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ORIGINAL CONTRIBUTION

Living radical miniemulsion polymerization by RAFT in the presence of beta-cyclodextrin

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Abstract Living radical polymerization of styrene in a miniemulsion by reversible addition–fragmentation chain transfer (RAFT) was successfully realized in the presence of beta-cyclodextrin (CD), using sodium dodecyl sulfate and hexadecane as surfactant and costabilizer, respectively. The drawback of instability (red layer formation) encountered in the living radical polymerization in emulsion or miniemulsion was overcome. The linear relationship between the monomer conversion and the molecular weight, as well as lower molecular weight distribution (MWD), shows that the polymerization process was under control. The addition of CD was found to have little influence on the polymerization rate. However, MWD of the polymer synthesized is obviously decreased. The mechanism of stability and controllability improvement in the presence of CD proposed that the complex formation between CD and RAFT agent or RAFT agent-ended oligomer increased their diffusion ability from monomer droplet to polymerization locus and improved the homogeneity of the RAFT agent level among the polymerization loci.

Keywords Miniemulsion polymerization · Reversible addition–fragmentation chain transfer · beta-Cyclodextrin

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Introduction

Various homogeneous reversible addition–fragmentation chain transfer (RAFT) polymerizations in bulk and solution were widely investigated [1–8]. A common feature reported is the low polymerization rate for either styrene (St) [2–5, 7, 8] or methacrylate [2–7] monomer when keeping a narrow polydispersity of molecular weight. It could be attributed to the intrinsic drawback of the homogeneous living radical polymerization in which low concentration of free radical must be kept to avoid the bimolecular termination between the radicals.

Heterogeneous polymerization system, such as emulsion or miniemulsion, gives us a chance to prevent or reduce this bimolecular termination via its compartmentation effect on the active radicals [9–19].

Unexpectedly, the polymerization rates were significantly retarded by the addition of RAFT agent due to the exit of radicals produced by chain transfer to the RAFT agent and then fragmentation, and which then terminated in the aqueous phase or reentry to terminate a radical already growing inside particles [12–14]. Large polydispersity of molecular weight was reported in the ab initio and seeded emulsion polymerization in the presence of a RAFT agent, although the linear relationship between the molecular weight and conversion suggested the living character of the polymerization process [10–14, 17, 18]. The appearance of red oil layer in the vortex shortly after the commencement of polymerization is another problem confronted in emulsion polymerization [13]. The low diffusion rate of the RAFT agent oligomer through water phase or the formation of oligomers in droplets was assumed to be the culprit behind the problem [13, 16]. However, application of water-soluble RAFT agent in ab initio emulsion polymerization of methyl methacrylate

(MMA) and vinyl acetate was also unsuccessful [11]. Seeded emulsion polymerization was therefore adopted to avoid the transfer of RAFT agent through water phase to reaction loci [15, 16, 19].

Another option to bypass the transfer of monomer through water phase is miniemulsion polymerization [9, 20–26]. Miniemulsion polymerization is featured by its droplet nucleation and could copy the droplets into polymer particles during the polymerization process in ideal condition [27]. Therefore, the transfer of a monomer through water phase to reaction loci is not required during miniemulsion polymerization and homogeneous RAFT concentration in all polymerization loci is expected. It is the case that no instability phenomenon was observed in the RAFT living radical polymerization of St or alkyl methacrylate conducted in the miniemulsion stabilized by nonionic surfactant Igepal 890 or Brij 98 [28]. The molecular weight distribution (MWD) of the polymer prepared was as low as around 1.10–1.20 for St, ethylhexyl methacrylate, MMA, and *n*-butyl methacrylate. Unfortunately, an instability problem was still encountered in the RAFT living polymerization carried out in miniemulsion using anionic or cationic surfactant [20, 21]. The MWD of the polymer was also as high as 1.8–2.5 when sodium dodecyl sulfate (SDS) was used as surfactant [10, 21, 23, 25, 26]. Luo et al. [23] proposed that the superswelling effect caused by oligomer in RAFT living radical polymerization could play a significant role in the instability of living radical miniemulsion polymerization through simulation of the chemical potential difference between droplets and particles. Their simulation results suggested that the use of nonionic surfactant and high level of costabilizer to decrease the monomer diffusion through water phase would depress the superswelling effect and would benefit the miniemulsion stability. This was demonstrated by some experimental results in different groups [20, 24, 26, 29]. Macro-RAFT agent was used to eliminate the exit of short active radicals from the particle to better control the RAFT polymerization in miniemulsion [24, 26].

