Uncontrolled Polymerization Occurred during Photoinitiated RAFT Dispersion Polymerization of Acrylic Monomer Promotes the Formation of Uniform Raspberry-like Polymer Particles

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EXPERIMENTAL SECTION

Material

Diacetone acrylamide (DAAM, Aladdin), N, N-dimethylacrylamide (DMA, Aladdin), ethylene glycol (EG, Aladdin), trimethylolpropane (TMP, Aladdin), dicyclohexylcarbodiimide (DCC, Aladdin), 4-dimethylaminopyridine (DMAP, Aladdin), and 2,4,6-trimethylbenzoyldi-phenylphosphinate (TPO, Ciba) were used without further purification. 2,2-Azobisisobutyronitrile (AIBN, Aladdin) was recrystallized from ethanol prior to storage under refrigeration at 4 °C. Isobornyl acrylate (IBOA, Sigma-aldrich) and tert-butyl acrylate (tBA, Aladdin) were purified by passing through a basic alumina oxide (Aladdin) column prior to storage at 4 °C. 3-(Benzylthiocarbonothioylthio)propanoic acid (BTPA) was synthesized according to a published procedure\(^1\). Pentaerythritol tetrakis-(3-(S-benzyl trithiocarbonyl)propionate) was synthesized according to a published procedure\(^2\).

Characterization

*Transmission Electron Microscopy (TEM).* The polymerization reaction mixtures were diluted 100-fold with ethanol/water mixtures. A drop of the solution was placed on the copper grid for 1 min and then blotted with filter paper to remove excess solution. TEM observations were carried out on a HT7700 instrument operated at 100 kV. TEM images were analyzed by using the software program named Image pro Plus 6.0.

*Scanning electron microscopy (SEM).* SEM images were collected using a Hitachi SU8010 (Tokyo, Japan) electron microscope on samples sputter-coated with gold prior imaging. The sample for SEM imaging was prepared by drop casting the diluted dispersion on a clean mica films and
drying at room temperature prior to sputter-coating. SEM images were analyzed by using the software program named Image pro Plus 6.0. us

**Gel Permeation Chromatography (GPC).** The molar mass and polydispersity of polymers were measured by GPC at 35 °C using a Waters 1515 GPC inStrument with tetrahydrofuran (THF) as the mobile phase and Waters Styragel HR1, HR4 columns. The flow rate of THF was 1.0 mL/ min. Linear polystyrene polymers with narrow molar mass distributions were used as standards to calibrate the apparatus.

**1H NMR Spectroscopy.** 1H NMR spectra were recorded in CDCl3 using a Bruker Avance III 400 MHz NMR spectrometer at a temperature of 25 °C. Note: The samples prepared by PISA were first diluted with methanol, and then dissolved in CDCl3.

**Contact angle analyzer.** Water contact angles were recorded with an ultrapure water droplet of 8 μL on a contact angle analyzer (Chengde Jinhe Instrument Manufacturing Co., Ltd.) at room temperature. All the contact angle values were determined by averaging the values measured five different points on each sample surface.

### Synthesis of difunctional and trifunctional small molecular RAFT agent

**Synthesis of difunctional RAFT agent.** A solution of BTPA (8.41 g, 30.92 mmol) in 30 mL of anhydrous tetrahydrofuran was introduced in a dry flask containing EG (0.80 g, 12.88 mmol). Then a solution of DCC (6.37 g, 30.92 mmol) and DMAP (0.377 g, 3.092 mmol) in 5 mL of anhydrous tetrahydrofuran was added dropwise to the reaction mixture at 0 °C. The esterification reaction proceeded under stirring at room temperature for 24 h. After the removal of solvent in vacuo, the crude product was purified using column chromatography on silica eluting with petroleum ether/dichloromethane (1: 1) and finally dried at 45 °C under vacuum to obtain a viscous orange oil.
Synthesis of trifunctional RAFT agent. A solution of BTPA (5.84 g, 21.47 mmol) in 25 mL of anhydrous tetrahydrofuran (THF) was introduced in a dry flask containing TMP (0.80 g, 5.96 mmol). Then a solution of DCC (4.12 g, 21.47 mmol) and DMAP (0.244 g, 2.15 mmol) in 5 mL of anhydrous tetrahydrofuran was added dropwise to the reaction mixture at 0 °C. The esterification reaction proceeded under stirring at room temperature for 24 h. After the removal of solvent in vacuo, the crude product was purified using column chromatography on silica eluting with dichloromethane and finally dried at 45 °C under vacuum to obtain a viscous orange oil.

