min, the miniemulsion was heated to 70 °C to start the polymerization. Samples were taken at regular time intervals throughout the reaction for analysis.

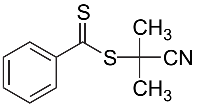

Fig. 2. Chemical structure of 2-cyanoprop-2-yl dithiobenzoate (CPDB).

Table 1
Experimental recipes for the RAFT polymerization of MMA in emulsion and miniemulsion systems

Exp.	Polymerization technique	Initiator (mmol)		Me-β-CD (g)	CPDB (mmol)	SDS (g)	HD (g)
		AIBN	KPS				
1	Emulsion	–	0.2	–	0.6	0.25	–
2	Emulsion	–	0.2	–	0.6	0.60	–
3	Emulsion	–	0.2	0.10	0.6	0.60	–
4	Emulsion	0.2	–	–	0.6	0.60	–
5	Miniemulsion	–	0.2	–	0.6	0.25	0.40
6	Miniemulsion	0.2	–	–	0.6	0.25	0.40
7	Miniemulsion	0.2	–	0.10	0.6	0.25	0.40
8	Miniemulsion	–	0.2	–	0.6	0.60	0.40
9	Miniemulsion	0.2	–	–	0.6	0.60	0.40
10	Miniemulsion	0.2	–	0.10	0.6	0.60	0.40

The recipes used in the RAFT/emulsion and RAFT/miniemulsion polymerization are listed in Table 1. The amounts of monomer MMA and deionized water were kept as 20 g (0.20 mol) and 80 g, respectively. The molar ratio of [MMA]:[CPDB]:[Initiator] was kept as 1000:3:1.

2.4. Characterization

The conversion of the monomer to the polymer was determined by a gravimetric method. Samples were drawn from the reactor at different times, immediately quenched with hydroquinone in a bath of ice water, and then dried in an oven at 50 °C.

The M_n values and PDIs of the dried polymers were recorded on a Waters 1515 gel permeation chromatographer (GPC) instrument with a PLgel 5.0 μm-bead-size guard column (50 × 7.5 mm), followed by two linear PLgel columns (500 Å and Mixed-C) and a differential refractive-index detector. The eluent was tetrahydrofuran at 30 °C with a flow rate of 1.0 mL min^{-1}. The molecular weights of dried PMMA samples were determined with standard poly(methyl methacrylate) calibration.

The mean particle sizes and size distributions of the polymer latexes were determined with an HPPS 5001 high-performance particle size instrument (Malvern) at 25 °C. Before the measurements, the original latex samples were diluted with deionized water to adjust the light strength suitable to the measurement condition. The cumulant method was chosen for measuring the *z*-average hydrodynamic diameter (D_z) and size polydispersity (denoted size PDI).

Transmission electron microscopy (TEM) was performed with instrument (TECNAI $G^2$20, FEI Co.) at 200 kV. The synthesized latex was diluted with deionized water and then dropped to a 400-mesh carbon-coated copper grid, followed by air drying at room temperature for 1 day before measurement. The morphology of latexes was ready to be observed.

3. Results and discussion

3.1. Comparison of polymerization kinetics and living characters in two systems

In the case of low concentration of the surfactant SDS, comparison was done about the RAFT polymerization of MMA in both conventional emulsion and miniemulsion systems. Due to the different nucleation mechanisms in these two systems, the polymerization kinetics and the character of living free radical polymerization were quite different, as shown in Figs. 3 and 4.

In the case of RAFT polymerization of MMA in conventional emulsion, 0.25 g of SDS was used (Exp. 1 in Table 1). Phase separation always occurred at the early stage of the polymerization. Although the monomer conversion increased linearly with the reaction time, the conversion of MMA only reached 31% after 150 min, and the conversion could not get higher even when the polymerization time was prolonged. It is reasonable to be ascribed to the low amount of surfactant used in this experiment. Landfester et al. found that less surfactant could lead to less micelle formation in water, and thus the corresponding polymerization loci and polymerization rate were both lowered [31]. The living/controlled character of the RAFT polymerization in conventional emulsion with less surfactant was not so good that the molecular weight did not increase with the monomer conversion, and the molecular weight distribution was quite broad. Sometimes dual peaks appeared in GPC curves, indicating that there were two living propagating centers in RAFT/emulsion polymerization. Besides the polymerization in micelles, some larger particles also formed. These large particles coagulated with the monomer droplets, caused by the shear force or buoyancy force, and finally formed the oil bulk layer. With the polymerization marched on, the oil layer became more viscous and deposited from the aqueous phase. As a result, when the conversion of MMA was over 25%, the PDI value decreased sharply from 1.93 to 1.45.

