1. Introduction

Since the advent of reversible addition–fragmentation chain transfer (RAFT) polymerization in 1998, it has been an effective and robust method to prepare not only well-controlled polymers with pre-designed molecular weight and narrow polydispersity, but also varied topologies, such as block copolymers, grafting polymers, star polymers, etc. RAFT polymerization is a popular method because of its high tolerance to different conditions and convenient operation to carry out heterogeneous reactions, such as suspension, dispersion, emulsion, miniemulsion, and microemulsion polymerization.

In the initial work of RAFT mediated emulsion polymerization, only hydrophobic control agents with low chain transfer constants (dithiocarbonate) can lead to successful synthesis (i.e., good control over the polymerization along with formation of stable latexes) while more reactive chain transfer agents proved to be unsuccessful. Significant headway hadn’t been made until strategies employing macromolecular chain transfer agents were put forward. Charleux et al. first reported an approach to carry out miniemulsion polymerization by using amphiphilic diblock copolymer to emulsify the monomer phase in water, stabilize the particles and polymerize a third monomer for the preparation of triblock copolymers.

In recent years, polymerization-induced self-assembly (PISA) first proposed by Hawkett et al. attracts many scientists’ attention since it has excellent advantages, such as high polymer content at a low viscosity, convenient operation and producing diblock copolymer nano-objects in situ. In this work, a soap-free emulsion with high solid content (60%) was successfully prepared in a semi-batch monomer addition manner. High monomer conversion can also be obtained by adjusting the dripping time. At first, a hydrophilic polymer, poly(poly(ethylene glycol)monomethyl ether methacrylate) (PPEGMA) was synthesized at almost complete monomer conversion in order to be used as a macroRAFT agent without any purification in the following step. Then PPEGMA was chain extended by the second monomer, methyl methacrylate (MMA), added at a very slow rate to form diblock copolymers and further self-assembled into nanoparticles in situ. The resulting latexes were very stable and the particle sizes remained at the nanoscale.
Some literatures have reported polymerization system at high solids up to 50% obtained by aqueous dispersion PISA while few reports about that by aqueous emulsion PISA. However, only few vinyl monomers are amenable to aqueous dispersion polymerization, including 2-isopropylacrylamide (NIPAM), \(^{20}\) \(N,N\)-diethylacrylamide (DEAA), \(^{21}\) 2-methoxymethyl acrylate (MEA), \(^{22}\) 2-hydroxypropyl methacrylate (HPMA) \(^{23}\) and \(N\)-ethyl methacrylate (DEGMA). \(^{24}\) Therefore aqueous emulsion PISA is more extensive with respect to monomer species and it is highly appreciated to develop high solids aqueous emulsion PISA. Semi-batch or monomer starved addition manner have been normally used in conventional emulsion to achieve small particle size at a low content of surfactant. The advantage of this addition manner can keep low concentration of monomer at the system during the polymerization.

In this work, we adopted semi-batch addition manner in the PISA process to prepare soap-free emulsion with high solid content and high monomer conversion. Hydrophilic PPEGMA was firstly prepared and then acted as macroRAFT agent to mediate the polymerization of MMA whose addition rate was precisely controlled by a dosing pump. Herein, the conversion of PEGMA in the first step reached nearly 100%, so no purification was needed, which dramatically simplified the synthetic process.

2. Experimental section

2.1. Materials

Poly(ethylene glycol)monomethyl ether methacrylate (PEGMA), average molecular weight is 500 g mol\(^{-1}\), 99%, Sigma-Aldrich) and methyl methacrylate (MMA, 99%, Shanghai Chemical Reagents Co. Ltd (Shanghai, China)) were passed through a neutral alumina column to remove inhibitor. 4-Cyano-4-(thiobenzoylthio)pentanoic acid (CTBCOOH) was purchased from J&K Chemical Co. Pure water (H\(_2\)O, Hangzhou Wahaha Group Co. Ltd) was obtained from the supermarket. Tetrahydrofuran (THF, analytical reagent), \(n\)-hexane (analytical reagent) and all other chemicals were purchased from Shanghai Chemical Reagents Co. Ltd. and used as received.