It is known that CD has a cyclic structure with special conformation in which hydrophilic hydroxyl groups are faced outside and formed a hydrophilic exterior and leaves a hydrophobic cavity of 6.5 Å in diameter. Therefore it can enclose smaller molecules to form water-soluble host–guest complexes. It was reported that CD could be used as phase transfer catalyst to overcome the solubility barrier in emulsion polymerization of highly water-insoluble monomers [30–35]. The proposed mechanism is that water-soluble complex formation among CD and hydrophobe reduces the kinetic barrier and makes it easier for the monomer to leave the monomer droplet. After arriving at the surface of the growing particle, the monomer is released from the complex and is able to enter the particle. Now the free CD can start its transportation again [33]. The peculiar complex-forming ability of CD in water phase could provide a new way to surmount the diffusion barrier of the RAFT agent or RAFT agent-ended oligomer through water phase and realize a homogeneous concentration of RAFT agent in the polymerization loci. In this contribution, we wish to report the successful RAFT miniemulsion polymerization of St and MMA in the presence of CD. The effects of initiator polarity, reaction temperature, and the amounts of CD and RAFT agent on the polymerization were investigated.

Experimental section

Reagents

St, MMA, and butyl acrylate were supplied by Dongfang Chemical (China) and were distilled in reduced pressure and stored in a refrigerator before use. 2,2′-Azobisisobutyronitrile (AIBN) was the chemical reagent and was recrystallized from methanol. Ammonium persulfate (APS), SDS, hexadecane (HD), and hydroquinone were of synthetic grade and were used as received. Beta-cyclodextrin (CD) was purchased from Shanghai Reagent and was recrystallized twice in water at 70 °C before use. Deionized water was used throughout the research.

Synthesis of RAFT agent

Dithiobenzoyl disulfide was synthesized according to Mitsukami et al. [36]. The RAFT agent 2-(2-cyano) propyl dithiobenzoate (CPDB) was prepared by the method of Thang et al. [37]. Distilled ethyl acetate (80.0 ml) was added to a 250-ml round-bottomed flask. Then dry 2,2′-azobissiobutyronitrile (3.44 g, 21.0 mmol) and dithiobenzoyl disulfide (4.25 g, 14.0 mmol) were added. The reaction solution was heated at reflux for 18 h. Most of the ethyl acetate was removed by rotating it in an evaporator and then was completely removed in a vacuum oven at room temperature. The crude product was isolated by column chromatography (silicone gel, chromatography grade) using ethyl acetate and hexane (2:3) as eluent. Fractions that were red in color were combined and dried by anhydrous sodium sulfate overnight. The solvent mixture was removed using a vacuum oven at room temperature overnight, and the red oily residue was placed in a freezer at −20 °C, whereupon it crystallized. The target compound was recrystallized from benzene. The ^{1}H NMR spectrum of CPDB is shown in Fig. 1.

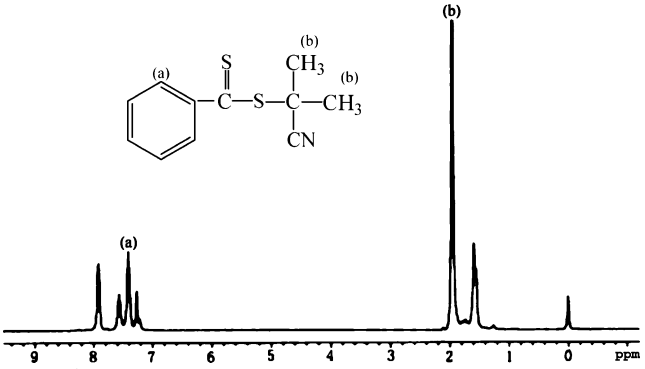

Fig. 1 ^{1}H NMR spectrum of CPDB

Preparation and polymerization of miniemulsion

A typical recipe for miniemulsion is composed of the following: deionized water 80 g, St 20 g, SDS 0.25 g, AIBN 0.05 g, CPDB 0.20 g, HD 0.40 g, and CD 0.205 g. Miniemulsion was prepared by dissolving SDS and CD in water and HD, AIBN, and CPDB in monomer St. Oily phase and aqueous phase were mixed with a magnetic stirrer for 15 min. The preemulsion was then sonicated at 60% of output in pulse mode for 5 min (Branson ultrasonic disintegrator, Shanghai Branson Ultrasonic, China). Immediately after sonication, the miniemulsion produced was transferred into a 250-ml four-necked flask equipped with a mechanical stirrer, thermometer, nitrogen inlet, and reflux condenser. The miniemulsion was purged with nitrogen for 10 min before it was put into the thermostat at reaction temperature. The polymerization temperature was kept constant at 70 °C if not specified.

