Supporting information

One Polymer with Multifunction: α, ω-Macromolecular Photoinitiator/Chain Transfer Agent used in Aqueous Photoinitiated Polymerization-Induced Self-Assembly

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EXPERIMENTAL SECTION

Materials.

Glycidyl methacrylate (GlyMA, Aladdin) was passed through a column of basic alumina (Aladdin) prior to storage under refrigeration at 4 ℃. 2-Hydroxypropyl methacrylate (HPMA, Aladdin), dicyclohexylcarbodiimide (DCC, Aladdin), 4-dimethylaminopyridine (DMAP, Aladdin), ethylene glycol (EG, Aladdin), 2-hydroxyethyl disulfide (Aladdin), ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate (TPO-L, Tianjin Jiuri Chemical Co.LTD), and *N*, *N*-dimethylformamide (DMF, Tianjin Damao) were used as received. 2,2-Azobisisobutyronitrile (AIBN, Aladdin) was recrystallized from ethanol prior to storage under refrigeration at 4 ℃. 4-Cyano-4-(dodecylsulfanylthiocarbonyl) sulfanylpentanoic acid (CDPA) was synthesized according to a literature procedure [1].

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 3 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 3 min, and then blotted with filter paper to remove excess stain. TEM observations were carried out on a Hitachi 7700 instrument operated at 100 kV.

^{1}H NMR Spectroscopy. Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$, D_2O or d_6-DMSO using a Bruker Avance III HD 400 MHz NMR spectrometer at a temperature of 25 °C.

Gel Permeation Chromatography (GPC). Molecular weights and polydispersities of samples were measured by gel permeation chromatography (GPC) at 50 ℃ using a Waters 1515 GPC instrument with dimethylformamide (DMF) as the mobile phase and Waters styragel HR1 and HR4 columns. The eluent used was HPLC grade DMF containing 10 mM LiBr and was filtered prior to use. The flow rate of DMF was 1.0 mL/min. Linear poly(methyl methacrylate) polymers with narrow molecular weight distributions were used as standards to calibrate apparatus.

Ultraviolet visible photometer. UV-visible spectra were recorded with a 1.0 cm quartz

cuvette using a UV2450 spectrometer.

Synthesis of CDPA-OH.

A solution of CDPA (15.00 g, 37.16 mmol) in anhydrous tetrahydrofuran (50 mL) was added into a dry flask containing anhydrous ethylene glycol (4.61 g, 74.31 mmol). Then a solution of DCC (23 g, 114.47 mmol) and DMAP (0.91 g, 7.45 mmol) in anhydrous THF (65 mL) was added dropwise to the reaction mixture at 0 ℃ . The esterification reaction proceeded with stirring at room temperature for 10 h. The product was further purified by a silica chromatography (v(ethyl acetate): v(*n*-hexane) = 1: 3), and finally dried at 40 ℃ under vacuum to obtain an orange oil. Yield: 67%.

Synthesis of sodium 2,4,6-trimethylbenzoylphenylphosphinate (TPO-Na).

A mixture of TPO-L (20.00 g, 63.20 mmol), NaI (10.50 g, 70.06 mmol) and 2-butanone (100 mL) was stirred at 40 ℃ for 30 min. The resulting solution was heated at 65 ℃ for 24 h. The suspension was cooled to room temperature and filtered, washed with cold 2-butanone (80 mL) and dried under vacuum.

Synthesis of 2,4,6-trimethylbenzoylphenylphosphinic acid (TPO-OH).

A solution of TPO-Na (7.20 g, 23.22 mmol) in distilled water (50 mL) was stirred at the room temperature. The aqueous solution of H_2SO_4 (0.5 M, 20 mL) was added to reach the pH of 1, and the product was precipitated gradually. Ethyl acetate (200 mL) was added to the solution, and the organic phase was separated. The aqueous layer was extracted with ethyl acetate (2 × 100 mL). The total organic layers were washed with water (2 × 100 mL) and dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, TPO-OH was obtained as a pale yellow solid. Yield: 65.5%.

Synthesis of 2,4,6-trimethylbenzoylphenylphosphinic acid chloride (TPO-Cl).

