

Supporting information

Polymerization-induced Self-assembly mediated by Vinyl-functionalized Macromolecular Chain Transfer Agents: A Straightforward Approach for Cross-linked Block Copolymer Nanoparticles with tunable Morphologies

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Experimental Section

1. Materials

Glycidyl methacrylate (GlyMA, Aladdin), allyl methacrylate (AMA, Aladdin), *tert*-butyl acrylate (*t*BA, Aladdin), hydroquinone (Aladdin), hydroxypropyl methacrylate (HPMA, Aladdin), dichloromethane (DCM, Aladdin), *N,N*-dimethylformamide (DMF, Aladdin), 4,4'-azobis(4-cyanovaleric acid) (ACVA, Aladdin), and 1,3,5-trioxacyclohexan (Aladdin) were used as received. Sodium phenyl-2,4,6-trimethylbenzoylphosphinate (SPTP) was synthesized according to a published procedure.¹ 2,2-Azobisisobutyronitri (AIBN, Aladdin) was recrystallized from ethanol prior to storage under refrigeration at 4 °C. 4-Cyano-4-(ethylthiocarbonothioylthio)pentanoic acid (CEPA) was synthesized based on a published procedures.² Purple light LED lamps ($\lambda_{\max} = 405$ nm) were purchased from Huaenopto (Zhejiang). HPLC grade DMF and PTFE needle filters were purchased from Shanghai Ampel Technology Co., Ltd.

2. 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.

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

Size Exclusion Chromatography (SEC). Molar mass and polydispersity of samples were measured by SEC at 50 °C using a Waters 1515 SEC instrument with DMF (containing 10 mM LiBr) as the mobile phase and Waters styragel HR1, HR2, and HR4 columns. The flow rate of DMF was 1.0 mL/min. Linear PMMA standard polymers with narrow molar mass distributions were used as the standards to calibrate the apparatus.

Dynamic light scattering (DLS). Intensity-average hydrodynamic diameters of the dispersions (0.1% v/v) were obtained using a Malvern Instrument Zetasizer NANO ZS.

Synthesis of glycerol methacrylate (GMA)

Glycidyl methacrylate (GlyMA, 40.00 g) was added to water (360.00 g, 10% w/w) in a 1000 mL round bottom flask connected with a condenser and stirred for 9 h at 80 °C. A transparent aqueous solution was formed. The resulting solution was then saturated with NaCl and extracted with dichloromethane. The organic phase was dried with Na₂SO₄ overnight, filtered, and concentrated under reduced pressure. The obtained monomer was further purified by silica column chromatography (CH₂Cl₂: CH₃OH = 20: 1).

Synthesis of PGMA_n-CEPA (n = 30, 45, 56)

In a typical experiment for the synthesis of PGMA₄₅-CEPA: GMA (30.00 g, 0.187 mol), ACVA (0.23 g, 0.81 mmol), and CEPA (1.07 g, 4.07 mmol), and 1,3,5-trioxacyclohexane (1.68 g, 0.19 mol) were added into a 150 mL round-bottom flask, and then dissolved with anhydrous ethanol (45.00 g, 40% w/w) to form a homogeneous solution. The reaction mixture was purged with nitrogen for 30 min, sealed, and then immersed in a pre-heated oil bath at 70 °C for 6 h. The polymerization was quenched by immersion in ice-water and exposure to air and analyzed by ¹H NMR spectroscopy, which indicated a mean degree of polymerization of 45 (monomer conversion was 98.3% as judged by ¹H NMR). The polymer was precipitated by adding excess petroleum ether and washed with additional petroleum ether for several times. The obtained product was dried at 45 °C under vacuum overnight, and then analyzed by DMF SEC. PGMA₃₀-CEPA and PGMA₅₆-CEPA were synthesized following the same protocol.