Conversion

Samples were taken regularly during the polymerization, quenched with a few crystals of hydroquinone. The monomer conversion was measured by gravimetric method after evaporation of all volatile compounds of the dispersion at 50 °C during 24 h.

TEM analysis

The synthesized latexes were diluted with deionized water to about 100:1. One drop of the latex was placed on the coated side of a 200-mesh copper grid. After 18–24 h of drying, the samples were ready to be observed by transmission electronic microscope (TEM; Hitachi H-600).

GPC analysis

Gel permeation chromatography (GPC) analysis was carried out with Waters Corporation Model 1515 instrument. Tetrahydrofuran was used as eluent (flow rate=1.0 ml min^{-1}), and calibration was done with polystyrene standards. Data acquisition was performed with Waters software. The ratio of weight and number average molecular weight (M_w/M_n) was used to characterize the MWD.

Results and discussion

Preliminary experiments were carried out to make sure the effectiveness of CD in the RAFT radical polymerization of styrene in miniemulsion using water-soluble and oil-soluble initiator. The results show that the instability phenomenon of red layer or coagulum reported in literatures was not observed during all the polymerization processes whether anionic or anionic/nonionic surfactant mixture was used as emulsifier. The following discussion concentrates on the miniemulsion polymerization when anionic surfactant SDS was used as emulsifier.

Initiator solubility

The results of RAFT radical polymerization of styrene in miniemulsion initiated by water-soluble APS and oil-soluble AIBN are shown in Fig. 2. It is seen that CD has a different effect on the miniemulsion polymerization initiated by APS and AIBN. The miniemulsion polymerization rate was little affected by the introduction of CD when AIBN was used as initiator. However, the styrene miniemulsion containing CD shows a higher polymerization rate than that without CD when the polymerization was initiated by APS. The water-soluble and the surface-active characteristics of CD may result in the increase of polymerization rate [32]. The relationship between the molecular weight and conversion of monomer was kept linear and MWD was less than 1.8 at most of the polymerization process when the polymerization was initiated by either AIBN or APS as shown in Fig. 2b,c. This means that the miniemulsion polymerization of styrene was under control. The MWD of polystyrene formed in the presence of CD was much lower than that in the absence of CD when AIBN was used as initiator. This demonstrates the efficiency of CD in improving the controllability of the living radical polymerization of styrene in miniemulsion. When APS was used as initiator, however, the effectiveness was reduced. The increase in MWD with conversion, which was not observed when styrene was replaced by MMA (refer to the results in "Availability in other monomers"), may be due to the low propagation rate constant of styrene.

As mentioned in the "Introduction", the hydrophobic interior or cavity of CD molecules could encapsulate smaller molecules to form water-soluble complexes [30–35]. The formation of CD complexes is supposed to increase the diffusion ability of the RAFT agent or RAFT