Synthesis of PDAAM-based macro-RAFT agents

In a typical experiment for the synthesis of 4-arm star macro-RAFT agent, DAAM (20.0 g, 118.2 mmol), tetrafunctional small molecular RAFT agent (1.55 g, 1.41 mmol), AIBN (184.6 mg, 1.13 mmol), 1, 3,5-trioxacyclohexane (1.064 g, 11.82 mmol), and 1, 4-dioxane (46.67 g) were weighed into a 100 mL round bottom flash and purged with nitrogen for 30 min. The flask was then immersed into a preheated oil bath at 70 °C for 100 min (Monomer conversion = 95% as judged by 1H NMR). The polymerization was then quenched by immersion in ice water and exposure to air. The product was precipitated by adding excess of hexane and washed several times with additional hexane. The precipitated product was then dried at 45 °C under vacuum overnight. Other macro-RAFT agents were synthesized following the same protocol.

Photoinitiated RAFT dispersion polymerization of IBOA

In a typical experiment for the synthesis of (PDAAM20-PIBOA350-TTC)4 (30% w/w), IBOA (3.0 g, 14.4 mmol), (PDAAM20-TTC-Z)4 (0.151 g, 0.0103 mmol), and TPO (4.8 mg, 0.014 mmol) were weighed into a 25 mL round bottom flask. Then an ethanol/water mixture (5.95 g/1.05 g, 85/15, w/w) was added into the flask to dissolve all reagents. The reaction mixture was purged with
nitrogen for 20 min and immersed into a water bath at 40 °C for 5 min, then irradiated by a visible light LED lamp (405 nm, 0.45 mW/cm²) for 1.5 h. The reaction was quenched by exposure to air and the addition of a small amount of hydroquinone.

**Kinetic study of photoinitiated RAFT dispersion polymerization**

IBOA (5.0 g, 24.0 mmol), (PDAAM_{20-TTC})₄ (0.294 g, 0.020 mmol), TPO (9.3 mg, 0.027 mmol) and 1,3,5-trioxacyclohexane (0.21 g, 2.4 mmol) were weighed into a 25 mL round bottom flask. Then an ethanol/water mixture (9.92 g/1.75 g, 85/15, w/w) was added into the flask to dissolve all reagents. The reaction mixture was purged with nitrogen for 20 min and immersed into a water bath at 40 °C for 8 min, and then irradiated by a visible light LED lamp (405 nm, 0.45 mW/cm²). Samples were withdrawn at predetermined time intervals by syringes under nitrogen, and the reaction was quenched by exposure to air and the addition of a small amount of hydroquinone. The samples were then analyzed by ¹H NMR spectroscopy, THF GPC and TEM.
Additional results

Table S1. GPC data of polymer particles prepared by photoinitiated RAFT dispersion polymerization of IBOA (30% w/w) mediated by (PDAAM<sub>20</sub>-TTC)<sub>4</sub> in ethanol/water (85/15, w/w) with different DPs of PIBOA

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Figure S1. TEM images of polymer particles prepared by photoinitiated RAFT dispersion polymerization of IBOA (30% w/w) in ethanol/water (85/15, w/w) mediated by (PDAAM<sub>20</sub>-TTC)<sub>4</sub> (target DP of 400) at different monomer conversions.
Figure S2. TEM images of polymer particles prepared by photoinitiated RAFT dispersion polymerization of IBOA (30% w/w) mediated by (PDAAM_{20}-TTC)_4 in ethanol/water (85/15, w/w) at 70 °C with different DPs of PIBOA: (a) DP = 245, (b) DP = 347.

Figure S3. TEM images of polymer particles prepared by photoinitiated RAFT dispersion polymerization of IBOA mediated by (PDAAM_{20}-TTC)_4 in ethanol/water (85/15, w/w) at 40 °C with different IBOA concentrations: (a) 25%, (b) 35%. 
Figure S4. TEM images of polymer particles prepared by photoinitiated RAFT dispersion polymerization of IBOA (30% w/w) in ethanol/water mediated by (PDAAM$_{20}$-TTC)$_4$ at 40 °C with different ethanol/water ratios (w/w): (a) 80/20, (b) 90/10.

Figure S5. TEM image of polymer particles prepared by thermally initiated RAFT dispersion polymerization of IBOA (30% w/w, target DP of 400) mediated by (PDAAM$_{20}$-TTC)$_4$ in ethanol/water (85/15, w/w) at 70 °C using AIBN as a thermal initiator.

REFERENCES