

Supporting Information

From RAFT Emulsion Polymerization to RAFT Dispersion Polymerization: A Facile Approach to tune Dispersities and Self-assembled behaviors of Block Copolymers

Junpeng Cao^a, Yanling Li^a, Yingxin Tan^a, Li Zhang^{a,b}, Jianbo Tan^{*a,b}

a. Department of Polymeric Materials and Engineering, School of Materials and Energy,

Guangdong University of Technology, Guangzhou 510006, China.

b. Guangdong Provincial Key Laboratory of Functional Soft Condensed Matter, Guangzhou

510006, China.

Junpeng Cao, Yanling Li, and Yingxin Tan contributed equally to this work.

**Corresponding author: tanjianbo@gdut.edu.cn*

EXPERIMENTAL SECTION

Materials

Methyl methacrylate (MMA, Aladdin), *n*-butyl methacrylate (*n*BMA, Aladdin), glycidyl methacrylate (GlyMA, Aladdin), benzyl methacrylate (BzMA, Aladdin), *tert*-butyl acrylate (*t*BA, Aladdin), and isobornyl acrylate (IBOA, Sigma-Aldrich) were passed through a column of basic alumina (Aladdin) prior to storage under refrigeration at 4 °C. Poly(ethylene glycol) methyl ether methacrylate (PEGMA, $M_n = 475$ g/mol, Sigma-Aldrich), methyl isobutyrate (MIB, Aladdin), dicyclohexylcarbodiimide (DCC, Aladdin), 4-dimethylaminopyridine (DMAP, Aladdin), and hydroquinone (Aladdin) were used as received. Azodiisobutyronitrile (AIBN, Aladdin) was recrystallized from ethanol prior to storage under refrigeration at 4 °C. 4-Cyano-4-(dodecylsulfanylthiocarbonyl) sulfanylpentanoic acid (CDPA) was synthesized according to a literature procedure.¹ Sodium phenyl-2,4,6-trimethylbenzoylphosphinate (SPTP) was synthesized according to a literature.²

Characterization

¹H NMR Spectroscopy. Nuclear magnetic resonance (NMR) spectra were recorded in CDCl₃, D₂O or *d*₆-DMSO using a Bruker Avance III HD 400 MHz NMR spectrometer at a temperature of 25 °C.

Size Exclusion Chromatography (SEC). Molecular weight and polydispersity of samples were measured by size exclusion chromatography (SEC) at 35 °C using a Waters 1515 GPC instrument with tetrahydrofuran (THF) as the mobile phase and Waters styragel HR1 and HR4 columns. The flow rate of THF was 1.0 mL/min. Linear polystyrene polymers with narrow molecular weight distributions were used as the standards to calibrate the apparatus.

Transmission Electron Microscopy (TEM). The obtained dispersions were diluted 100-fold with water. A drop of the solution was placed on a copper grid for 5 min and then blotted with filter paper to remove excess solution. A drop of uranyl acetate solution (0.5 wt %) was soaked on the same copper grid for 5 min, and then blotted with filter paper to remove excess stain. All samples were stained with uranyl acetate

to obtain TEM images with high quality. TEM observations were carried out on a Hitachi 7700 instrument operated at 100 kV.

1. Methylation of CDPA chain transfer agent.

CDPA (4.00 g, 9.90 mmol) and anhydrous methanol (0.63 g, 19.69 mmol) were dissolved with 10 mL anhydrous DCM in a 50 mL dry round bottom flask. A solution containing DCC (4.08 g, 19.81 mmol) and DMAP (0.24 g, 1.98 mmol) in anhydrous DCM (20 mL) was added dropwise to the reaction mixture at 0 °C. The esterification reaction was stirred at room temperature for 24 h. The reaction mixture was filtered and dried under vacuum. The obtained product was further purified by silica gel column chromatography ($v(\text{CH}_2\text{Cl}_2): v(n\text{-hexane}) = 1: 3$) and finally dried under vacuum at 40 °C to obtain an orange oil.

2. Synthesis of PPEGMA_{7,6}-CDPA-Me.

PEGMA (25.00 g, 0.05 mol), CDPA-Me (2.61 g, 6.25 mmol), AIBN (0.21 g, 1.28 mmol), 1,3,5-trioxacyclohexane (0.45 g, 5.00 mmol), and 1,4-dioxane (25.00 g) were weighed into a 100 mL round bottom flask and purged with nitrogen for 60 min. The flask was then immersed into a preheated oil bath at 70 °C for 5 h (Monomer conversion = 95.1% as judged by ¹H NMR). The polymerization was then quenched by immersion in ice water and exposure to air. The product was precipitated with excess *n*-hexane (500 mL) and washed several times with additional *n*-hexane. The precipitated product was then dried at 45 °C under vacuum overnight. The polymer was analyzed by THF SEC with $M_n = 4.80$ kg/mol and $M_w/M_n = 1.10$ (against polystyrene standards). The PPEGMA_{10,2}-CDPA-Me macro-RAFT agent was synthesized in the same way.