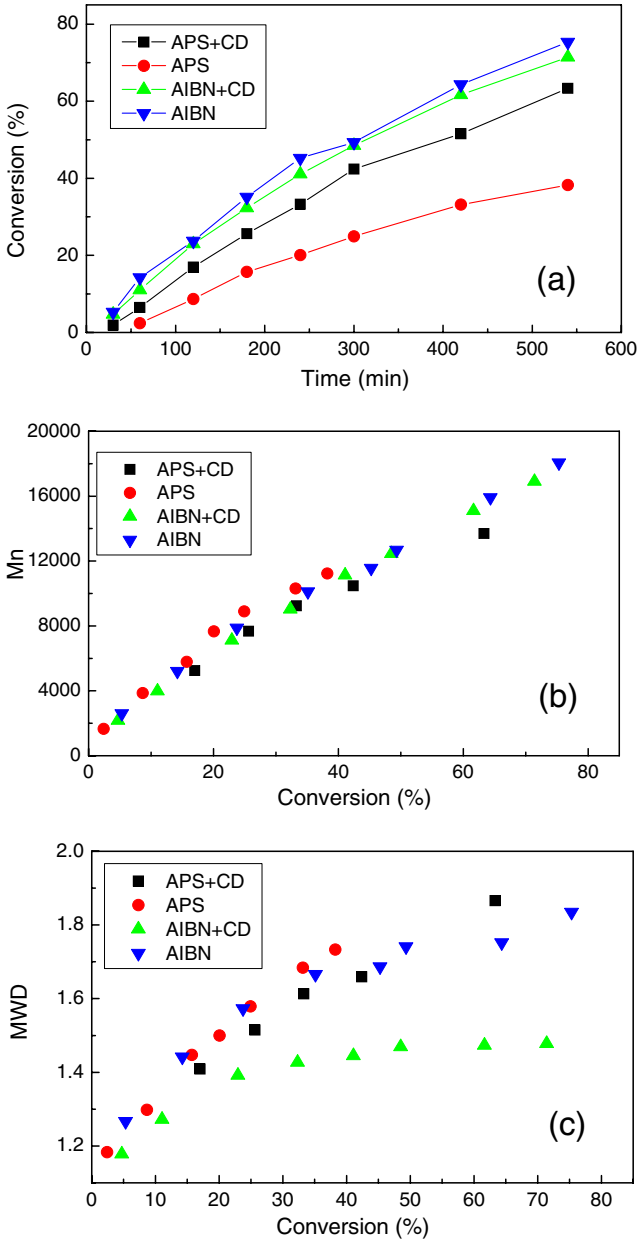

Fig. 2 Effects of CD on the RAFT polymerization of styrene miniemulsion initiated by APS or AIBN

agent-ended oligomer through water phase to the nucleated particles and improve the homogeneity of RAFT agent level among polymerization loci [38]. Therefore, the formation of a complex between CD in the water phase and various RAFT agents, including CPDB and dithiobenzoyl-capped oligomers (macro-RAFT agent) diffused out from the particle or droplet, may be the key factor that determines the efficiency in the RAFT/miniemulsion polymerization. When the miniemulsion polymerization was initiated by hydrophobic initiator AIBN, the dithiobenzoyl-capped oligomers diffused out from droplet are hydrophobic and are easily enclosed by CD and transferred to other particles or droplets. The concentration of the CPDB in polymerization loci was kept even. Whereas the CPDB-capped oligomers initiated by APS is of relatively higher hydrophilicity than that by AIBN. Therefore the formation of CD complexes was depressed, which resulted in the efficiency reduction of CD.

Amount of beta-CD

The effect of the amount of CD on the miniemulsion polymerization initiated by AIBN is shown in Fig. 3 (from this section, AIBN was used as initiator). The polymeriza-

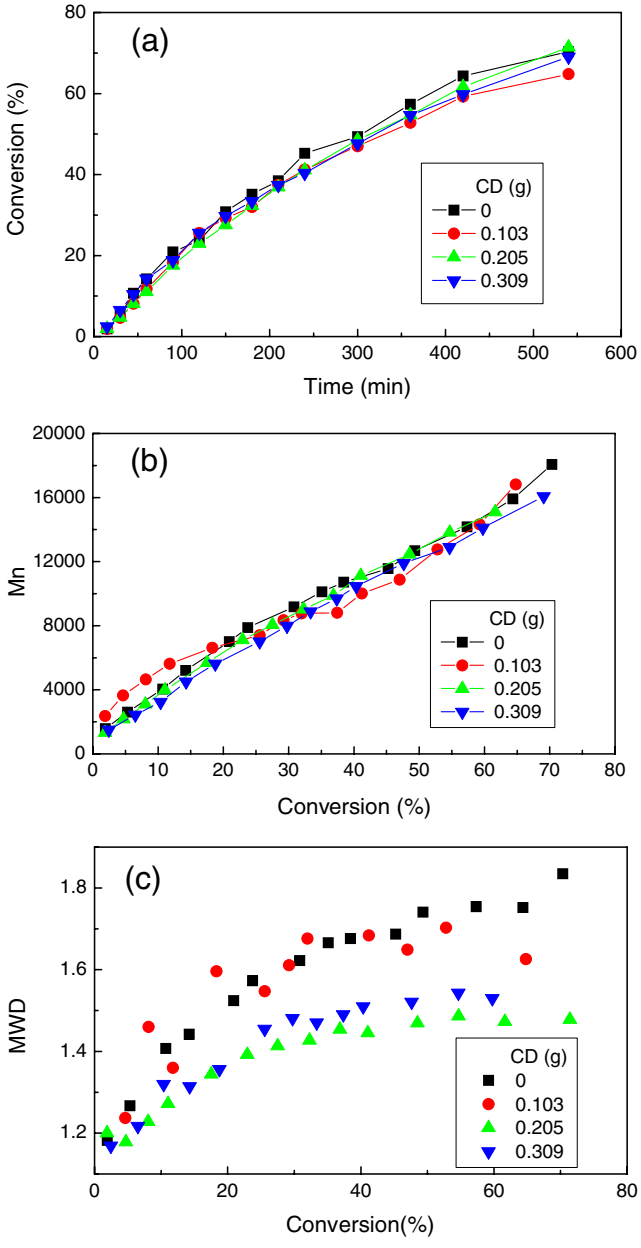

Fig. 3 Effects of CD amounts on the RAFT polymerization of styrene miniemulsion initiated by AIBN