Synthesis of PGMA_m-PAMA_n-CEPA

In a typical experiment for the synthesis of PGMA₄₅-PAMA_{4.5}-CEPA: PGMA₄₅-CEPA (7.00 g, 0.93 mmol), AMA (2.35 g, 18.66 mmol), AIBN (30.70 mg, 0.19 mmol), 1,3,5-trioxacyclohexane (0.17 g, 1.86 mmol), and anhydrous ethanol (13.30 g) were introduced into a 25 mL round bottom flask and purged with nitrogen for 30 min. The flask was then immersed into a preheated oil bath at 70 °C for 60 min. The polymerization was then quenched

by immersion in ice water and exposure to air (The conversion of the methacrylic unit was 22.22% as judged by ^1H NMR). The product was precipitated by adding excess petroleum ether and washed several times with additional petroleum ether to remove unreacted monomer. The precipitated product was then dried at room temperature under vacuum overnight and then analyzed by DMF SEC and ^1H NMR spectroscopy. PGMA₄₅-PAMA_{8.3}-CEPA, PGMA₃₀-PAMA_{8.9}-CEPA, and PGMA₅₆-PAMA_{9.5}-CEPA were synthesized following the same protocol.

Synthesis of P(GMA_{44-co}-AMA₅)-CEPA

GMA (41.00 g, 0.26 mol), AMA (6.91 g, 54.76 mmol), CEPA (0.45 g, 1.71 mmol), ACVA (9.60 mg, 0.034 mmol), 1,3,5-trioxacyclohexane (1.40 g, 15.50 mmol), and anhydrous ethanol (72.00 g) were introduced into a 250 mL round bottom flask and purged with nitrogen for 30 min. The flask was then immersed into a preheated oil bath at 70 °C for 2.5 h. The polymerization was then quenched by immersion in ice water and exposure to air. As analyzed by ^1H NMR, the conversion of the methacrylic unit of GMA was 29.1% and the conversion of the methacrylic unit of AMA conversion was 16.4%. The product was precipitated by adding excess petroleum ether and washed several times with additional petroleum ether to remove unreacted monomer. The precipitated product was then dried at room temperature under vacuum overnight and then analyzed by DMF SEC and ^1H NMR spectroscopy.

Aqueous photoinitiated RAFT dispersion polymerization of HPMA using PGMA_m-PAMA_n-CEPA

In a typical experiment by using PGMA₄₅-PAMA_{4.5}-CEPA ([HPMA]/[macro-RAFT] = 200): HPMA (0.536 g, 3.72 mmol, 20% w/w), PGMA₄₅-PAMA_{4.5} (0.15 g, 18.60 μmol), DMF (0.027g), and SPTP (1.9 mg, 6.00 μmol) were weighed into a 5 mL round bottom flask. Then a certain amount of water (2.14 g in this case) was added to the flask to dissolve all reagents. 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 of 0.45 mW/cm²) at room temperature for 60 min. The

polymerization was quenched by exposure to air. Other RAFT dispersion polymerizations were performed following the same protocol.

Aqueous photoinitiated seeded RAFT emulsion polymerization of *t*BA using PGMA₄₅-PAMA_{4.5}-PHPMA₁₂₅ worms as seeds.

In a typical experiment by using PGMA₄₅-PAMA_{4.5}-PHPMA₁₂₅ worms (prepared at 20% w/w HPMA) as seeds ($[tBA]/[PGMA_{45}\text{-PAMA}_{4.5}\text{-PHPMA}_{125}]$ ratio of 300, solids content of 10% w/w): A solution of *t*BA (0.20 g, 1.56 mmol) in water (2.05 g) was added into the dispersion of PGMA₄₅-PAMA_{4.5}-PHPMA₁₂₅ copolymer nanoparticles (1.00 g, containing 0.13 g (5.20 μmol) PGMA₄₅-PAMA_{4.5}-PHPMA₁₂₅). Then additional SPTP (0.54 mg, 1.74 μmol) was added into the reaction mixture. The reaction mixture was purged with nitrogen for 30 min, sealed, and then irradiated by a visible light LED lamp (405 nm, 0.45 mW/cm²) at room temperature for 1 h. The polymerization was quenched by exposure to air. Other seeded RAFT polymerizations of *t*BA using PGMA₄₅-PAMA_{4.5}-PHPMA₁₂₅ worms as seeds were performed following the same protocol.