2.2. Synthesis of PEGMA macroRAFT agents

The typical procedure to prepare PPEGMA with a molar ratio of [PEGMA]_0/[CTBCOOH]_0/[AIBI]_0 = 20/1/0.2 was as follows: CTBCOOH (90.6 mg, 0.325 mmol), AIBI (21.0 mg, 0.065 mmol), PEGMA (3.0 mL, 6.48 mmol) and water (3.0 mL) were added in a flask with a magnetic stir bar. After three freeze–pump–thaw cycles, the flask was put into an oil bath with temperature held at 70 °C. After 1.5 h, the polymerization was quenched by immersing the flask in an iced water bath. The monomer conversion was determined by \(^1\)H NMR spectroscopy in D\(_2\)O. A little amount of sample was freeze-dried and then dissolved in THF, and precipitated out from \(n\)-hexane. The molecular weight and dispersity values of polymers were determined by GPC in THF.

2.3. Synthesis of PPEGMA-b-PMMA amphiphilic diblock copolymer nanoparticles by RAFT emulsion polymerization

The typical procedure with a molar ratio of [MMA]_0/[PEGMA]_0/[AIBI]_0 = 100/1/0.2 was as follows: a little amount of MMA (0.14 mL, 1.32 mmol), and AIBI (4.2 mg, 0.013 mmol) were added to a solution of previously synthesized PPEGMA macroRAFT (\(M_n = 6900 \text{ g mol}^{-1}, M_w/M_n = 1.29\)) agent and the amount of water was adjusted according to different solid contents. The reaction mixture was placed in a rubber-sealed flask with a magnetic stir bar. The remainder monomer (0.56 mL, 5.28 mmol) was purged with argon for 15 min to remove the dissolved oxygen prior to addition. After purged with argon for 30 min in an ice bath, the flask was heated at 60 °C in a thermostated oil bath under stirring, and at the same time, the remainder monomer was added into the flask at a given rate monitored by a syringe pump (TJ-3A, Baoding Longerpump Co. Ltd). A balloon filled with argon was linked to the flask to provide only slight overpressure. When monomer was added completely, the polymerization was quenched by immersing the flask in an iced water bath. A small amount of sample was freeze-dried, dissolved in 2 mL of THF, and then precipitated out from \(n\)-hexane. The monomer conversion was determined by gravimetric analysis. The molecular weight and molecular weight distribution were determined by GPC with THF as a mobile phase.

2.4. Characterization

Number average molecular weight (\(M_n,\text{GPC}\)) and molecular weight distribution (\(M_w/M_n\)) of resulting polymers were determined by TOSOH HLC-8320 gel permeation chromatography (GPC) comprised of a Waters 717plus autosampler, a refractive index detector (TOSOH), TSKgel guard column SuperMP-N (4.6 × 20 mm) and two TSKgel SupermultipleHZ-N (4.6 × 150 mm). THF was used as the mobile phase, eluting at 0.35 mL min\(^{-1}\) at 40 °C. The narrow PMMA standards with molecular weights ranging from 5 × 10^2 g mol\(^{-1}\) to 5 × 10^5 g mol\(^{-1}\) were used as calibration. \(^1\)H NMR spectra of the synthesized polymers were recorded on a Bruker 300 MHz nuclear magnetic resonance (NMR) instrument using D\(_2\)O or DMSO as the solvent. Dynamic light scattering (DLS, Nano ZS from Malvern Instruments) was used to determine the intensity-average hydrodynamic diameter (\(d_h\)) and the dispersity in size of latex (indicated by the polydispersity index, PDI) at 25 °C. The latex was diluted in deionized water and data were averaged over three measurements. The nanoparticles images were taken by using transmission electron microscopy (TEM, Hitachi H-7000) at an acceleration of 120 kV. Diluted solution was dropped on a copper grid and excess solution was drawn off the edge of the grid with tissue paper. Then the grid was stained with 1% (w/v) phosphotungstic acid and dried under air before observation.