tion rate of styrene was kept the same within the experimental error at a different amount of CD. The molecular weight increased linearly with the increase of styrene conversion at all CD amounts, indicating the living characteristic of polymerization. Lowest MWD value was obtained at the 1:1 ratio of CD to CPDB in the miniemulsion. TEM micrographs of the latex particles at different amounts of CD were given in Fig. 4. It can be seen that the particle size distribution of the latex was broad when no CD existed in the miniemulsion. When some CD was added into the miniemulsion, the particle size distribution became narrower, although the particle size was increased to some extent. This may be contributed to the enclosure of some emulsifier into CD cavity and may reduce the surfactant level in the miniemulsion. The shelf life of the latex was also found to be longer when the amount of CD added was increased.

Polymerization temperature

It is well known that the higher the temperature, the higher the polymerization rate and the lower the molecular weight of the polymer formed in the conventional free radical polymerization. Only a few reports were published on the effect of temperature on the RAFT polymerization and the conclusions were inconsistent [1, 38–40]. Bai et al. [39] reported that higher polymerization rate was obtained at higher temperature in the bulk polymerization of methyl acrylate using dithiobenzoic acid as RAFT agent. However, the MWD was obviously increased with the increase of temperature. In the bulk polymerization of 4-acetoxystyrene using *S*-thiobenzoylthioglycolic acid as RAFT agent, the MWD of the poly(4-acetoxystyrene) formed was found to be constant at temperatures of 60, 80, and 90 °C [1]. Recently, Shim et al. [40] reported that the MWD of poly (methyl methacrylate) (PMMA) was reduced at high temperature in the MMA miniemulsion polymerization when 4-thiobenzoyl sulfonyl methyl benzoic acid was used as RAFT agent. According to our experiments, the results are different from the above-mentioned conclusions. The polymerization rate increased at higher temperature, whereas the molecular weight of polystyrene decreased as shown in Fig. 5, which is a common phenomenon in the free radical polymerization. The MWD value of the polystyrene formed was lowest at 70 °C and highest at 75 °C in most conversion ranges. It seemed that 70 °C was an optimal temperature for this polymerization system. The efficient chain transfer balance at high temperature tended to reduce the MWD. However, the following two factors would result in the broad MWD at high temperature: (1) the high diffusion ability, which induced the exit of the oligomer radical to water phase, and (2) the high radical concentration, which caused the high chance of termination between the monomer radicals. The efficiency of CD–CPDB complex or CD–macro-RAFT formation at different temperature may also contribute to it.

The UV spectrophotometer was used to explain the effect of the temperature on the partition of the CPDB between water phase and oil phase. Forty milliliters of CD solution of 0.25 g/l and CPDB hexane solution of 20 ml was added into a 100-ml flask with stop. The mixture was then stirred for 30 min in a water bath at 65, 70, and 75 °C. The solution mixture was kept static until phase separation was finished. The oil phase was separated out for UV spectrophotometer measurement at 231 nm. The residual CPDB in hexane phase was then calculated according to the