Oxalyl chloride (0.79 mL, 8.93 mmol) was added into a solution containing TPO-OH (1.29g, 4.47 mmol) and anhydrous dichloromethance (13 mL) at 0 ℃. The mixture was stirred at room temperature for 24 h. After evaporation of the solvent under reduced pressure, a pale-yellow oil was obtained and used in next step without further purification.

Synthesis of TPO-CDPA.

TPO-Cl (1.37 g, 4.47 mmol) was added into a solution containing CDPA-OH (2.00 g, 4.47 mmol) and anhydrous dichloromethane (13 mL) at room temperature. The resulting

mixture was stirred at room temperature for 9 h. The product was further purified by a silica chromatography (v(ethyl acetate): v(dichloromethane) = 1: 5), and finally dried at 35 ℃ under vacuum to obtain an orange oil. Yield: 44.51%.

Synthesis of glycerol monomethacrylate (GMA).

Glycidyl methacrylate (50.00 g) was added to water (450.0 g, 10% w/w) in a round bottom flask connected with a condenser. The reaction mixture was stirred at 80 ℃ for 10 h, and a transparent aqueous solution was formed. The resulting solution was then saturated with NaCl, and extracted with dichloromethane. The organic phase was dried with Na_2SO_4 overnight, filtered, and concentrated under reduced pressure. The obtained monomer was then further purified by silica column chromatography (v(dichloromethane): v(methanol) = 20: 1).

Synthesis of PGMA-based macro-RAFT agents.

Synthesis of $PGMA_n$-CDPA. A typical protocol for the synthesis of $PGMA_{45}$-CDPA is given below: GMA (10.00 g, 62.43 mmol), AIBN (0.041 g, 0.25 mmol), 1,3,5-trioxacyclohexane (0.56 g, 6.22 mmol), and CDPA (0.50 g, 1.24 mmol) were added into a round bottom flask. A certain amount of anhydrous ethanol (15.00 g) was added into the round bottom flask to form a homogeneous solution. The reaction mixture was then purged with nitrogen for 1 h, sealed, and then immersed in a 70 ℃ pre-heated oil bath for 250 min. The polymerization was quenched by immersion in ice-water and exposure to air. The polymer was precipitated by adding excess hexane (300 mL) and washed several times with additional hexane. The obtained product was then dried 35 ℃ under vacuum overnight, and then analyzed by DMF gel permeation chromatography (GPC). ^{1}H NMR measurement indicated a mean degree of polymerization of 45 for this macro-RAFT agent (denoted as $PGMA_{45}$-CDPA), and DMF GPC measurement confirmed its M_n = 17.7 kg/mol and M_w/M_n = 1.22.

Synthesis of TPO-$PGMA_n$-CDPA. A typical protocol for the synthesis of TPO-$PGMA_{47}$-CDPA is given below: GMA (20.00 g, 0.12 mol), AIBN (0.082 g, 0.50 mmol), 1,3,5-trioxacyclohexane (1.12 g, 12.44 mmol), and TPO-CDPA (1.79 g, 2.49 mmol) were added into a round bottom flask. A certain amount of anhydrous ethanol (30.00 g) was added into the round bottom flask to form a homogeneous solution. The

reaction mixture was then purged with nitrogen for 1 h, sealed, and then immersed in a 70 ℃ pre-heated oil bath for 250 min. The polymer was precipitated by adding excess hexane (500 mL) and washed several times with additional hexane. The obtained product was then dried 35 ℃ under vacuum overnight, and then analyzed by DMF gel permeation chromatography (GPC). ^{1}H NMR measurement indicated a mean degree of polymerization of 47 for this macro-RAFT agent (denoted as TPO-PGMA$_{47}$-CDPA), and DMF GPC measurement confirmed its M_n = 18.0 kg/mol and M_w/M_n = 1.19. Other macro-RAFT agents were synthesized following the same protocol.

Aqueous photo-PISA of HPMA using TPO-PGMA$_{47}$-CDPA.

In a typical experiment (25% w/w HPMA, [HPMA]/[TPO-PGMA$_{47}$-CDPA] = 300): HPMA (0.80 g, 5.55 mmol), TPO-PGMA$_{47}$-CDPA (0.15 g, 0.019 mmol), and water (2.40 g) were weighted into a 10 mL round bottom flask. A tiny amount of DMF (20 μL) was added to the reaction mixture as an internal standard. The reaction mixture was purged with nitrogen for 20 min, and then exposed to a LED lamp (λ = 405 nm, 0.45 mW/cm^2) for 1 h. The polymerization was quenched by exposure to air.

