

`R-RAFT or Z-RAFT? Well-defined Star Block Copolymer

Nano-objects prepared by RAFT-Mediated

Polymerization-Induced Self-Assembly

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EXPERIMENTAL SECTION

Material

N,N-Dimethylacrylamide (DMA, Aladdin), ethylene glycol (EG, Aladdin), trimethylolpropane (TMP, Aladdin), dicyclohexylcarbodiimide (DCC, Aladdin), 4-dimethylaminopyridine (DMAP, Aladdin), and hydroquinone (Aladdin) were used as received. 2, 2-Azobisisobutyronitrile (AIBN, Aladdin) was recrystallized from ethanol prior to storage under refrigeration at 4 °C. 2, 4, 6-trimethylbenzoyldi-phenylphosphinate (TPO, Ciba) was used without further purification. *N*-isopropylacrylamide (NIPAM, Aladdin) was recrystallized from hexane prior to storage under refrigeration at 4 °C. Styrene (St, Aladdin) and isobornyl acrylate (IBOA, Sigma-Aldrich) 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 Pentaerythritoltetrakis-(3-(S-benz-yltrithiocarbonyl)propionate) ((TTC-Z)₄) was synthesized according to a published procedure.² 1, 2, 4, 5-tetrakis-(butyltrithiomethyl)benzene ((TTC-R)₄) was synthesized according to a published procedure.³

Characterization

Transmission Electron Microscopy (TEM). The polymerization reaction mixtures were diluted 100-fold with methanol/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.

Gel Permeation Chromatography (GPC). The molecular weight 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 molecular weight distributions were used as the 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.

Ultraviolet visible photometer. UV-Visible spectra were recorded with a 1.0 cm quartz cuvette using a UV2450 spectrometer.

Synthesis of Multifunctional Trithiocarbonates

Synthesis of (TTC-Z)₂. 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 (TTC-Z)₃. 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 1-, 2-, 3-, and 4-arm star macro-RAFT agents

In a typical experiment for the synthesis of 4-arm star macro-RAFT agent, DMA (15.0 g, 151.3 mmol), (TTC-Z)₄ (2.09 g, 1.89 mmol), AIBN (25 mg, 0.15 mmol), 1, 3, 5-trioxacyclohexane (1.37 g, 15.13 mmol), and 1, 4-dioxane (35.0 g) were weighed into a 100 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 4 h (Monomer conversion = 97% 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.

Star block copolymer nano-objects prepared by RAFT-mediated dispersion polymerization

In a typical experiment for the synthesis of (PDMA₂₀-PSt₁₅₀-TTC-Z)₄ (20% w/w St), St (1.50 g, 14.4 mmol), (PDMA₂₀-TTC-Z)₄ (0.217 g, 0.024 mmol), and AIBN (5.2 mg, 0.032 mmol) were weighed into a 25 mL round bottom flask. Then a methanol/water mixture (4.8 g/1.2 g) was added into the flask to dissolve all reagents. The reaction was purged with nitrogen for 20 min, and then immersed into a pre-heated oil bath at 70 °C for 24 h. The reaction was quenched by immersing into an ice-water bath.

Kinetic Study of RAFT-mediated dispersion polymerization

In a typical experiment, St (2.50 g, 24.0 mmol), (PDMA₂₀-TTC-Z)₄ (0.269 g, 0.030 mmol), AIBN (6.6 mg, 0.040 mmol) and 1,3,5-trioxacyclohexane (0.21 g, 2.4 mmol) were weighed into a 25 mL round bottom flask. Then a methanol/water mixture (8.0 g/2.0 g) was added into the flask to dissolve all reagents. The reaction mixture was purged with nitrogen for 20 min, and then immersed into a pre-heated oil bath at 70 °C for 24 h. Samples were withdrawn at predetermined time intervals by syringes under nitrogen, and the reaction was quenched by immersing into an ice-water batch and adding a small amount of hydroquinone. The samples were then analyzed by ¹H NMR spectroscopy and gel permeation chromatography (GPC).