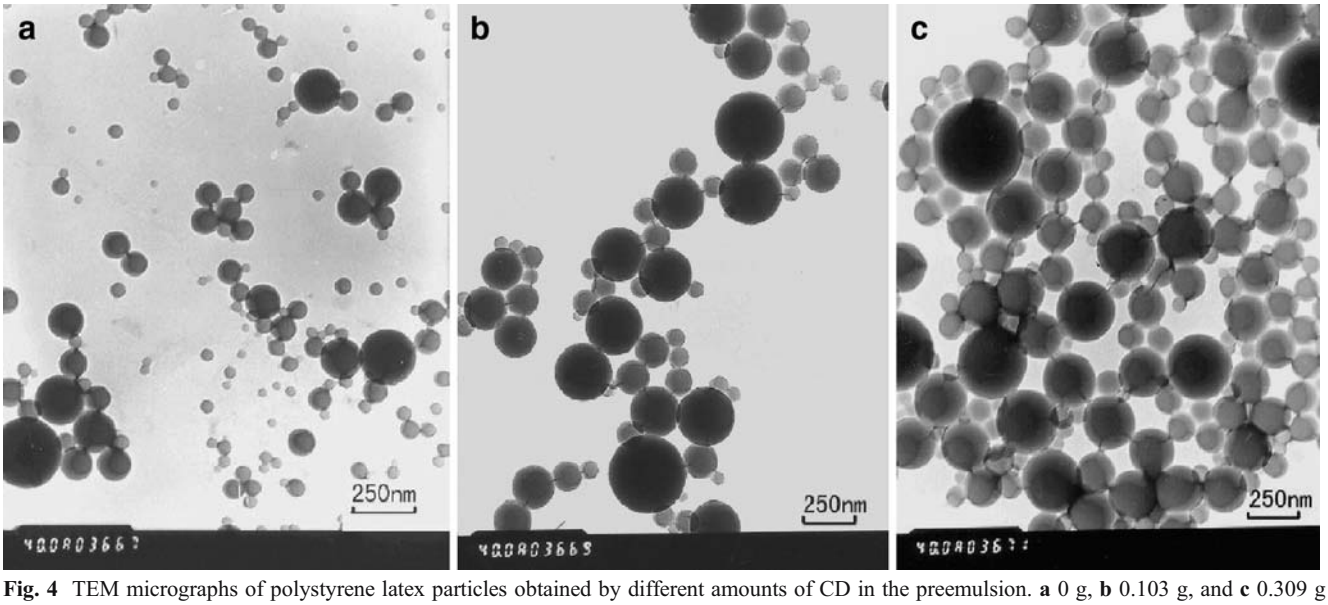

Fig. 4 TEM micrographs of polystyrene latex particles obtained by different amounts of CD in the preemulsion. **a** 0 g, **b** 0.103 g, and **c** 0.309 g

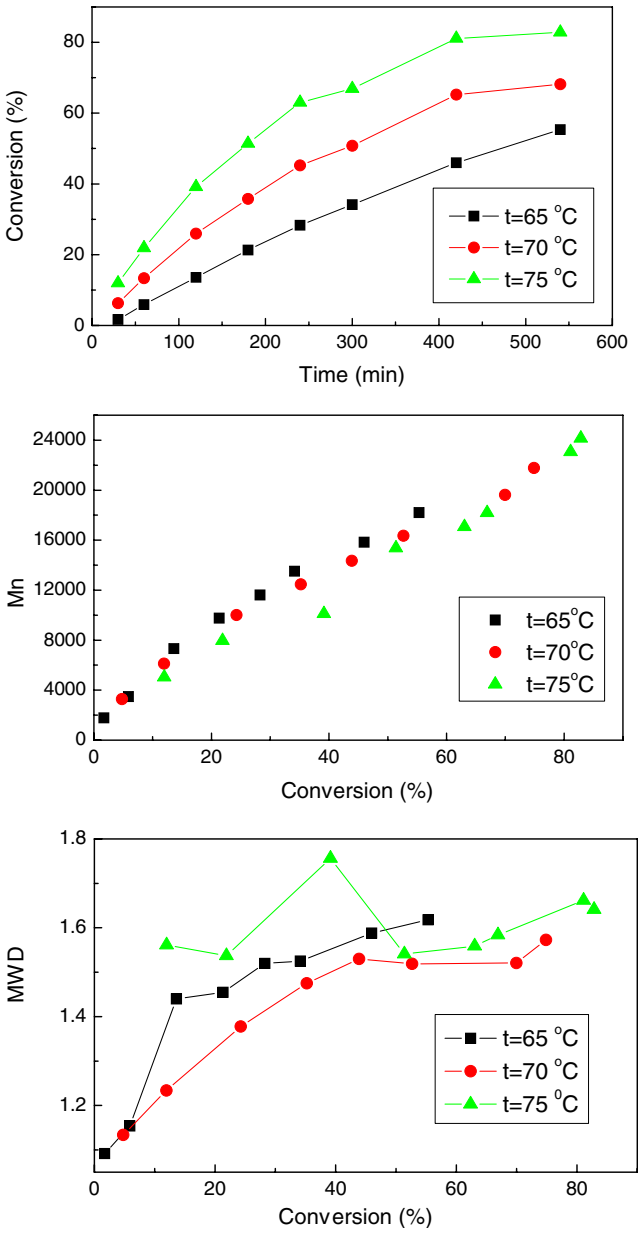

Fig. 5 Effects of reaction temperatures on the styrene RAFT miniemulsion polymerization in the presence of CD

adsorption value by means of calibration curve. The results in Table 1 indicate that the residual CPDB in oil phase was lowest at 70 °C although the difference among them was not very obvious. This partition result and the polymerization result as mentioned above suggest that the complex formed plays an important role in improving the controllability of the miniemulsion polymerization.