Aqueous thermally initiated PISA of HPMA using TPO-PGMA$_{92}$-CDPA.

In a typical experiment (25% w/w HPMA, [HPMA]/[TPO-PGMA$_{92}$-CDPA] = 300): HPMA (0.80 g, 5.55 mmol), TPO-PGMA$_{92}$-CDPA (0.29 g, 0.019 mmol), ACVA (1.73 mg, 0.006 mmol). and water (2.40 g) were weighted into a 10 mL round bottom flask. A tiny amount of DMF (20 μL) was added to the reaction mixture as an internal standard. The reaction mixture was purged with nitrogen for 20 min, sealed, and then immersed into a pre-heated oil bath at 70 ℃ for 12 h. The polymerization was quenched by exposure to air.

Aqueous photo-PISA of HPMA at 70 ℃ using TPO-PGMA$_{92}$-CDPA.

In a typical experiment (25% w/w HPMA, [HPMA]/[TPO-PGMA$_{92}$-CDPA] = 300): HPMA (0.80 g, 5.55 mmol), TPO-PGMA$_{92}$-CDPA (0.29 g, 0.019 mmol), and water (2.40 g) were weighted into a 10 mL round bottom flask. A tiny amount of DMF (20 μL) was added to the reaction mixture as an internal standard. The reaction mixture was purged with nitrogen for 20 min, sealed, and then immersed into a pre-heated oil bath at 70 ℃ by exposure to a LED lamp (λ = 405 nm, 0.45 mW/cm^2) for 1h. The polymerization was

quenched by exposure to air.

Kinetic study of aqueous photo-PISA of HPMA using TPO-PGMA$_{47}$-CDPA.

HPMA (2.00 g, 13.87 mmol), TPO-PGMA$_{47}$-CDPA (0.38 g, 0.046 mmol), and water (18.00 g) were weighed into a 25 mL round bottom flask. A tiny amount of DMF (40 μL) was added to the reaction mixture as an internal standard. The reaction mixture was purged with nitrogen for 30 min, sealed, and then exposed to a LED lamp (λ = 405 nm, 0.45 mW/cm^2). Sample were withdrawn at predetermined time intervals by syringes under nitrogen. Polymerizations were quenched by exposure to air and the addition of a small amount of hydroquinone. The samples were then analyzed by ^{1}H NMR spectroscopy and DMF GPC.