Synthesis of 4-arm triblock copolymer nano-objects by seeded RAFT dispersion polymerization

Synthesis of (PDMA₂₀-PSt₁₅₀-TTC-Z)₄ vesicles. St (1.50 g, 14.4 mmol), AIBN (5.2 mg, 0.032 mmol), and (PDMA₂₀-TTC-Z)₄ (0.217 g, 0.024 mmol) were weighed into a 25 mL round bottom flask. Then a methanol/water mixture (4.8 g/1.2 g) was added into the flask to dissolve all reagents. The reaction mixture was purged with nitrogen for 20 min, and then immersed into a pre-heated oil bath at 70 °C for 24 h.

Synthesis of (PDMA₂₀-PSt₁₄₈-PNIPAM₂₀₀-TTC-Z)₄ assemblies. NIPAM (2.1735 g, 19.2 mmol) and AIBN (5.2 mg, 0.032 mmol) were dissolved in a methanol/water mixture (12.83 g/3.21 g). The solution was purged with nitrogen for 20 min, and then injected into the dispersion of (PDMA₂₀-PSt₁₄₈-TTC-Z)₄ vesicles at 70 °C. The polymerization was continued for another 24 h. The reaction was quenched by exposure to air and immersing in an ice-water bath.

Synthesis of (PDMA₂₀-PSt₁₄₈-PIBOA₁₀₀-TTC-Z)₄ assemblies. IBOA (2.00 g, 9.6 mmol) and AIBN (5.2 mg, 0.032 mmol) were dissolved in a methanol/water mixture (12.03g/ 3.01 g). The solution was purged with nitrogen for 20 min, and then injected into the dispersion of (PDMA₂₀-PSt₁₄₈-TTC-Z)₄ vesicles at 70 °C for 24 h. The reaction was quenched by exposure to air and immersing in an ice-water bath.

Removal of trithiocarbonate group from the 4-arm star block copolymers

(PDMA₂₀-PSt₂₀₀-TTC-Z)₄ (0.87g) was dissolved in 4.33 g THF in a 10 mL round bottom flask. Then 50-fold photoinitiator (2,4,6-trimethylbenzoyldiphenyl phosphine oxide) was

added to the reaction mixture. The reaction was then purged with nitrogen for 20 min, and then irradiated by a visible light LED lamp (405 nm, 3 mW/cm²) for 5 h. The samples were then analyzed by GPC directly.

Additional results

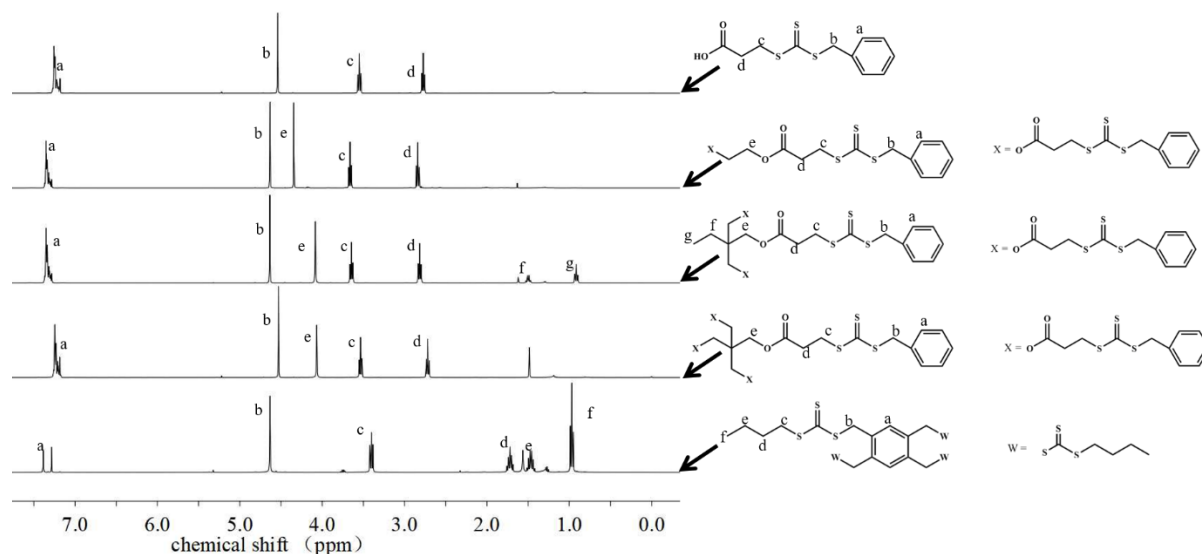


Figure S1. ¹H NMR spectra of small molecular RAFT agents used in the present study.

