Supporting Information

Photoinitiated Polymerization-induced Self-Assembly via Visible Light-induced RAFT-mediated Emulsion Polymerization

Jianbo Tan*., a, b, Xiaocong Dai a, Yuxuan Zhang a, Liangliang Yu a, Hao Sun c, Li Zhang*, 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.
c. Department of Chemistry, Northwestern University, Evanston, IL, 60208, United States.

*Corresponding authors: tanjianbo@gdut.edu.cn, lizhang@gdut.edu.cn
EXPERIMENTAL SECTION

Materials. Tert-butyl acrylate (tBA, Aladdin) and tert-butyl methacrylate (tBMA, Aladdin) were purified by passing through a basic alumina oxide (Aladdin) column prior to storage at 4 °C. Poly(ethylene glycol) methyl ether methacrylate (PEGMA, $M_n = 500$ g/mol, Sigma-Aldrich), glucose oxidase (GOx, Aladdin, lyophilized powder, > 180 U/mg), D- (+)-glucose (Aladdin), 2-(2-methoxyethoxy)ethyl methacrylate (MEO2MA, Sigma-Aldrich), 1,3,5-trioxacyclohexane (Aladdin), and hydroquinone (Aladdin) were used as received. Azobisisobutyronitrile (AIBN, Aladdin) was recrystallized from ethanol prior to storage under refrigeration at 4 °C. 4-Cyano-4-(dodecylsulfanylthiocarbonylsulfonyl)pentanoic acid (CDPA) and 4-cyano-4-(ethylthiocarbonothioylthio)pentanoic acid (CEPA) were synthesized according to the literature. Sodium phenyl-2,4,6-trimethylbenzoylphosphinate (SPTP) was synthesized according to a literature procedure. LUDOX®AM colloidal silica (20 nm, 30 wt.% suspension in H2O, Sigma-Aldrich) was dialyzed against water prior to use and the final solids was 13.72 wt.%. LED lamps (405 nm) were purchased from Huaenopto (Zhejiang).

Characterization. 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 1 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 1.5 min, and then blotted with filter paper to remove excess strain. TEM observations were carried out on a Hitachi 7700 instrument operated at 120 kV.
**Gel permeation chromatography (GPC).** The molecular weight and polydispersity of the block copolymers were measured by gel permeation chromatography (GPC) 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 apparatus.

**$^1$H NMR spectroscopy.** Nuclear magnetic resonance (NMR) spectra were recorded in CDCl$_3$ or DMSO-$d_6$ using a Bruker Avance III HD 400 MHz NMR spectrometer at a temperature of 25 °C.

**Rheological experiment.** Rheological experiments were carried out on a HAAKE rheometer at room temperature. The measurements were performed in an oscillatory shear mode using a parallel plate geometry with a diameter of 20 mm. The gel-like dispersion was placed between the plates with a 1 mm gap. Frequency sweep in the range 5-100 rad s$^{-1}$ was applied at an oscillatory strain value of 0.5 %, checked to be in the linear domain.

**UV-vis spectroscopy.** The UV-vis spectra were recorded using a PGENERAL TU-1901 UV/vis spectrophotometer.

**Dynamic light scattering (DLS).** The particle size and particles size distribution was measured by a Brookhaven nanoparticle size–zeta potential and molecular weight analyzers.

1. **Synthesis of PPEGMA$_{15}$-CDPA**

   The synthesis of PPEGMA$_{15}$-CDPA is given below: PEGMA (20.0 g, 40 mmol), CDPA (0.95 g, 2.35 mmol), AIBN (0.077 g, 0.47 mmol), and 1,3,5-trioxacyclohexane (0.36 g, 4.00 mmol), and 1,4-dioxane (20.0 g) were weighed into a 100 mL round bottom flask and purged with nitrogen for 45 min. The flask was then immersed into a preheated oil bath at 70 °C for 4 h (Monomer conversion...
= 88.9 % as judged by $^1$H NMR). The polymerization was then quenched by immersion in ice water and exposure to air. The product was precipitated by excess hexane (300 mL) and washed several times with additional hexane. The precipitated product was then dried at 45 °C under vacuum overnight. The polymer was analyzed by THF GPC with $M_n = 7.2$ kg/mol and $M_w/M_n = 1.13$ as determined by reference to polystyrene standards.

2. **Synthesis of PPEGMA$_{10}$-CDPA**

The synthesis of PPEGMA$_{10}$-CDPA is given below: PEGMA (30.0 g, 60.0 mmol), CDPA (2.02 g, 5.00 mmol), AIBN (0.164 g, 1.00 mmol), and 1,3,5-trioxacyclohexane (0.54 g, 6.00 mmol), and 1,4-dioxane (30.0 g) were weighed into a 100 mL round bottom flask and purged with nitrogen for 45 min. The flask was then immersed into a preheated oil bath at 70 °C for 140 min (Monomer conversion = 83 % as judged by $^1$H NMR). The polymerization was then quenched by immersion in ice water and exposure to air. The product was precipitated by excess hexane (300 mL) and washed several times with additional hexane. The precipitated product was then dried at 45 °C under vacuum overnight. The polymer was analyzed by THF GPC with $M_n = 5.8$ kg/mol and $M_w/M_n = 1.13$ as determined by reference to polystyrene standards.