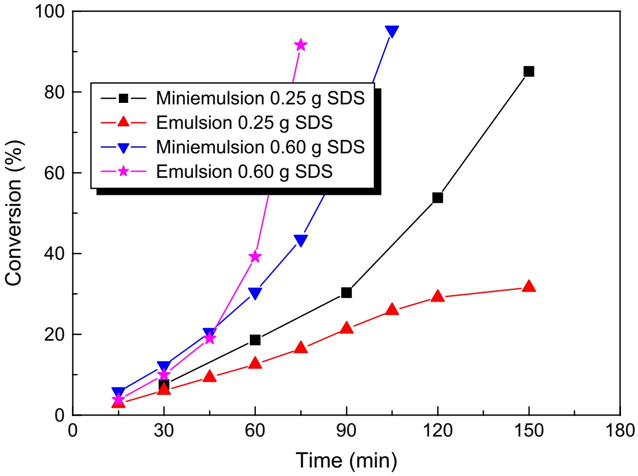

Fig. 3. Comparison of RAFT polymerizations of MMA in emulsion and miniemulsion on the evolution of monomer conversion as a function of reaction time.

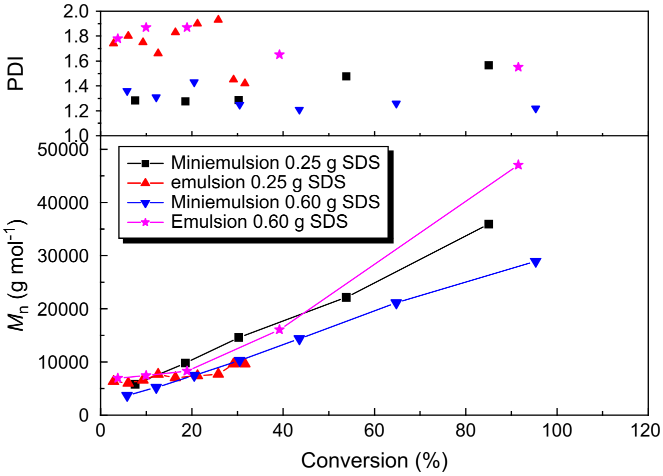

Fig. 4. Comparison of RAFT polymerizations of MMA in emulsion and miniemulsion on the evolution of M_n and PDI as a function of conversion.

It has been reported that increasing the amount of surfactant could enhance the stability of RAFT polymerization in both emulsion and miniemulsion systems [21,32]. Considering this point, we increased the amount of SDS from original 0.25 g to 0.60 g (Exp. 2 in Table 1) in the RAFT/emulsion polymerizations of MMA. The experimental results showed that the polymerization rate in RAFT/emulsion system increased rapidly when the conversion was above 20% (that is, in interval II of the emulsion polymerization), and the final conversion reached much higher of about 88%. Meanwhile, the colloidal stability was greatly improved. Although the red coagulum was still observed on the stirrer, the level was much lower than the case of 0.25 g of SDS, which was in good agreement with the report by Luo and Cui [32]. As shown in Fig. 4, the molecular weight distribution of PMMA was still broad. Before the conversion of 41%, the PDI was always above 1.75, and afterwards, it leveled off to 1.57.

With the comparison of RAFT/emulsion polymerization, RAFT/miniemulsion polymerizations of MMA were performed with 0.25 g and 0.60 g of SDS, respectively (Exp. 5 and Exp. 8 in Table 1). No coagulum was observed during the course of polymerization. It seemed more stable than the conventional emulsion/RAFT polymerization with 0.25 g of SDS (Exp. 1) and even with 0.60 g of SDS (Exp. 2). This indicated that the transport of water-insoluble RAFT agent played an important role in the heterogeneous RAFT polymerization. In Exp. 5, when the monomer conversion was lower than 30%, conversion increased linearly with polymerization time. And later on, the polymerization rate increased a little. It is worth noting that Monteiro et al. used a non-ionic surfactant Brij98 to conduct successfully the RAFT-mediated emulsion polymerization of styrene [33]. They postulated that the rapid transportation of RAFT agent from the monomer swollen micelles to the growing particles was fast on the polymerization timescale, and the high nucleation rate from the high rate of exit (of the R radical from the RAFT agent) and high entry rate from water-phase radicals (high APS concentration) reduced the effects of 'superswelling' and therefore a similar molar ratio of RAFT agent to monomer was maintained in all growing particles.

Compared with the RAFT/emulsion polymerization, the RAFT/miniemulsion system exhibited a better living polymerization character in the whole polymerization procedure. The molecular weight increased with the conversion in a linear fashion. Although the PDI of the polymer increased steadily with the conversion, it was still below 1.5, except for the conversion of above 50%. It can be observed in Fig. 4 that increasing the amount of SDS to 0.60 g could obviously improve the latex stability and decrease the value of PDI in RAFT/miniemulsion polymerization systems.