3. Synthesis of PPEGMA_{10,2}-PMMA_n diblock copolymer in a water/ethanol mixture with different ethanol contents at different temperatures.

In a typical experiment for the synthesis of PPEGMA_{10,2}-PMMA₁₀₀ (10% w/w MMA) in water at 25 °C: PPEGMA_{10,2}-CDPA-Me (0.17 g, 0.03 mmol) and SPTP (1.90 mg, 6.13 μmol) were dissolved with water (2.70 g) in a 10 mL round bottom flask. Then MMA (0.30 g, 3.00 mmol) were added into the reaction mixture. The reaction mixture was degassed with nitrogen for 20 min at 25 °C under magnetic stirring, and then irradiated by a visible light LED lamp (405 nm, 0.45 mW/cm²) for 1 h. The obtained sample was then analyzed by ¹H NMR spectroscopy, TEM and THF SEC. Other samples were prepared following the same protocol using water/ethanol mixture with

different ethanol contents at different temperatures.

4. Kinetic study of photoinitiated RAFT heterogeneous polymerization using PPEGMA_{10,2}-CDPA-Me in a water/ethanol mixture with different ethanol contents at 25 °C.

Kinetic study of RAFT heterogeneous polymerization of MMA (10% w/w, [MMA]/[PPEGMA_{10,2}-CDPA-Me] = 100) mediated by PPEGMA_{10,2}-CDPA-Me in water was given as follows: PPEGMA_{10,2}-CDPA-Me (0.66 g, 0.12 mmol) and SPTP (7.4 mg, 23.87 μmol) were dissolved with water (10.80 g in this case) in a 25 mL round bottom flask. Then MMA (1.20 g, 11.99 mmol) and a trace amount of DMF (0.09 g, 1.20 mmol) were added into the flask. The reaction mixture was degassed with nitrogen for 25 min at 25 °C under magnetic stirring, and then irradiated by a visible light LED lamp (405 nm, 0.45 mW/cm²) for 1 h. Samples were withdrawn at predetermined time intervals by syringes under nitrogen. Each aliquot was quenched by exposure to air and the addition of a small amount of hydroquinone. The samples were then analyzed by ¹H NMR spectroscopy and THF SEC. Other kinetic studies were performed following the same protocol at different ethanol contents.

5. Synthesis of PPEGMA_{7,6}-PMMA_n diblock copolymer nanoparticles in a water/ethanol mixture with different ethanol contents at different temperatures.

In a typical experiment for the synthesis of PPEGMA_{7,6}-PMMA₁₀₀ (20% w/w MMA) in water at 30 °C: PPEGMA_{7,6}-CDPA-Me (0.25 g, 0.06 mmol) and SPTP (3.70 mg, 11.94 μmol) were dissolved with water (2.40 g) in a 10 mL round bottom flask. Then MMA (0.60 g, 5.99 mmol) and a trace amount of DMF (0.04 g, 0.60 mmol) were added into the flask. The reaction mixture was degassed with nitrogen at 25 °C for 20 min under magnetic stirring before immersion into a preheated water bath at 30 °C. After equilibration at 30 °C for 5 min, the reaction mixture was irradiated by a visible light LED lamp (405 nm, 0.45 mW/cm²) for 1 h. The obtained product was then analyzed by ¹H NMR spectroscopy and TEM. Other samples were prepared following the same protocol at different temperatures with different ethanol contents.

ADDITIONAL RESULTS

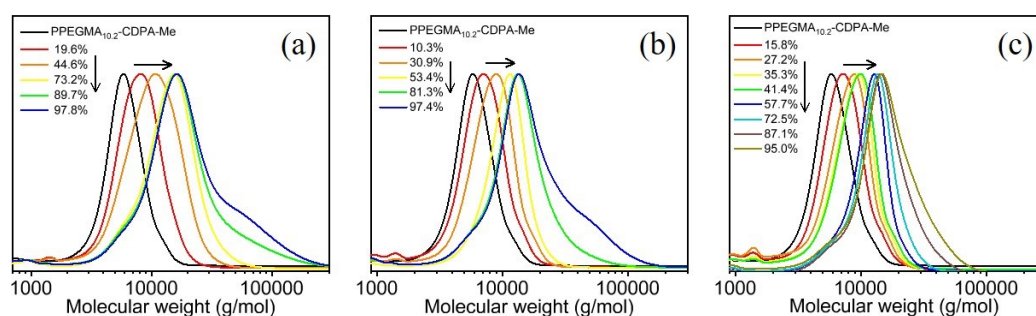


Figure S1. THF SEC traces of PPEGMA_{10.2}-CDPA-Me and samples obtained at different monomer conversions during the kinetic study of heterogeneous RAFT polymerization of MMA (10% w/w, targeted DP of 100) mediated by PPEGMA_{10.2}-CDPA-Me in a water/ethanol mixture with different ethanol contents: (a) 0 wt.%, (b) 15 wt.%, (c) 30 wt.%.