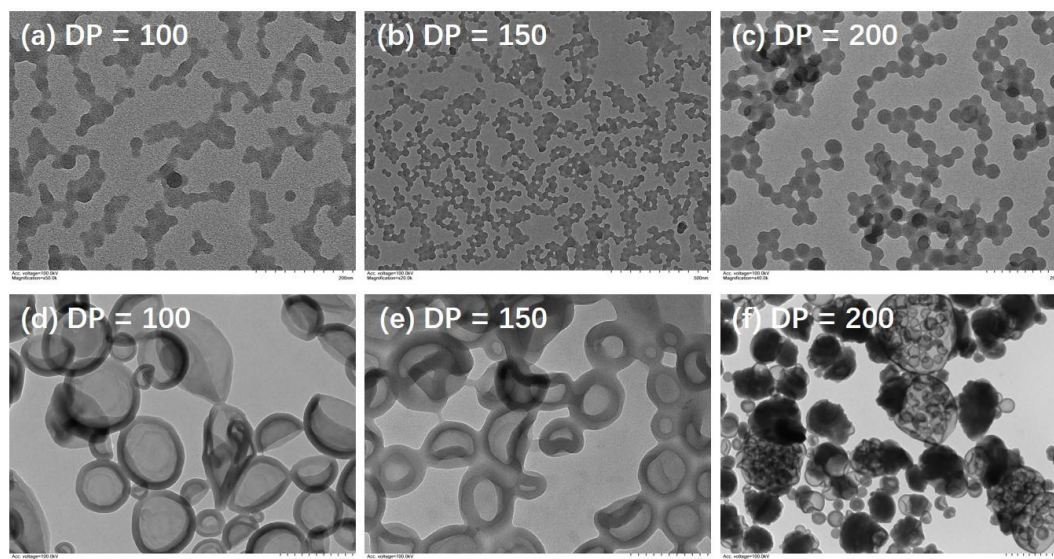


Figure S2. (a-c) TEM images of (PDMA₂₇-PSt_n-TTC-Z)₄ star block copolymer nano-objects prepared by RAFT-mediated PISA of St using (PDMA₂₇-TTC-Z)₄. (d-f) TEM images of (PDMA₁₃-PSt_n-TTC-Z)₄ star block copolymer nano-objects prepared by RAFT-mediated PISA of St using (PDMA₁₃-TTC-Z)₄.

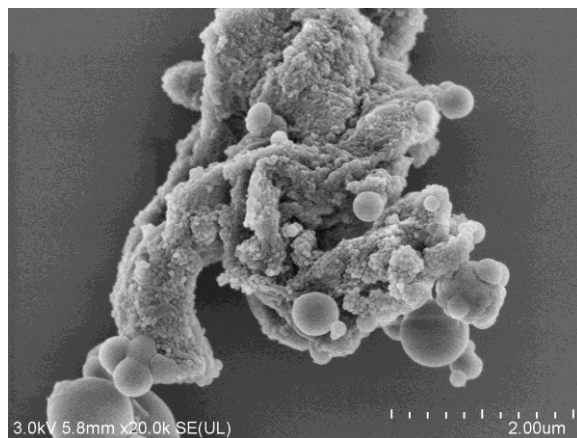


Figure S3. SEM image of $(\text{TTC-PSt}_{200}\text{-PDMA}_{27}\text{-R})_4$ prepared by RAFT-mediated PISA of St using $(\text{TTC-PDMA}_{27}\text{-R})_4$.