3.2. Effect of Me-β-CD on RAFT/emulsion and RAFT/miniemulsion polymerizations

3.2.1. Comparison of latex stability

In RAFT/emulsion polymerization of MMA, a red bulk layer could always be observed floating on the surface of the emulsion in Exp. 1 and Exp. 2. Even in RAFT/miniemulsion polymerization of MMA (Exp. 5), a small amount of red layer could still be observed in the early stage of the polymerization. But no coagulum was observed. It has been reported that methyl-β-cyclodextrin (Me-β-CD) is an amphiphilic cyclic substance with a hydrophobic cavity and a hydrophilic shell. Therefore, it could encapsulate a hydrophobe and facilitate its transport in an aqueous phase. In our previous work, β-cyclodextrin (β-CD) was applied to the RAFT/miniemulsion polymerization of BMA and MMA. The experimental results demonstrated that it can act as a solubilizer to facilitate the transportation of the water-insoluble RAFT agent into the polymerization loci, and thereby the PDI of the final polymer was lowered [19]. In the current study, Me-β-CD was used to replace β-CD to investigate the effects of a small amount of Me-β-CD on the RAFT/emulsion and RAFT/miniemulsion polymerization of MMA. Because the crystal structure of β-CD was damaged after methylation, the solubility of Me-β-CD in water was improved. Our experimental results show that Me-β-CD can act sufficiently in the RAFT heterogeneous polymerization (see Table 2).

Table 2
Influence of Me-β-CD on the stability of polymerizations of MMA in emulsion and miniemulsion

Exp.	Polymerization technique	Me-β-CD (g)	Conversion (%)	M_n (g mol^{-1})	M_w/M_n	D_z (nm)	Size PDI
2	Emulsion	0	88	36,700	1.78	49	0.24
3	Emulsion	0.10	92	47,000	1.55	53	0.24
6	Miniemulsion	0	65	22,200	1.73	184	0.12
7	Miniemulsion	0.10	78	31,200	1.40	199	0.08
9	Miniemulsion	0	70	21,900	1.30	210	0.25
10	Miniemulsion	0.10	81	26,500	1.26	195	0.17

3.2.2. Comparison of effect of Me-β-CD on polymerization kinetics, molecular weight and PDI

When Me-β-CD was added to RAFT/emulsion polymerization, although the red coagulum could still be observed, the amount was quite smaller than the case without Me-β-CD. In RAFT/emulsion polymerization, Me-β-CD had little influence on the living polymerization character. As shown in Fig. 5, the molecular weight of PMMA was higher than the theoretical molecular weight because of the red coagulum, and the PDI of PMMA was still broad.

In RAFT/miniemulsion polymerization of MMA, the red float was also observed during the course of the polymerization (Exp. 5) in the absence of Me-β-CD. The instability of RAFT polymerization in miniemulsion could be explained by the superswelling theory proposed by Luo et al. [23]. It was stated as follows: not all the droplets are nucleated in the early stage of the RAFT/miniemulsion polymerization. The nucleated particles containing oligomers would extract monomers from the unnucleated droplets because of the different potentials between them. The direct consequence of superswelling is the disappearance of a large number of monomer droplets and the formation of a few super-swollen particles. The broad particle size distribution leads to the different concentrations of RAFT agent in each particle. Therefore, the polymerization rate and the molecular weights of polymers were quite different in each particle. The PDI of the polymer measured by GPC would be high. It is supposed that partial RAFT agents initially existing in the droplets would deposit from the water phase because of superswelling effect. Luo et al. also indicated that the consumption rate of the RAFT agents for the whole miniemulsion polymerization was much slower, and the RAFT agents were still observed even at higher conversion [34]. If the unreacted RAFT agents could transport to the other particles in the late stage of the polymerization, maybe this would have good effect on the PDI. Considering this point, we used a small amount of Me-β-CD as solubilizer in the RAFT/miniemulsion polymerization of MMA. No red

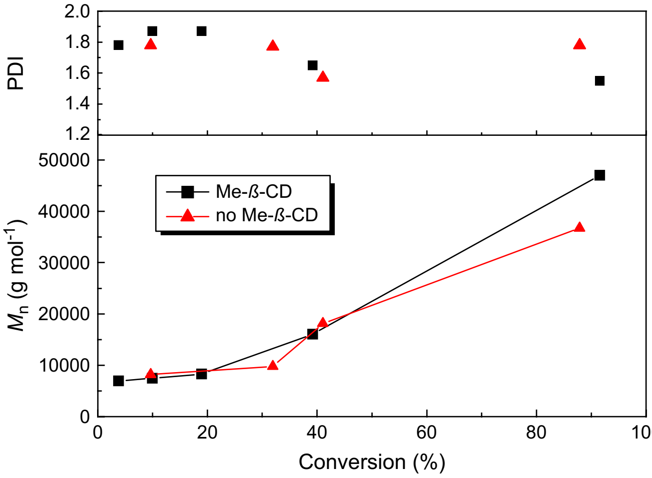

Fig. 5. Comparison of RAFT polymerizations of MMA in emulsion with and without Me-β-CD on the evolution of M_n and PDI as a function of conversion (0.25 g SDS).