Aqueous photoinitiated seeded RAFT emulsion polymerization of *t*BA using PGMA₄₅-PHPMA₁₀₀ worms as seeds.

In a typical experiment by using PGMA₄₅-PHPMA₁₀₀ worms (prepared at 20% w/w HPMA) as seeds ($[tBA]/[PGMA_{45}\text{-PHPMA}_{100}]$ ratio of 300, solids content of 10% w/w): A solution of *t*BA (0.24 g, 1.88 mmol) in water (2.83 g) was added into the dispersion of PGMA₄₅-PHPMA₁₀₀ copolymer nanoparticles (1.05 g, containing 0.14 g (6.28 μmol) PGMA₄₅-PHPMA₁₀₀). Then additional SPTP (0.64 mg, 2.09 μmol) was added into the reaction mixture. The reaction mixture was purged with nitrogen for 30 min, sealed, and then irradiated by a visible light LED lamp (405 nm, 0.45 mW/cm²) at room temperature for 1 h. The polymerization was quenched by exposure to air. Other seeded RAFT polymerizations of *t*BA using PGMA₄₅-PHPMA₁₀₀ worms as seeds were performed following the same protocol.

Aqueous photoinitiated seeded RAFT emulsion polymerization of GlyMA using P(GMA₄₄-*co*-AMA₅)-PHPMA₂₅₀ vesicles as seeds

In a typical experiment by using P(GMA₄₄-*co*-AMA₅)-PHPMA₂₅₀ vesicles (prepared at 10% w/w HPMA) as seeds ([GlyMA]/[P(GMA₄₄-*co*-AMA₅)-PHPMA₂₅₀] ratio of 300, solids content of 10% w/w): A solution of GlyMA (0.18 g, 1.27 mmol) in water (1.88 g) was added into the dispersion of P(GMA₄₄-*co*-AMA₅)-PHPMA₂₅₀ copolymer nanoparticles (1.55 g, containing 0.19 g (4.24 μmol) P(GMA₄₄-*co*-AMA₅)-PHPMA₂₅₀). Then additional SPTP (0.44 mg, 1.40 μmol) was added into the reaction mixture. The reaction mixture was purged with nitrogen for 30 min, sealed, and then irradiated by a visible light LED lamp (405 nm, light intensity of 0.45 mW/cm²) at room temperature for 1 h. Other seeded RAFT polymerization of GlyMA using P(GMA₄₄-*co*-AMA₅)-PHPMA₂₅₀ vesicles as seeds were performed following the same protocol.

Kinetic study of aqueous photoinitiated RAFT dispersion polymerization using PGMA₄₅-PAMA_{8.3}-CEPA

HPMA (1.054 g, 7.31 mmol), PGMA₄₅-PAMA_{8.3}-CEPA (0.25 g, 29.24 μmol), DMF (0.077 g), and SPTP (3.02 mg, 9.74 μmol) were weighed into a 10 mL round bottom flask. Then a certain amount of water (5.97 g) was added to the flask to dissolve all reagents. The reaction mixture was purged with nitrogen for 30 min, sealed, and then irradiated by a visible light LED lamp (405 nm, light intensity of 0.45 mW/cm²) at room temperature. Samples were withdrawn at predetermined time intervals by syringes under nitrogen, and the samples were quenched by exposure to air and the addition of a small amount of hydroquinone. The samples were then analyzed by ¹H NMR spectroscopy, DMF SEC, DLS, and TEM.