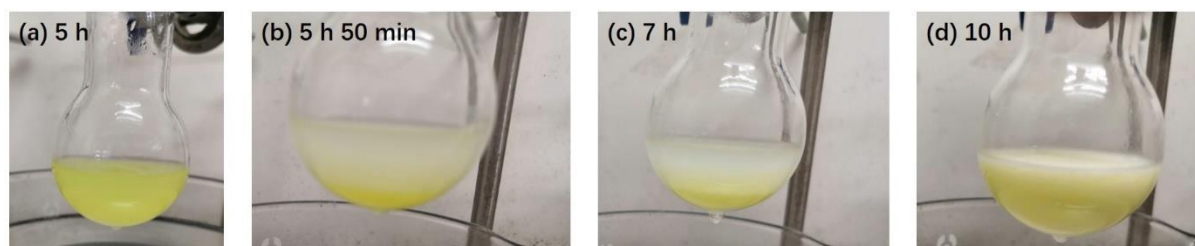


Figure S4. Optical images of reaction mixture of RAFT-mediated PISA of St (20% w/w) using $(\text{TTC-PDMA}_{20}\text{-R})_4$ in a methanol/water (80/20, w/w) mixture.

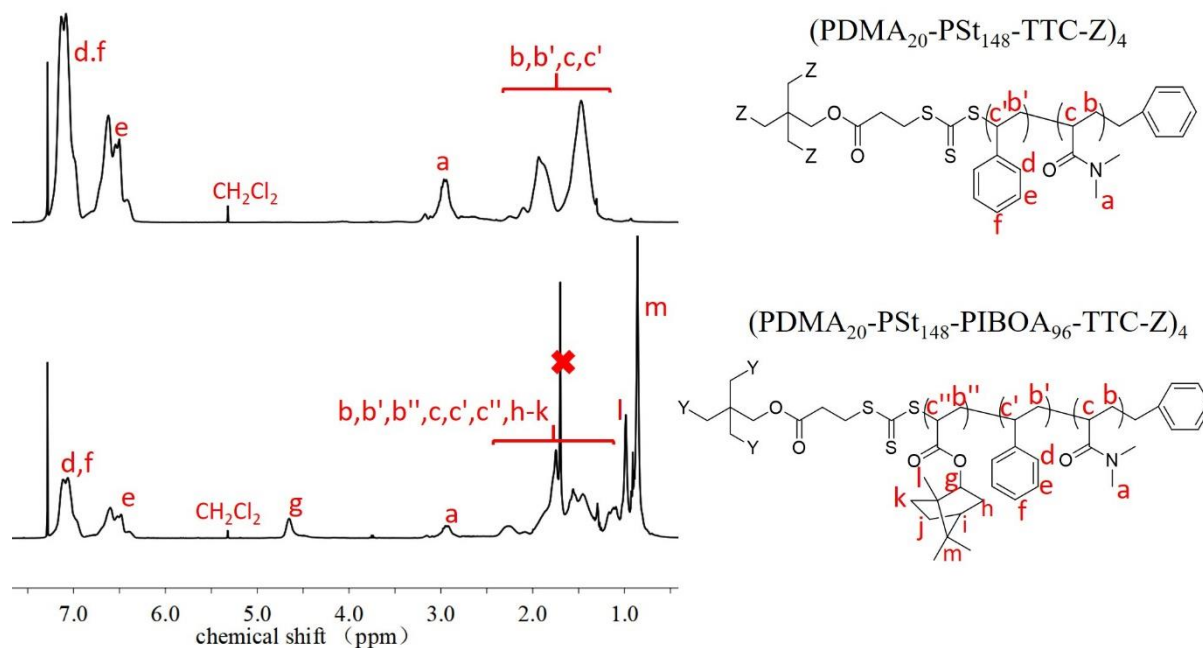


Figure S5. ^1H NMR spectra of $(\text{PDMA}_{20}\text{-PSt}_{148}\text{-TTC-Z})_4$ and $(\text{PDMA}_{20}\text{-PSt}_{148}\text{-PIBOA}_{96}\text{-TTC-Z})_4$.