float was observed throughout the whole polymerization, indicating that the stability of the miniemulsion was indeed improved. When compared the two systems with and without Me-β-CD (Exp. 6 and Exp. 7), it was found that the polymerization rate and monomer conversion were both elevated with the addition of Me-β-CD. Moreover, the PDI value was significantly decreased, as can be seen in Fig. 6. All these solid experimental results indicated that the transport of RAFT agent and its oligomer in aqueous phase was indeed facilitated with the aid of Me-β-CD. The distribution of RAFT agents among the polymerization loci (droplets or particles) plays an important role in the RAFT/miniemulsion polymerization. The equal distribution of the RAFT agents could lead to lower value of PDI.

The effect of Me-β-CD on the RAFT/miniemulsion polymerization with 0.6 g SDS was also evaluated through Exp. 9 and Exp. 10 in terms of latex stability, polymerization kinetics, molecular weight and PDI, particle size and size PDIs. The polymerization rate was greatly accelerated at a higher surfactant concentration. As can be seen in Fig. 7, the ultimate conversion reached in 240 min with AIBN as an initiator, irrespective of the addition of Me-β-CD. Meanwhile, the increase of conversion with polymerization time was in a straight line, which indicated a good living polymerization character. Comparing these two systems, we could find that the polymerization rate with the addition of Me-β-CD, as well as the conversion, was somewhat higher than that without Me-β-CD. The reason for this observation was that Me-β-CD acted not only as solubilizer but also as a good stabilizer in the RAFT/miniemulsion, so it could help to enhance the stability and promote the polymerization kinetics.

The concentration of SDS affected both the kinetics of RAFT/miniemulsion polymerization and the molecular weight and PDI. When RAFT/miniemulsion polymerization of MMA in the presence of 0.6 g SDS was conducted, it exhibited a better living polymerization character. The experimental molecular weight fits well with the theoretical molecular weight, and the values of PDIs were fairly below the benchmark of 1.5. Although the difference in PDI between the two systems was not significant, we could still find out from Fig. 8, in which the PDI was little reduced with the addition of Me-β-CD.

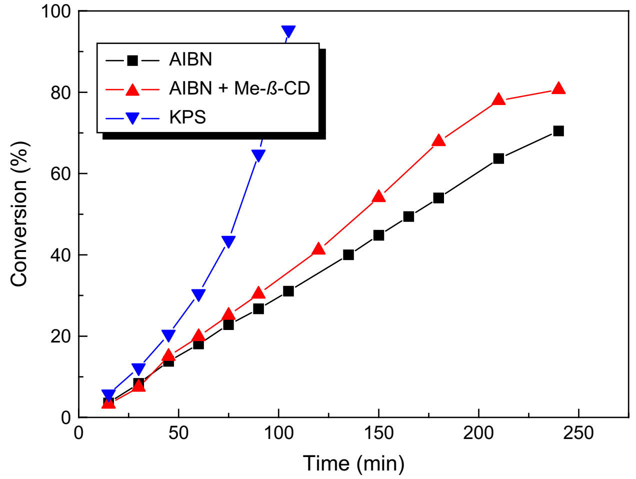

Fig. 7. Comparison of RAFT/miniemulsion polymerization of MMA with different initiators on the evolution of monomer conversion as a function of reaction time (0.60 g SDS).

3.2.3. Comparison of particle size and size PDI

The particle size and particle size distribution (size PDI) of the PMMA latexes were also monitored after the polymerization. Generally, the particle size in conventional emulsion was always smaller than that in miniemulsion. Here, we would like to see whether the addition of Me-β-CD into the RAFT/emulsion or RAFT/miniemulsion polymerization systems could make the particle size distribution lower. In RAFT/emulsion polymerization, the addition of Me-β-CD hardly changed the particle size and particle size distribution, as shown in Table 2. However, when it came to RAFT/miniemulsion of MMA with 0.25 g SDS, as we expected, the particle

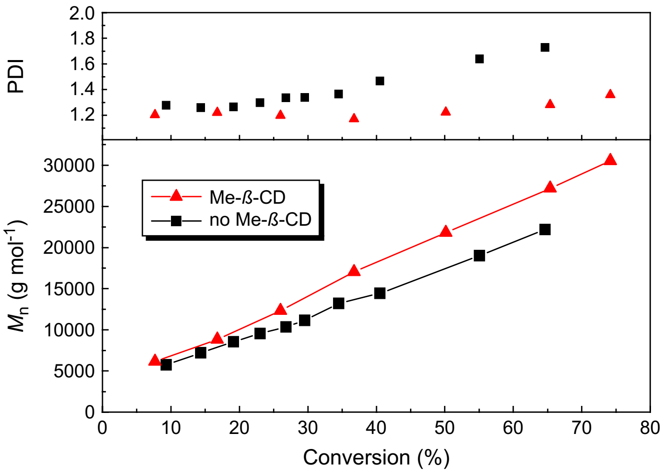

Fig. 6. Comparison of RAFT polymerizations of MMA in miniemulsion with and without Me-β-CD on the evolution of M_n and PDI as a function of conversion (0.25 g SDS).