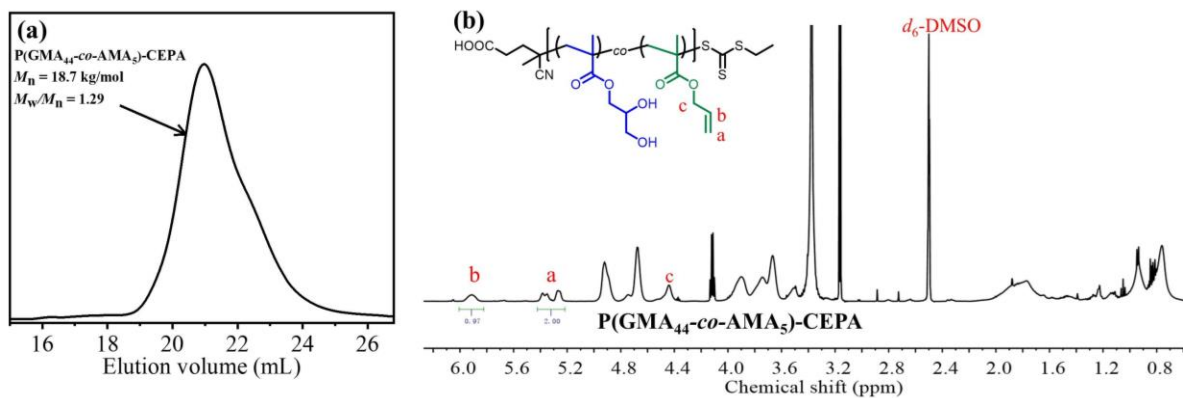


Figure S1. (a) DMF SEC trace and (b) ^1H NMR spectrum of P(GMA₄₄-co-AMA₅)-CEPA.