3. Results and discussion

3.1. Synthesis of PPEGMA macroRAFT agent

The RAFT polymerizations of PEGMA were conducted in water using in all cases CTB–COOH as the control agent and AIBI as the initiator to synthesize macroRAFT agents (PPEGMA), which
were subsequently chain extended using MMA as the monomer under PISA conditions. As shown in Table 1, PPEGMA with different molecular weights were prepared by changing molar ratios of [PEGMA]₀/[CTB–COOH]₀. In order to use the polymer solution of PPEGMA directly without further purification in the subsequent PISA process, all the polymerizations were not stopped until the monomer conversion reached close to 100% (at least >96%). It is also found that the values of \( M_n,GPC \) by GPC analysis are close to the theoretical \( M_n,th \) ones and the values of molecular weight distribution (MWD) are rather low which indicate a well-controlled polymerization process. Furthermore, \(^1\text{H} \) NMR was also employed to calculate the molar mass of the polymer chains \( (M_n,NMR) \) and in all cases, the values of \( M_n,NMR \) are very close to the theoretical \( M_n,th \).

### 3.2. Soap-free emulsion RAFT polymerization in semi-batch way

Emulsion polymerizations were carried out with MMA as a hydrophobic monomer, AIBI as a water-soluble initiator and PPEGMA as macroRAFT agent. The polymer solution of PPEGMA was used directly followed by the addition of calculated amount of water according to the desired solid content of the system. At first, one fifth of total monomer was added to the system, so that hydrophilic chain of PPEGMA could react with MMA to form block copolymer, PPEGMA-\( b \)-PMMA, which may facilitate the formation of nanoparticles in the subsequent PISA process. The other part of monomer was injected slowly to the system in a semi-batch way with dripping rate precisely monitored, which can prevent high viscosity of emulsion and ensure the polymerization goes smoothly. As a consequence, the monomer was gradually consumed to form longer block copolymers.  

![Fig. 1](image1.png)

**Fig. 1** GPC curves of macroRAFT agent, PPEGMA-2 and block copolymer, PPEGMA-2-\( b \)-PMMA.

![Fig. 2](image2.png)

**Fig. 2** \(^1\text{H} \) NMR spectrum (300 MHz, DMSO-\( d_6 \)) of PPEGMA-\( b \)-PMMA prepared by emulsion RAFT polymerization in semi-batch way.

### Table 1  RAFT polymerization of PEGMA mediated by CTB–COOH in water

| Entry | PPEGMA code | \( R^b \) | Time (min) | Conv.\(^c\) (%) | \( M_n,th \)\(^d\) (g mol\(^{-1}\)) | \( M_n,NMR \) (g mol\(^{-1}\)) | \( M_n,GPC \) (g mol\(^{-1}\)) | \( M_w/M_n \) |
|-------|-------------|---------|-----------|--------------|-----------------|-----------------|-----------------|-----------------|
| 1     | PPEGMA-1    | 15/1/0.2| 140       | 98.0         | 7600            | 8500            | 7800            | 1.11            |
| 2     | PPEGMA-2    | 20/1/0.2| 90        | 99.0         | 10 100          | 10 200          | 9200            | 1.10            |
| 3     | PPEGMA-3    | 25/1/0.2| 140       | 99.3         | 12 680          | 13 700          | 11 000          | 1.09            |
| 4     | PPEGMA-4    | 35/1/0.2| 150       | 99.6         | 17 700          | 17 500          | 14 000          | 1.07            |

\(^a\) Polymerization conditions: \( V_{PEGMA} = 3.0 \text{ mL}, V_{PEGMA}/V_{water} = 1/1 \text{ (v/v)}, T = 70^\circ \text{C.} \)

\(^b\) \( R = \text{[PEGMA]}_0/\text{[CTB–COOH]}_0/\text{[AIBI]}_0 \).

\(^c\) Calculated from the data of \(^1\text{H} \) NMR spectra.

\(^d\) \( M_n,th = (\text{[PEGMA]}_0/\text{[CTB–COOH]}_0) \times M_w,PPEGMA \times \text{conversion\%} + M_w,\text{CTB–COOH} \).