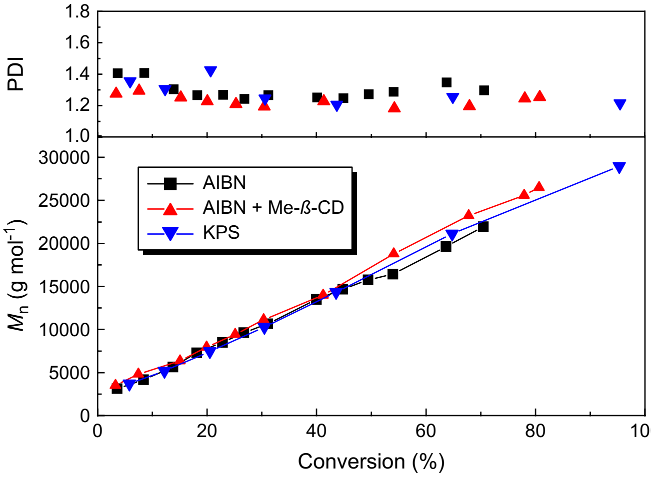

Fig. 8. Comparison of RAFT polymerizations of MMA in miniemulsion with different initiators on the evolution of M_n and PDI as a function of conversion (0.60 g SDS).

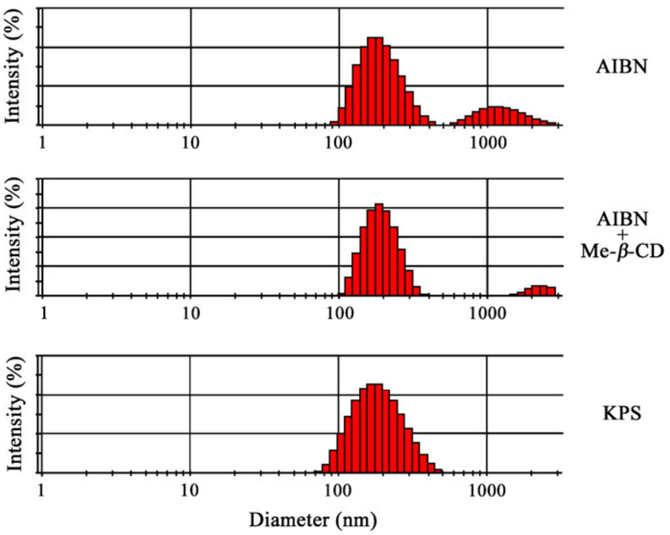

Fig. 9. Particle size and particle size distribution of PMMA particles prepared in RAFT/miniemulsion polymerizations with 0.6 g SDS.

size distribution was lowered from 0.12 to 0.08 with the addition of Me-β-CD, and the particle size was a little larger than the case without Me-β-CD.

When the amount of SDS was increased to 0.6 g, the main peaks both appeared at 194 nm with and without Me-β-CD, but a large particle peak could still be seen in Fig. 9. It was found that adding 0.1 g Me-β-CD could help decrease the amount of larger particles, and the size PDIs measured by laser light scattering (LLS) were decreased from 0.25 to 0.17. The kinetics of polymerization would do effect on the particle size. As explained above, Me-β-CD could help the transportation of RAFT agent to the polymerization loci in the RAFT/miniemulsion polymerization, so the distribution of RAFT agent could become even. As a result, the polymerization in each particle could proceed simultaneously and the diffusion of monomer could also be alleviated. To our mind, it could help decrease the particle size distribution.

To further study the effect of Me-β-CD on the stability and morphology of polymer latexes, we compared TEM images of PMMA particles prepared with and without Me-β-CD, as shown in Fig. 10a and b, respectively. The TEM photographs show that PMMA particles produced in the presence of Me-β-CD have smooth surface and relative uniform particle size than those prepared in the absence of any Me-β-CD.

3.3. Effect of initiator type on RAFT polymerizations in emulsion and miniemulsion

3.3.1. Effect of initiator type on polymerization kinetics in two systems

In this section, a water-soluble initiator KPS and an oil-soluble initiator AIBN were selected to initiate the RAFT polymerization of MMA in both emulsion and miniemulsion systems. We would like to see which initiator on earth was more suitable for each system.