ADDITIONAL RESULTS

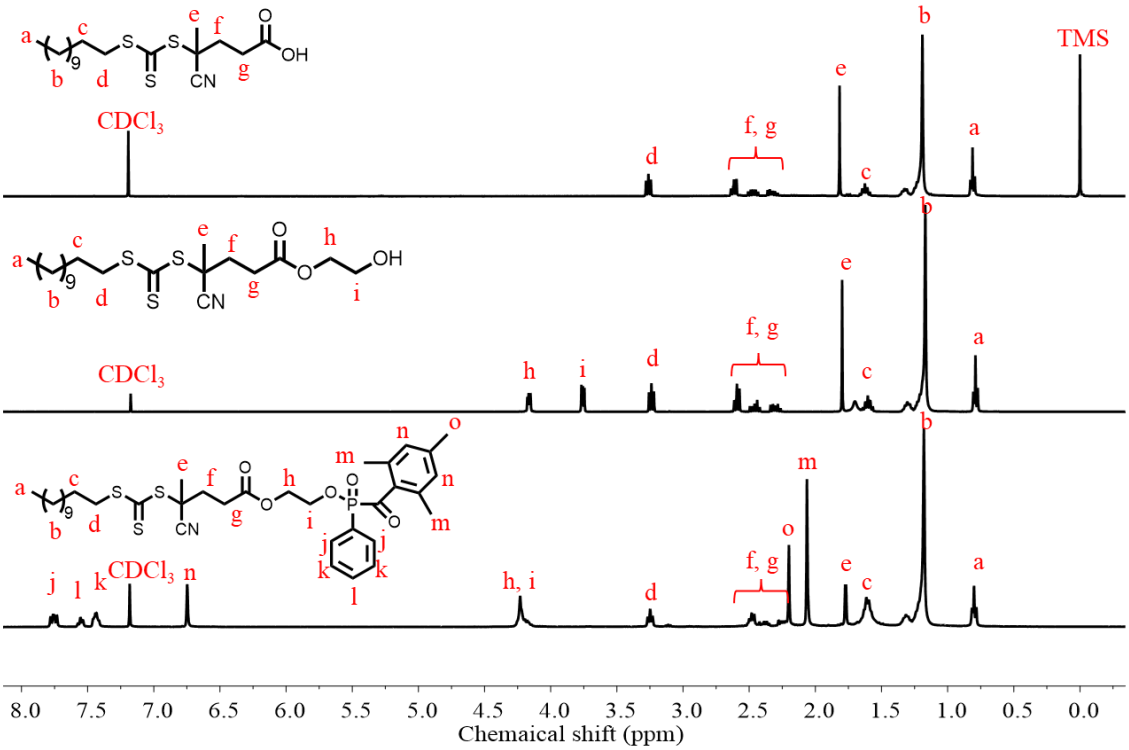

Figure S1. ^{1}H NMR spectra of CDPA、CDPA-OH, and TPO-CDPA.

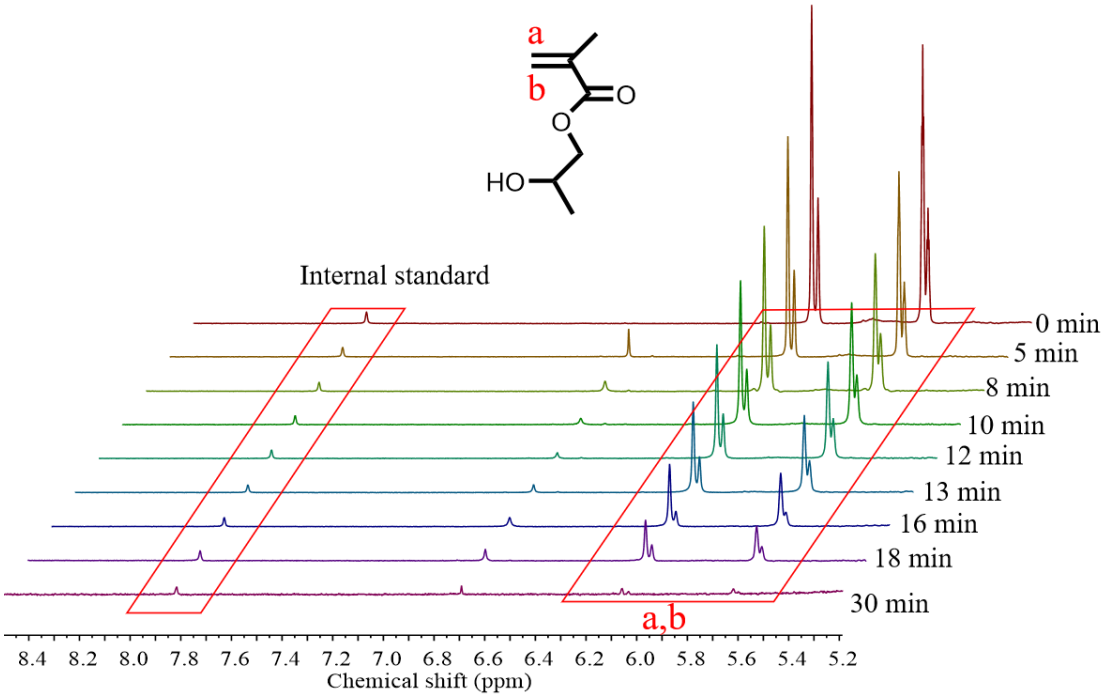

Figure S2. ^{1}H NMR spectra of reaction mixtures withdrawn during aqueous photo-PISA of HPMA (10% w/w) using TPO-PGMA$_{47}$-CDPA ([HPMA]/[TPO-PGMA$_{47}$-CDPA] = 300/1) under purple light irradiation (λ = 405 nm, 0.45 mW/cm^2).

REFERENCE

[1] Shen, W, et al. Biocompatible, Antifouling, and Thermosensitive Core-shell Nanogels Synthesized by RAFT Aqueous Dispersion Polymerization. *Macromolecules*, 2011,44(8):p. 2524-2530.