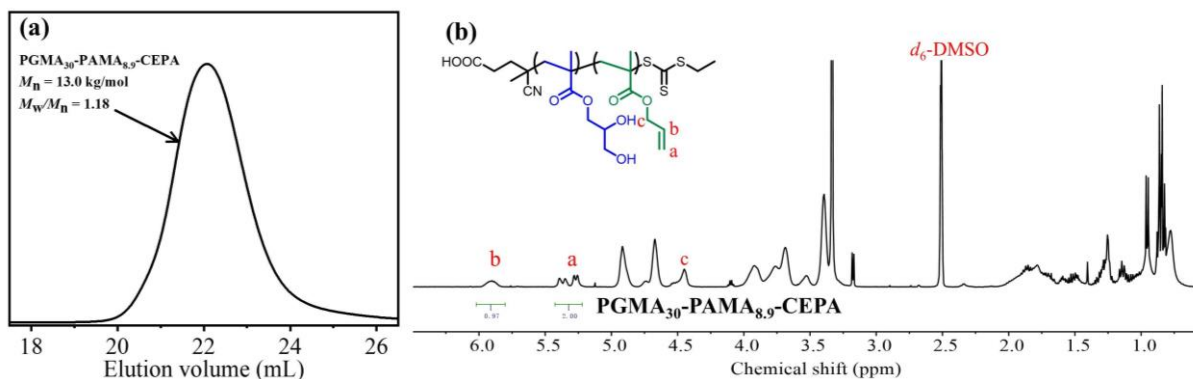


Figure S2. (a) DMF SEC trace and (b) ^1H NMR spectrum of PGMA₃₀-PAMA_{8.9}-CEPA

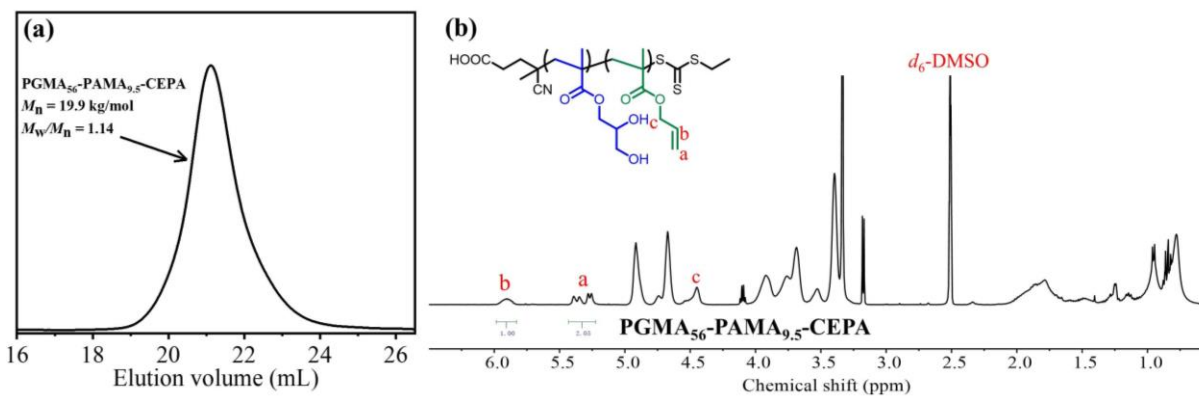


Figure S3. (a) DMF SEC trace and (b) ^1H NMR spectrum of PGMA₅₆-PAMA_{9.5}-CEPA

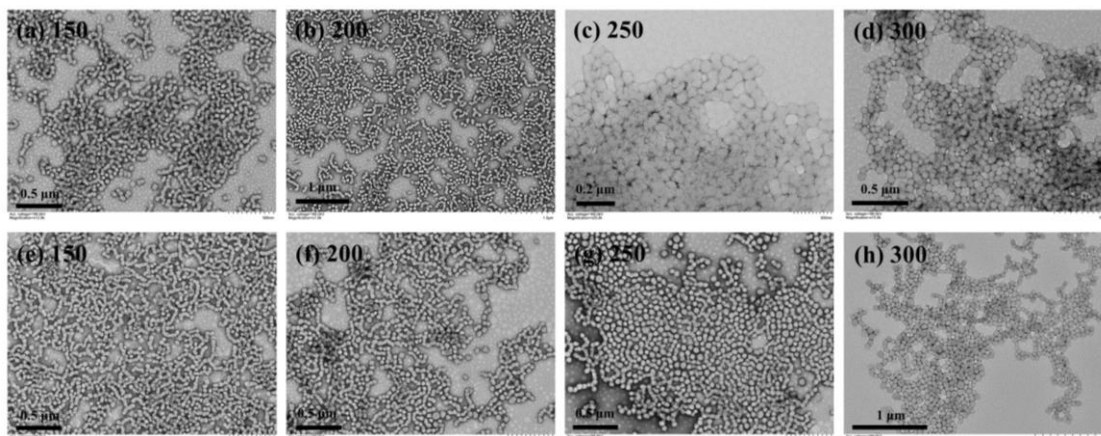


Figure S4. (a-d) TEM images of block copolymer nanoparticles prepared by aqueous photoinitiated RAFT dispersion polymerization of HPAM (10% w/w) using PGMA₄₅-PAMA_{8.3}-CEPA with different [HPMA]/[macro-RAFT] ratios. (e-h) TEM images of block copolymer nanoparticles prepared by aqueous photoinitiated RAFT dispersion polymerization of HPAM (10% w/w) using PGMA₄₅-PAMA_{4.5}-CEPA with different [HPMA]/[macro-RAFT] ratios.

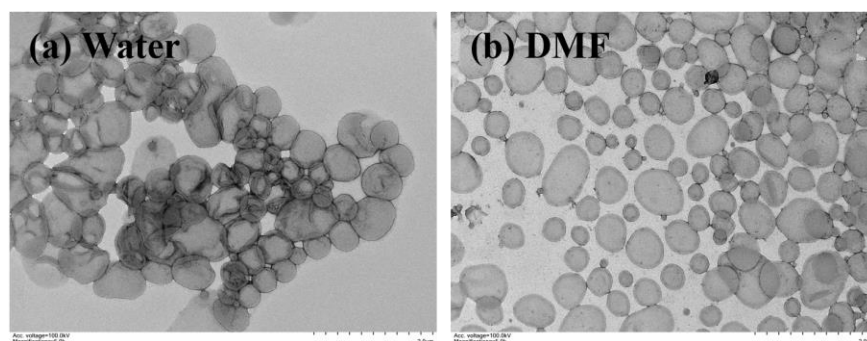


Figure S5. TEM images of P(GMA₄₄-co-AMA₅)-PHPMA₂₀₀ vesicles (after storage at room temperature for 6 months) dispersing in (a) water and (b) DMF.

References

- [1] G. Li, N. Xu, Q. Yu, X. Lu, H. Chen, Y. Cai, *Macromolecular Rapid Communications* **2014**, *35*, 1430–1435.
- [2] G. Moad, Y. K. Chong, A. Postma, E. Rizzardo, S. H. Thang, *Polymer* **2005**, *46*, 8458–8468.