In emulsion polymerization, water-soluble initiators are normally used. This kind of initiator decomposes in aqueous phase. The resulting free radicals enter the micelles to initiate the polymerization or directly initiate polymerization in the aqueous phase. Thus, micellar nucleation and homogeneous nucleation are considered as the main nucleation mechanisms. In Exp. 2, KPS was used as the initiator. The experimental results, as shown in Table 3, have demonstrated that more stable emulsion could be obtained with high level of surfactant. When an oil-soluble initiator AIBN was added to the RAFT/emulsion polymerization of MMA (see Exp. 4 in Table 3), the polymerization was directly initiated by the primary radicals which decomposed from AIBN in the droplets or micelles. When the monomer conversion reached high, the viscosity of the monomer droplet became so high that it could not be separated by mechanical stirring. The red bulk phase coagulated and most of them sticked to the stirrer. Therefore, AIBN was absolutely not suitable for the RAFT/emulsion polymerization of MMA.

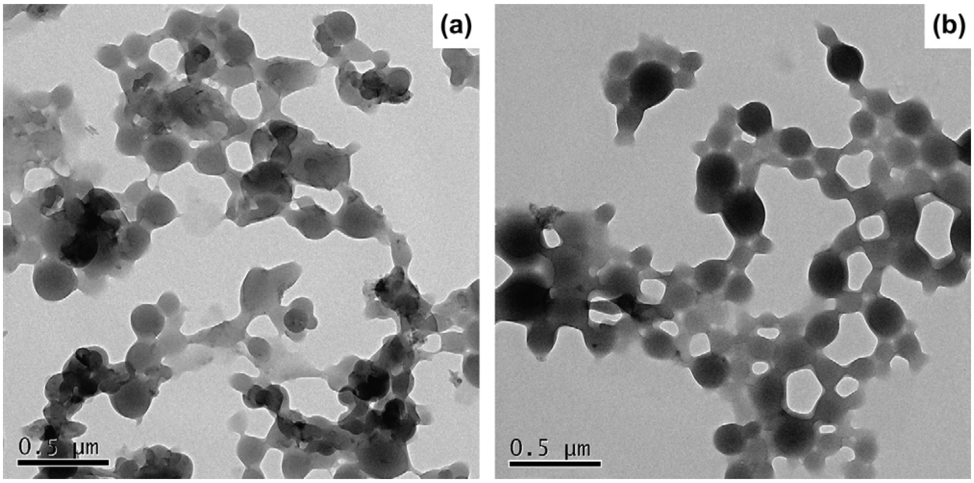

Fig. 10. TEM images of the latex particles of (a) without Me-β-CD and (b) with Me-β-CD. These latexes were prepared via RAFT/miniemulsion polymerizations using AIBN as an initiator.

Table 3
Results for RAFT polymerizations of MMA in emulsion and miniemulsion with different initiators

Exp.	Polymerization technique	Initiator	Conversion (%)	M_n (g mol^{-1})	M_w/M_n	$\overline{D}_z$ (nm)	Size PDI
2	Emulsion	KPS	92	47,000	1.55	50	0.24
4	Emulsion	AIBN	Coagulate	–	–	–	–
5	Miniemulsion	KPS	85	35,900	1.57	184	0.07
6	Miniemulsion	AIBN	65	22,200	1.73	184	0.12
8	Miniemulsion	KPS	95	29,000	1.22	170	0.12
9	Miniemulsion	AIBN	70	21,900	1.30	210	0.25

In contrast, both the oil-soluble initiator and water-soluble initiator could be used in the RAFT/miniemulsion polymerization of MMA (Exp. 5, 6 and Exp. 8, 9 in Table 3). The decomposition of the oil-soluble initiator AIBN and the following polymerization take place directly in the droplets. Each droplet equals a small bulk phase. The polymerization initiated by AIBN in miniemulsion has the analogous character of bulk polymerization. The water-soluble initiator KPS decomposed and then initiated the polymerization in the aqueous phase. Short chain radicals were first formed in water and then diffused to the monomer droplets or particles to make the particle grow.

The different initiation loci of KPS and AIBN would have different influences on the kinetics of RAFT polymerization of MMA in miniemulsion media. In Exp. 5 and Exp. 6, when 0.25 g SDS was used, it was found that the RAFT/miniemulsion polymerization rate with the water-soluble initiator KPS was faster than that system with the oil-soluble initiator AIBN, as shown in Fig. 11. However, at higher conversion, the curve of first-order kinetics was not linear for KPS. The reason for the observation may be that MMA is somewhat soluble in water, so the primary radicals decomposed from KPS could first initiate MMA in the aqueous phase. Meanwhile, because the oil-soluble RAFT agent CPDB was hardly soluble in water, the chain transfer reaction was less likely to occur in water phase. The free radicals would initiate the polymerization of MMA in the aqueous phase to some degree till the polymeric radicals were somewhat hydrophobic. And then these polymeric radicals diffused into the droplets or particles to initiate further polymerization.