### Table 2  Effect of dripping time of MMA on soap-free RAFT emulsion polymerization of MMA using PPEGMA-2 as the macroRAFT agent

| Entry | Dripping time (min) | Conv. (%) | \( M_n,th \)\(^b\) (g mol\(^{-1}\)) | \( M_n,NMR \) (g mol\(^{-1}\)) | \( M_n,GPC \) (g mol\(^{-1}\)) | \( M_w/M_n \) | \( d_\text{h} \)\(^c\) (nm) | PDI\(^c\) |
|-------|---------------------|-----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1     | 30                  | 19.0      | 12 100          | 20 000          | 16 000          | 1.16            | 173             | 0.10            |
| 2     | 90                  | 82.2      | 18 400          | 36 400          | 28 000          | 1.34            | 23              | 0.12            |
| 3     | 100                 | 92.9      | 17 800          | 35 600          | 28 000          | 1.33            | 33              | 0.13            |
| 4     | 110                 | 95.3      | 17 500          | 33 500          | 28 000          | 1.31            | 39              | 0.17            |
| 5     | 120                 | 93.0      | 17 400          | 32 800          | 28 000          | 1.27            | 39              | 0.15            |
| 6     | 140                 | 79.4      | 18 000          | 33 500          | 28 000          | 1.27            | 39              | 0.20            |

\(^a\) Polymerization conditions: \([\text{MMA}]_0/\text{[PPEGMA-2]}_0/\text{[AIBI]}_0 = 100/1/0.2, V_{MMA} = 0.7 \text{ mL}, \text{ solid content} = 10\%, T = 60^\circ \text{C.} \)

\(^b\) \( M_n,th = ([\text{MMA}]_0/\text{[PPEGMA-2]}_0) \times M_w,\text{MMA} \times \text{conversion\%} \).

\(^c\) \( d_\text{h} \) and PDI were obtained by dynamic light scattering (DLS).
Soap-free RAFT emulsion polymerization of MMA using PPEGMA-2 as the macroRAFT agent at varied solid content

Table 3 Soap-free RAFT emulsion polymerization of MMA using PPEGMA-2 as the macroRAFT agent at varied solid content

| Entry | Solid content (%) | Conv. (%) | $M_n,\text{th}$ (g mol$^{-1}$) | $M_n,\text{NMR}$ (g mol$^{-1}$) | $M_n,\text{GPC}$ (g mol$^{-1}$) | $M_n/M_n$ | $d_n$ (nm) | PDI |
|-------|------------------|-----------|-------------------------------|-------------------------------|-------------------------------|-----------|-----------|-----|
| 1     | 10               | 95.3      | 20 900                        | 16 500                        | 16 200                        | 1.30      | 36        | 0.17 |
| 2     | 20               | 93.4      | 20 700                        | 18 100                        | 15 700                        | 1.17      | 29        | 0.17 |
| 3     | 30               | 90.2      | 20 400                        | 17 800                        | 15 700                        | 1.14      | 27        | 0.19 |
| 4     | 40               | 65.6      | 17 900                        | 16 000                        | 14 000                        | 1.16      | 30        | 0.23 |
| 5$^c$ | 50               | 92.0      | 19 500                        | 20 700                        | 16 200                        | 1.22      | 36        | 0.24 |
| 6     | 60               | 74.3      | 18 800                        | 13 300                        | 13 100                        | 1.14      | 79        | 0.34 |

$^a$ Polymerization conditions: [MMA]/[PPEGMA-2]/[AIBI]$_0$ = 100/1/0.2, dripping time = 110 min, $V_{MMA} = 0.7 \text{ mL}$, $T = 60 \degree \text{C}$. $^b$ $M_{n,\text{th}} = ([\text{MMA}]_0/[\text{PPEGMA-2}]_0) \times M_{n,\text{MMA}} \times \text{conversion}\% + M_{n,\text{NMR(PPEGMA-2)}}$. $^c$ $d_n$ and PDI are obtained by dynamic light scattering (DLS). $^d$ Dripping time of self-assembled block copolymers at the conversion of 95.3% is shown in Fig. 3(A) and shows the nanoparticles size is around 30 nm.