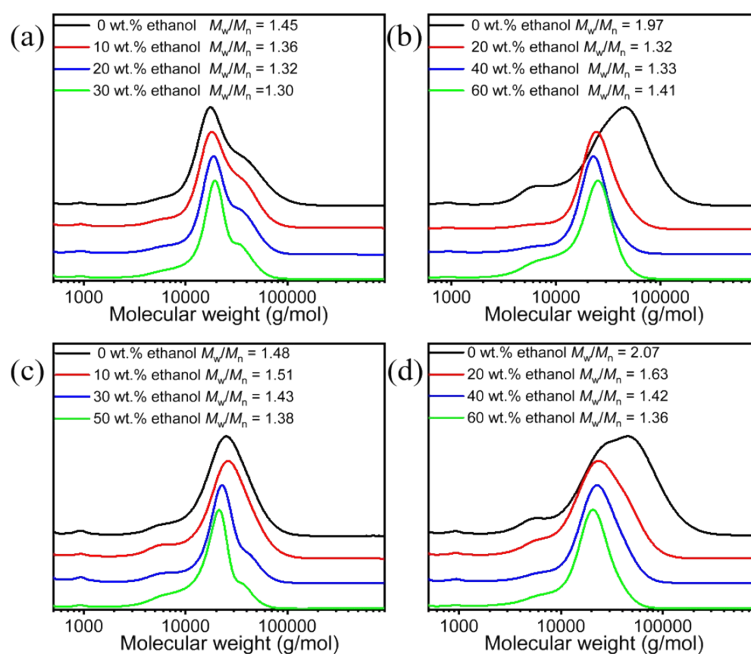


Figure S2. (a) THF SEC traces of PPEGMA_{10.2}-PGlyMA₁₀₀ block copolymers synthesized by photoinitiated heterogeneous RAFT polymerization of GlyMA (10% w/w) in ethanol/water at 45 °C with different ethanol contents. (b) THF SEC traces of PPEGMA_{10.2}-PBzMA₁₀₀ block copolymers synthesized by photoinitiated heterogeneous RAFT polymerization of BzMA (10% w/w) in ethanol/water at 45 °C with different ethanol contents. (c) THF SEC traces of PPEGMA_{10.2}-PtBA₁₀₀ block copolymers synthesized by photoinitiated heterogeneous RAFT polymerization of *t*BA (10% w/w) in ethanol/water at 45 °C with different ethanol contents. (d) THF SEC traces of PPEGMA_{10.2}-PIBOA₁₀₀ block copolymers synthesized by photoinitiated heterogeneous RAFT polymerization of IBOA (10% w/w) in ethanol/water at 45 °C with different ethanol contents.

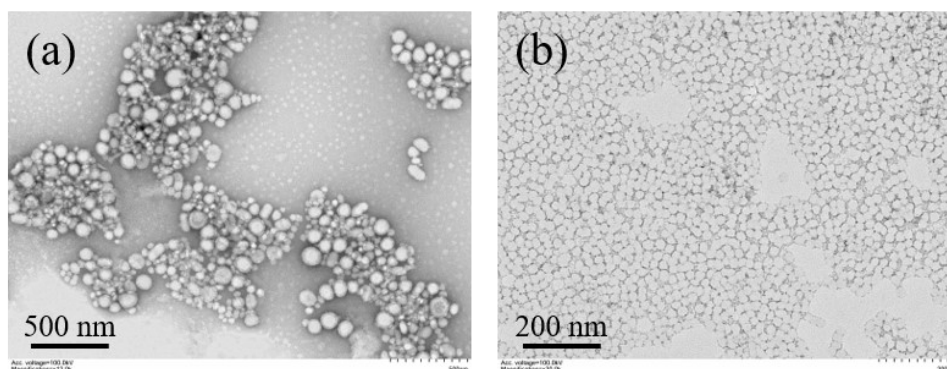


Figure S3. TEM images of PPEGMA_{10.2}-PMMA₂₀₀ block copolymer nanoparticles prepared by heterogeneous RAFT polymerization of MMA (10% w/w) at 50 °C in (a) water or (b) ethanol/water (20/80, w/w).

Table S1. Solubility of MMA in ethanol-water mixtures (measured in our lab).

m(ethanol): m(water)	Solubility of MMA
5: 95	2.13±0.09 g/ 100 g
15: 85	2.36±0.15 g/ 100 g
20: 80	3.18±0.29 g/ 100 g
30:70	8.40±0.22 g/ 100 g

REFERENCES

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- (2) Li, G.; Xu, N.; Yu, Q.; Lu, X.; Chen, H.; Cai, Y. Acceleration and Selective Monomer Addition during Aqueous RAFT Copolymerization of Ionic Monomers at 25 °C. *Macromol. Rapid Commun.* **2014**, *35* (16), 1430–1435. <https://doi.org/10.1002/marc.201400153>.