3. **Synthesis of PPEGMA$_6$-CDPA**

The synthesis of PPEGMA$_6$-CDPA is given below: PEGMA (20.0 g, 40 mmol), CDPA (2.31 g, 5.71 mmol), AIBN (0.188 g, 1.14 mmol), and 1,3,5-trioxacyclohexane (0.36 g, 4.0 mmol), and 1,4-dioxane (20.0 g) were weighed into a 100 mL round bottom flask and purged with nitrogen for 45 min. The flask was then immersed into a preheated oil bath at 70 °C for 140 min (Monomer conversion = 86% as judged by $^1$H NMR). The polymerization was then quenched by immersion in ice water and exposure to air. The product was precipitated by excess n-Hexane (300 mL) and
washed several times with additional hexane. The precipitated product was then dried at 45 °C under vacuum overnight. The polymer was analyzed by THF Gel Permeation Chromatography (GPC) with \( M_n = 4.7 \text{ kg/mol} \) and \( M_n/M_w = 1.11 \) as determined by reference to polystyrene standards.

4. Synthesis of PPEGMA\(_{5.7}\)-CDPA

The synthesis of PPEGMA\(_{5.7}\)-CDPA is given below: PEGMA (10.0 g, 20 mmol), CDPA (1.15 g, 2.86 mmol), AIBN (0.156 g, 0.952 mmol), and 1,3,5-trioxacyclohexane (0.18 g, 2.0 mmol), and 1,4-dioxane (10.0 g) were weighed into a 100 mL round bottom flask and purged with nitrogen for 45 min. The flask was then immersed into a preheated oil bath at 70 °C for 3.5 h (Monomer conversion = 82% as judged by \(^1\)H NMR). The polymerization was then quenched by immersion in ice water and exposure to air. The product was precipitated by excess n-Hexane (300 mL) and washed several times with additional hexane. The precipitated product was then dried at 45 °C under vacuum overnight. The polymer was analyzed by THF Gel Permeation Chromatography (GPC) with \( M_n = 3.9 \text{ kg/mol} \) and \( M_n/M_w = 1.11 \) as determined by reference to polystyrene standards.

5. Visible light-induced RAFT-mediated emulsion polymerization

In a typical experiment for the synthesis of PPEGMA\(_{15}\)-PBA\(_{150}\), tBA (1.50 g, 11.70 mmol), PPEGMA\(_{15}\)-CDPA (0.621 g, 0.078 mmol), and SPTP (8.1 mg, 0.026 mmol) were weighed into a 10 mL round bottom flask. A certain amount of water (6.0 g in this case) was added into the flask, purged with nitrogen for 20 min, and then irradiated by a visible light LED lamp (405 nm, 0.45 mW/cm\(^2\)) for 1 h. The reaction was quenched by exposure to air.

6. In situ encapsulation of silica nanoparticles into vesicles

A typical protocol for the synthesis of hybrid vesicles is given below: tBA (0.80 g, 6.24 mmol), POEGMA\(_{5.7}\)-CDPA (0.204 g, 0.062 mmol), SPTP (6.4 mg, 0.021 mmol), silica sol (1.28 g, 13.72%
w/w) and water (2.096 g) were added into a 10 mL round bottom flask. The reaction mixture was purged with nitrogen for 20 min, sealed, and irradiated by a LED lamp (405 nm, light intensity of 0.45 mW/cm²) for 1 h. The obtained vesicles were diluted with water, sedimented by centrifugation at 9000 rpm and resuspended in water. This washing process was repeated 6 times to remove free silica nanoparticles.

7. Visible light-induced RAFT-mediated emulsion polymerization at different volumes.

In a typical experiment (total volume of 1.0 mL), aqueous solution of PPEGMA₆-CDPA (247 μL, 0.2 g/mL, 0.0156 mmol), rBA (226.5 μL, 1.5604 mmol), aqueous solution of glucose (48 μL 0.1 M), and aqueous solution of GOx (130 μL, 3.0775 μM, to ensure the final concentration of GOx is 0.5 μM) and water (53 μL) were added into a 1.5 mL vial. The reaction mixture was incubated for 20 min to remove the dissolved oxygen. SPTP (322 μL, 0.0052 mmol) was then added to the reaction mixture, exposed to a LED lamp (0.45 mW/cm², 405 nm) for 1 h. The polymerization was under magnetic stirring during the whole process.