Soap-free RAFT emulsion polymerization of MMA using PPEGMA-2 as the macroRAFT agent with varied molecular weights

Table 4 Soap-free RAFT emulsion polymerization of MMA using PPEGMA with varied molecular weights

| Entry | PPEGMA code | Conv. (%) | $M_n,\text{th}$ (g mol$^{-1}$) | $M_n,\text{NMR}$ (g mol$^{-1}$) | $M_n,\text{GPC}$ (g mol$^{-1}$) | $M_n/M_n$ | $d_n$ (nm) | PDI |
|-------|-------------|-----------|-------------------------------|-------------------------------|-------------------------------|-----------|-----------|-----|
| 1     | PPEGMA-1    | 58.8      | 14 300                        | 11 900                        | 12 500                        | 1.12      | 19        | 0.12 |
| 2     | PPEGMA-2    | 95.3      | 19 700                        | 16 500                        | 16 200                        | 1.30      | 36        | 0.17 |
| 3     | PPEGMA-3    | 74.8      | 21 100                        | 18 600                        | 15 300                        | 1.14      | 20        | 0.09 |
| 4     | PPEGMA-4    | 85.5      | 26 000                        | 28 600                        | 18 600                        | 1.16      | 27        | 0.16 |

$^a$ Polymerization conditions: [MMA]/[PPEGMA-2]/[AIBI]$_0$ = 100/1/0.2, dripping time = 110 min, $V_{MMA} = 0.7 \text{ mL}$, solid content = 10%, $T = 60 \degree \text{C}$. $^b$ $M_{n,\text{th}} = ([\text{MMA}]_0/[\text{PPEGMA}]_0) \times M_{n,\text{MMA}} \times \text{conversion}\% + M_{n,\text{NMR(PPEGMA)}}$. $^c$ $d_n$ and PDI were obtained by dynamic light scattering (DLS).
20 nm, which is slightly broad than that obtained by DLS because of the swelling of the hydrophilic PPEGMA segment in water.

In order to exert the advantage of semi-batch addition manner, emulsions with high solid content from 20 to 60 per cent were also prepared. As can be seen from Table 3, high monomer conversion can still be obtained at dripping time of 110 min when solid content varied from 10% to 30%. However, monomer conversions were far from satisfaction at the solid content of 40% and 60%. This is because the higher the solid content, the higher the viscosity of the polymerization system, so shorter reaction time is needed to obtain high monomer conversion. When reducing the addition time to 60 min at 50% solid content, monomer conversion (entry 5 in Table 3) can be reached to 93%, which confirmed the above speculation. Besides, the values of \( M_n, \text{GPC} \) corresponded to theoretical ones \( (M_n, \text{th}) \) and the ones calculated by \( ^1H \) NMR \( (M_n, \text{NMR}) \). The values of \( M_d/M_n \) were also very narrow in each case. The nanoparticles sizes were all around 30 nm except that at 60% solid content. Additionally, stable latexes with transparent appearance were obtained except that macroscopic turbidity was observed for entry 6 in Table 3. The TEM image of latex at 60% solid content is shown in Fig. 3(B) and aggregation between nanoparticles is obvious. In fact, the size of every nanoparticle no matter in free or aggregation situation is about 20 nm, which indicates that there is no big nanoparticle formation, so nanoparticles can’t be distributed uniformly at high solid content can explain this phenomenon.

In order to investigate the extensity of semi-batch addition manner, varied molecular weights of PPEGMAs were used as macroRAFT agents. From Table 4, it can be observed that the molar mass of the copolymers analyzed by GPC are close to the theoretical ones the ones calculated by \( ^1H \) NMR \( (M_n, \text{NMR}) \). Besides, the dispersity values are low, which indicating well controlled effect of the macroRAFT agents. Moreover, stable latexes with transparent appearance were obtained in all cases and the average diameter of nanoparticles analyzed by DLS are all around 30 nm and the particles dispersities keep at a low level.

4. Conclusions

Soap-free emulsion with solid content up to 60% was prepared in differential semi-batch monomer addition way by polymerization induced self-assembly (PISA) process from PPEGMA-b-PMMMA. The obtained latex was very stable with particle size almost invariably at 20 nm at 10−50% solid content and narrow particle size distribution. This approach may provide an alternative way for preparing high solid content soap-free emulsion by a novel strategy of differential semi-batch monomer addition manner. At the same time, high monomer conversion (>95%) can be achieved by just adjusting the addition time, which facilitates to decrease the residue of monomer after a PISA process, and therefore facilitates its practical application.

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