When AIBN was used, it decomposed in the droplets. The transfer constant of free radicals to the RAFT agents was quite large that nearly all the free radicals were converted to dormant species. An AIBN-initiated RAFT polymerization of styrene in bulk was conducted by McLeary et al. [35]. They found that the reaction was extremely selective during the initiation period. Almost no RAFT-capped chains of degree of polymerization greater than unity were obtained until all the initial RAFT agent was converted into its single monomer adduct. Thereby, in the quite early stage of the RAFT/miniemulsion, the length of polymer chains initiated by AIBN was shorter than that by KPS. In fact, the length of polymeric radicals transferring to the RAFT agents in the droplets or particles has a significant effect on the kinetics of RAFT polymerization. Short dormant chains exhibit significantly shorter radical life times and hence have a slower overall rate of polymerization [36]. In addition, the RAFT/miniemulsion polymerization initiated with KPS was under zero-one condition [37]. Because of the compartment effect in emulsion polymerization or miniemulsion polymerization, the lifetime of the free radical was longer and the RAFT polymerization rate in miniemulsion should be larger than that in bulk. It was mentioned above that the RAFT/miniemulsion polymerization with an oil-soluble initiator AIBN had some similar character of bulk polymerization. Therefore, the RAFT/miniemulsion polymerization rate with AIBN would be slower than that with KPS.

3.3.2. Effect of initiator type on molecular weights and PDIs

From Fig. 12, we can find that the molecular weights of PMMA prepared by RAFT/miniemulsion polymerization with KPS or AIBN as initiator increased linearly with the

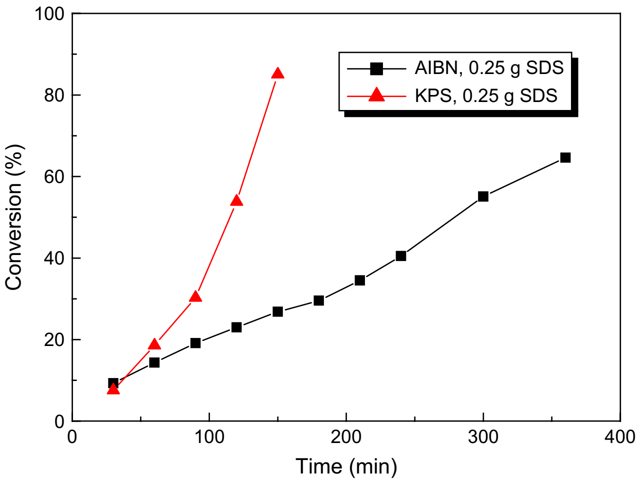

Fig. 11. Comparison of RAFT polymerizations of MMA in miniemulsion with different types of initiators on the evolution of monomer conversion as a function of reaction time (0.25 g SDS).

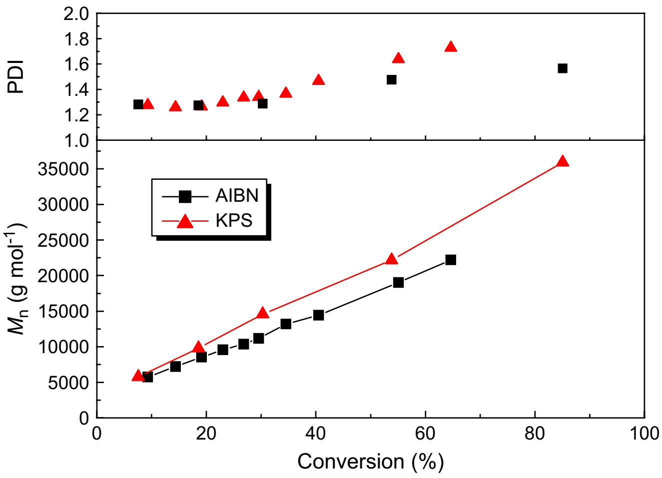

Fig. 12. Comparison of RAFT polymerizations of MMA in miniemulsion with different types of initiators on the evolution of M_n and PDI as a function of conversion. (0.25 g SDS).

conversion. However, the PDI values also increased steadily with the evolution of conversion, and even exceeded above 1.5 at the final conversion. A reasonable explanation for this result should be that the amount of surfactant SDS and co-stabilizer HD used in these experiments were only 1.25% and 2% based on the monomer, so that superswelling could not be avoided. This observation was in agreement with the results reported in the literature [33]. Comparing these two systems, we found that in the case of RAFT/miniemulsion polymerization initiated with AIBN, the obtained PDI value was higher than that with KPS. It was also due to the chain length of the polymers formed at the early stage of the RAFT/miniemulsion. Relatively short polymer chains were formed in the early stage of the RAFT/miniemulsion polymerization initiated by AIBN. Consequently, superswelling was much more likely to occur and inevitably led to higher PDI. Table 3 also gives summary results of RAFT polymerization with KPS and AIBN as initiators in emulsion and miniemulsion systems.