Table 1 The UV absorption of the CPDB in oil and water phase at different temperatures

Temperature (°C)	UV absorption	CPDB concentration (g/l)
65	1.57	0.086
70	1.48	0.079
75	1.58	0.088

Amount of RAFT agent

Figure 6 shows the results of miniemulsion polymerization in the presence of different amounts of CPDB while other parameters were kept constantly. It is seen that the polymerization rate reduced and the molecular weight of polystyrene decreased with the increase of CPDB content. At the same time the MWD was narrowed. This is in accordance with the results obtained by other researchers in the miniemulsion polymerization without CD [25, 40]. The

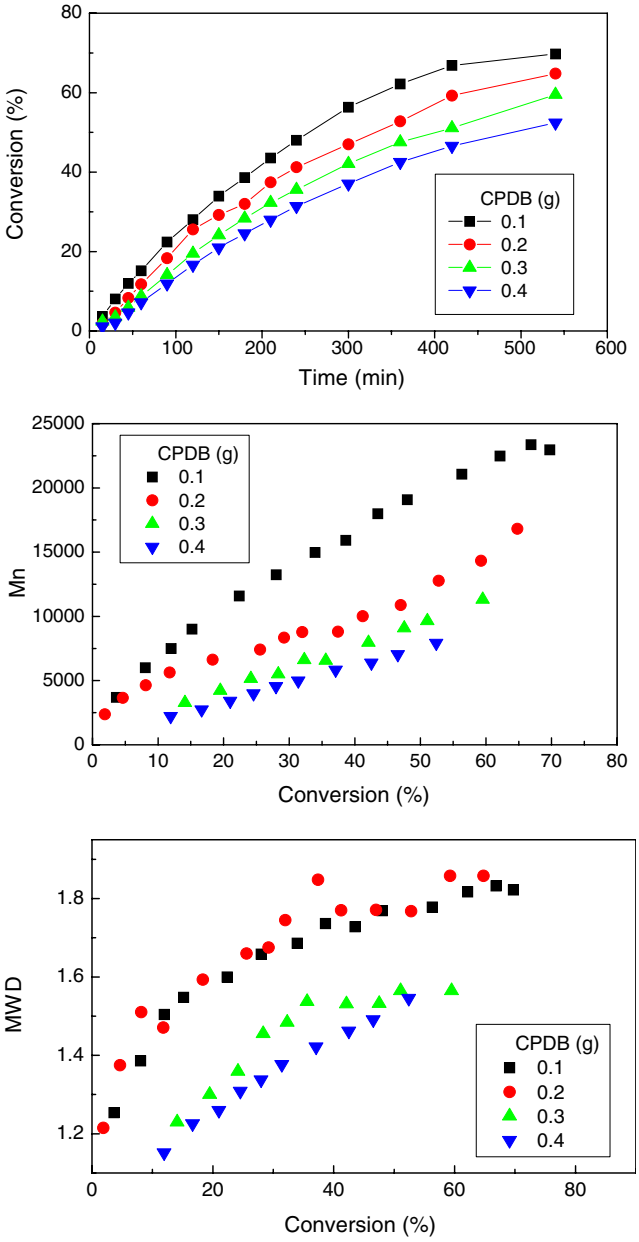

Fig. 6 Effect of CPDB amount on the styrene RAFT miniemulsion polymerization in the presence of CD

results of miniemulsion polymerization with CD at different AIBN content also show the same trend as that without CD in the miniemulsion.

Amount of costabilizer HD

It is well known that addition of costabilizer HD could reduce the Ostwald ripening between the droplets with different droplet size and endow the miniemulsion with stability. Effect of the amount of HD on the miniemulsion polymerization of St in the presence of CD is shown in Fig. 7. It is seen that the amount of HD has little effect on the polymerization rate when other experimental parameters were kept constantly. It, however, had some influence on the molecular weight, although no obvious trend could be obtained. The polydispersity of molecular weight at highest HD amount (0.8 g) was found to be smaller than that at lower HD amount, which could be ascribed to more stability of the miniemulsion at high HD amount and coincident with the prediction of Luo et al. [23].