8. Kinetics of visible light-induced RAFT-mediated emulsion polymerization

PPEGMA₆-CDPA (0.399 g, 0.117 mmol), rBA (1.50 g, 11.70 mmol), SPTP (0.012 g, 0.039 mmol) and water (6.0 g in this case) were weighed into a 10 mL round bottom flask. The reaction mixture was then purged with nitrogen for 20 min, sealed, and then irradiated by a visible light LED lamp (405 nm, light intensity 0.45 mW/cm²) at 25 °C. Samples were withdrawn at predetermined time intervals by syringes under nitrogen. The polymerizations were quenched by exposure to air and the addition of a small amount of hydroquinone. The samples (typically 0.5 g) were then analysis by gravimetry and GPC.
9. Kinetics of visible light-induced RAFT-mediated emulsion polymerization in an open vessel

In a typical experiment ([GOx] = 0.5 μM): PPEGMA₆-CDPA (0.3995 g, 0.117 mmol), tBA (1.5 g, 11.70 mmol), aqueous solution of glucose (0.108 g, 0.1 M), aqueous solution of GOx (26.7 μL, 18 mg/mL, to ensure the final concentration of GOx is 0.5 μM) and water (5.973 g) were added to a 10 mL round bottom flask. The reaction mixture was incubated for 20 min to remove the dissolved oxygen. SPTP (0.0121 g, 0.039 mmol) was then added to the reaction mixture, exposed to a LED lamp (405 nm, light intensity 0.45 mW/cm²). Samples were withdrawn at predetermined time intervals by syringes, and the reaction was quenched by exposure to air and the addition of a small amount of hydroquinone. The samples (typically 0.5 g) were then analysis by gravimetry and GPC.

Monomer conversion was calculated from the follow equation:

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\text{Conversion (\%)} = \frac{W_p - W_{CTA}}{W_m} \times 100 \%
\]  

Where \( W_p \) is the weight of the final sample, \( W_{CTA} \) is the weight of macro-RAFT agent added in the reaction and \( W_m \) is the weight of monomer added in the reaction.
ADDITIONAL RESULTS

Table S1. Summary of visible light-induced RAFT-mediated emulsion polymerization.

| Target composition | Monomer concentration (w/w%) | Conversion (%) | $M_n$ (kg/mol) | $M_n/M_a$ | Morphology |
|--------------------|-----------------------------|---------------|---------------|-----------|------------|
| PPEGMA$_{36}$-PrBA$_{50}$ | 20 | >99 | 12.2 | 1.45 | S |
| PPEGMA$_{36}$-PrBA$_{75}$ | 20 | >99 | 13.2 | 1.48 | W |
| PPEGMA$_{36}$-PrBA$_{100}$ | 20 | >99 | 16.5 | 1.53 | W+V |
| PPEGMA$_{36}$-PrBMA$_{50}$ | 20 | >99 | 9.25 | 1.40 | S |
| PPEGMA$_{36}$-PrBMA$_{75}$ | 20 | >99 | 12.2 | 1.47 | S |
| PPEGMA$_{36}$-PrBMA$_{100}$ | 20 | >99 | 14.5 | 1.52 | S |
| PPEGMA$_{20}$-PrBA$_{100}$ | 20 | >99 | 20.6 | 1.58 | W |
| PPEGMA$_{20}$-PrBA$_{150}$ | 20 | >99 | 25.9 | 1.77 | W+V |
| PPEGMA$_{20}$-PrBA$_{300}$ | 20 | >99 | 22.3 | 1.79 | S+W |

Figure S1. UV and RI GPC traces of PPEGMA$_{36}$-PrBA$_n$ diblock copolymer nano-objects prepared by visible light-induced RAFT-mediated emulsion polymerization of tBA (20% w/w): (a) $n =$ 50, (b) $n =$ 75, (c) $n =$ 100.
Figure S2. TEM images of PPEGMA$_{10}$-PtBA$_{150}$ or PPEGMA$_{15}$-PtBA$_{n}$ (n = 150, 200) diblock copolymer nano-objects prepared by visible light-induced RAFT-mediated emulsion polymerization with 20% w/w tBA.

Figure S3. GPC traces of PPEGMA$_6$-CDPA and PPEGMA$_6$-PtBA$_n$ diblock copolymers prepared by visible light-induced RAFT-mediated emulsion polymerization of tBA (20% w/w) in a closed vessel with the addition of GOx and glucose.
Figure S4. TEM image of PPEGMA$_6$-PtBA$_{100}$ diblock copolymer nano-objects prepared by the oxygen-tolerant visible light-induced RAFT-mediated emulsion polymerization of tBA (20% w/w) at different volumes.

Figure S5. Polymerization kinetics for visible light-induced RAFT-mediated emulsion polymerization of tBA (20% w/w, DP of 100) with nitrogen degassing or GOx deoxygenation in a closed round bottom flask.

REFERENCE

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