The criteria to evaluate a good living polymerization system is that the molecular weight should increase linearly with conversion and fit well with the theoretical value, also the PDI should be substantially below the benchmark of 1.5. However, the above results of RAFT/miniemulsion with 0.25 g SDS showed that the PDI steadily increased with conversion and the final PDI always exceeded the limitation of 1.5. Comparison was also done in RAFT/miniemulsion polymerization of MMA with AIBN or KPS as initiators in the presence of 0.60 g SDS. Compared with 0.25 g SDS, similar results were obtained in terms of polymerization kinetics and molecular weight increase with conversion, as can be seen in Figs. 7 and 8. The main difference was that the value of PDI was reduced when the amount of SDS was increased from 0.25 g to 0.60 g.

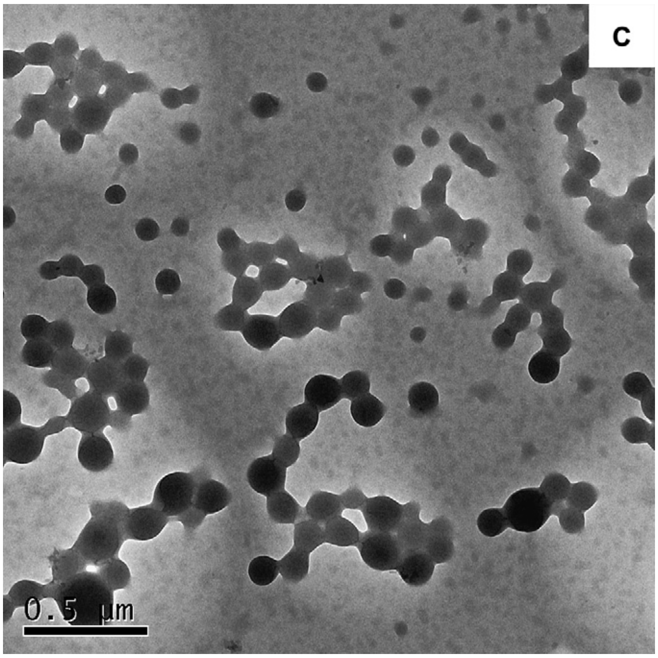

Fig. 13. TEM image of the latex particles synthesized in RAFT/miniemulsion polymerizations with KPS as an initiator.

3.3.3. Effect of initiator type on particle size and particle size distribution

The particle size and particle size distribution of the PMMA lattice were also affected by the type of initiator. As can be seen in Fig. 9, when KPS was used as the initiator, the particle size was more uniform than that with AIBN. There was only one main peak at 194 nm without any larger particles. TEM also provided the solid evidence about the uniform particle size shown in Fig. 13. This proved that when KPS was used as initiator, superswelling was less likely to take place than AIBN as initiator, and this is in good agreement with the results of kinetics, and molecular weight and molecular weight distribution.

4. Conclusions

Due to the different nucleation mechanisms of emulsion polymerization and miniemulsion polymerization, RAFT polymerizations of MMA in these two systems have different controlled/living polymerization characters. In RAFT/emulsion polymerization, a small amount of surfactant SDS would lead to large sum of coagulation. Increasing the amount of SDS could enhance the stability of RAFT/emulsion polymerization and reduce the amount of coagulation. In RAFT/miniemulsion polymerization, much stable latex was obtained even at low amount of surfactant SDS. No coagulation formed although a red bulk layer was observed at the early stage of the polymerization. The polymerization exhibited good living character. Adding a small amount of Me-β-CD as the solubilizer to the RAFT/miniemulsion polymerization could enhance the stability and controlled/living character of the RAFT polymerization of MMA in miniemulsion systems. For the RAFT/miniemulsion polymerization containing Me-β-CD, the common red bulk layer was eliminated and the PDIs of the polymers were reduced, compared to the system without Me-β-CD. Adding Me-β-CD to the RAFT/emulsion polymerization could reduce the amount of coagulation, but did not have any effect on the living polymerization character. The molecular weight distribution (PDI) was still high. In RAFT/miniemulsion polymerization of MMA, water-soluble initiator KPS and an oil-soluble initiator AIBN had different effects on the polymerization kinetics and living polymerization character. Experimental results indicated that KPS was better than AIBN with respect to the living polymerization character, monomer conversion, particle sizes and size PDIs.

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