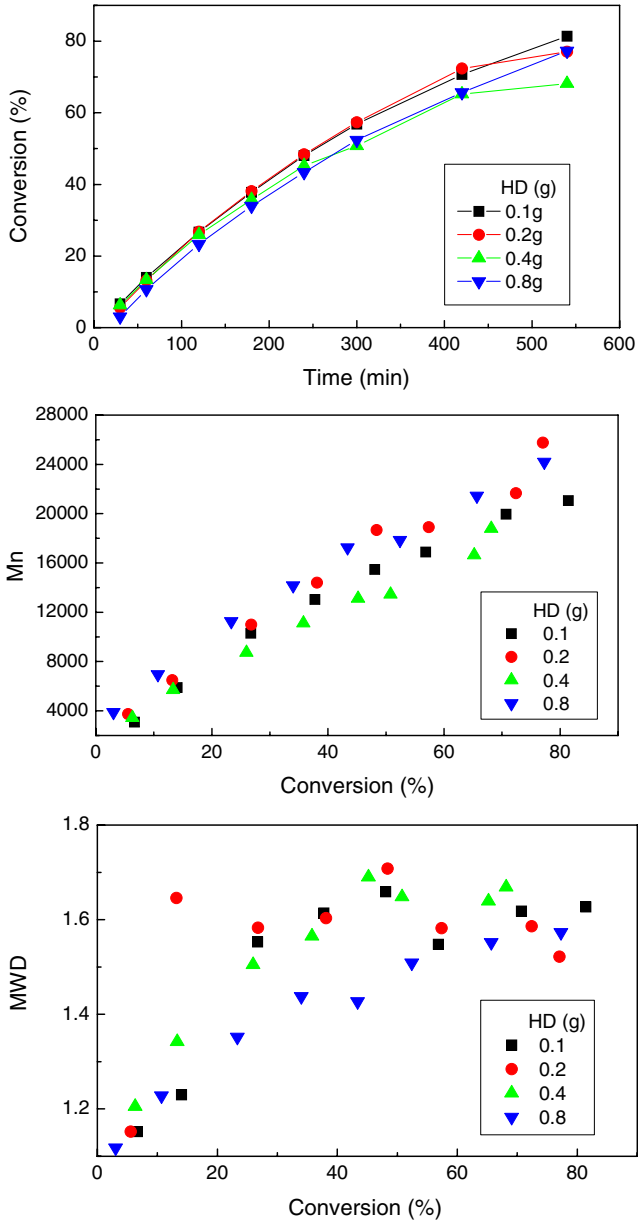

Fig. 7 Effects of the costabilizer HD amounts on the styrene RAFT miniemulsion polymerization in the presence of CD

Availability in other monomers

The results of miniemulsion polymerization of MMA in the presence and absence of CD are shown in Fig. 8 when CPDB was used as RAFT agent. The controllability of RAFT miniemulsion polymerization of MMA was greatly improved when a catalytic amount of CD was added into the preminiemulsion by comparing the MWD conversion curves and the MWD of the final polymer with and without CD. The phenomenon that MWD increases with conversion, as observed in the styrene miniemulsion polymerization, did not appear. The MWD of the PMMA formed was kept at a low value at high conversion (around 1.3) when CD was present in the recipe. The availability of the method for the miniemulsion polymerization of butyl methacrylate was also conformed and the results are disclosed elsewhere [38].

Conclusions

The complex formation of CD was successfully applied to improve the controllability of the styrene or MMA miniemulsion polymerization. The stability problem encountered in the RAFT miniemulsion polymerization was overcome and the controllability of the RAFT polymerization was successfully improved by the addition of a small amount of CD in the miniemulsion when the miniemulsion polymerization was initiated by water-soluble initiator APS. This was attributed to the complex formation between the CPDB or CPDB-ended oligomer that diffused out from

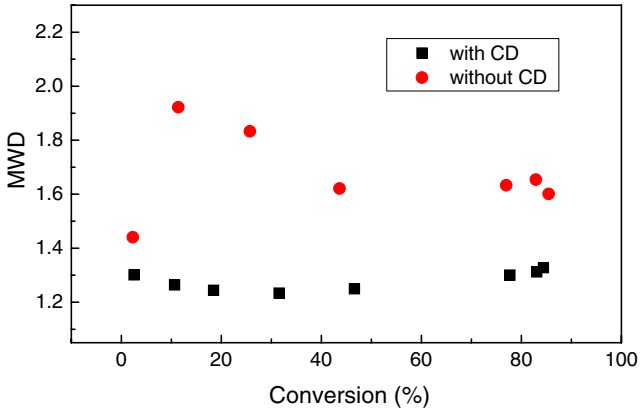

Fig. 8 MWD-conversion profile of the RAFT polymerization of MMA miniemulsion in the presence or absence of CD

droplet and the CD during polymerization, which improved the homogeneity of the RAFT agent level among the polymerizing loci.

Similar to miniemulsion without CD, an increase in the amount of RAFT agent or costabilizer HD was favorable to improve the controllability of the polymerization. Polymerization temperature affected both the MWD of polystyrene in the range of 65 to 75 °C and the polymerization rate. The best control of the polymerization was achieved with the CD to CDBP ratio of 1:1 (w/w) in the miniemulsion, although higher amount of CD was found to be beneficial to the stability of the polymer latex.

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