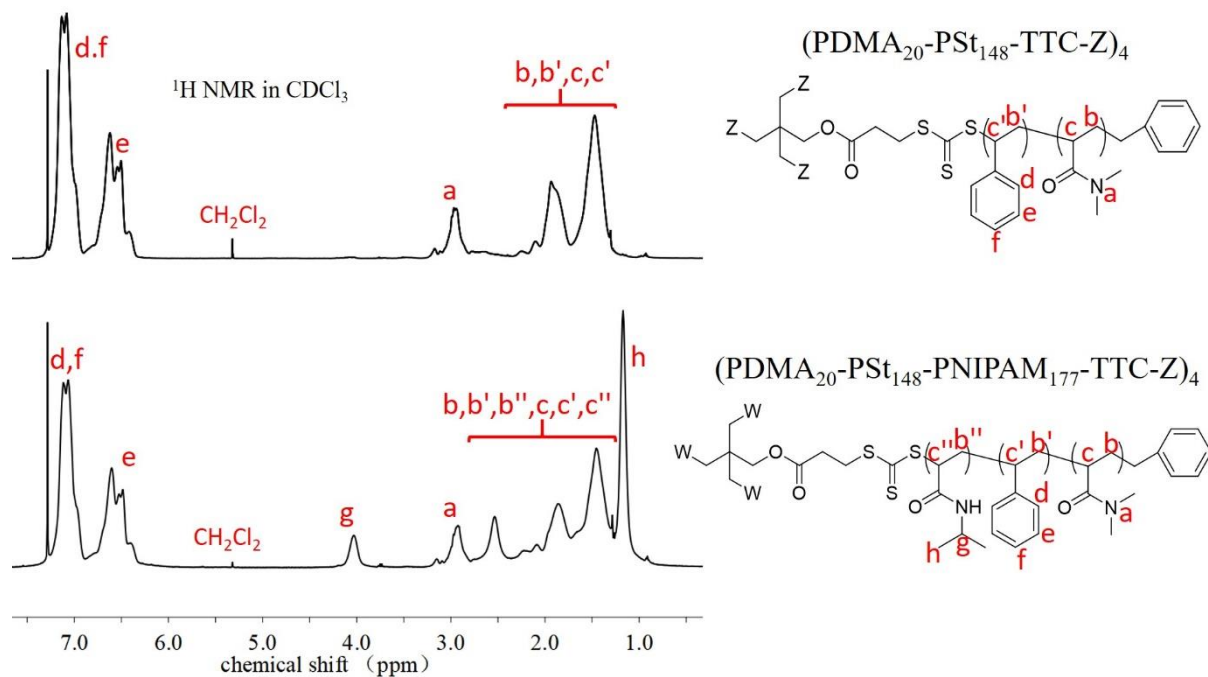


Figure S6. ^1H NMR spectra of $(\text{PDMA}_{20}\text{-PSt}_{148}\text{-TTC-Z})_4$ and $(\text{PDMA}_{20}\text{-PSt}_{148}\text{-PNIPAM}_{177}\text{-TTC-Z})_4$.

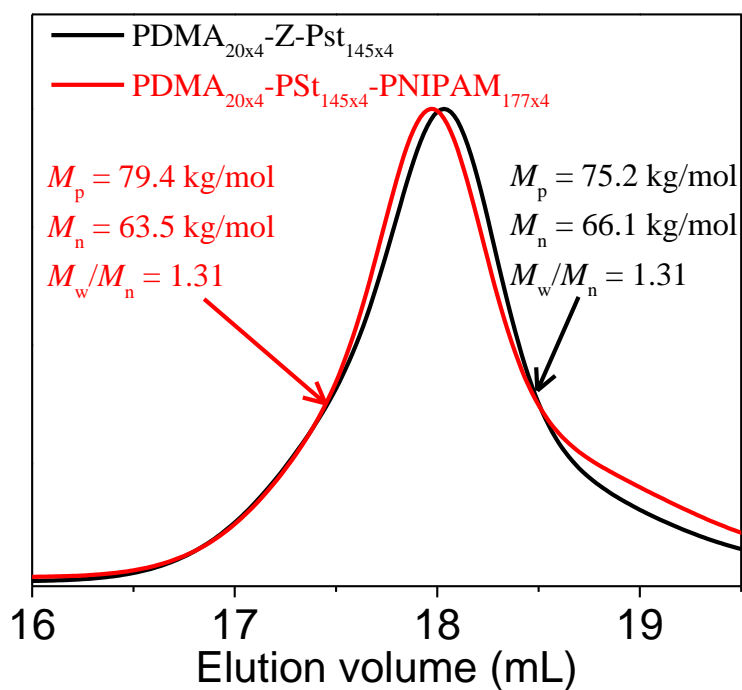


Figure S7. GPC traces of $(\text{PDMA}_{20}\text{-PSt}_{148}\text{-TTC-Z})_4$ and $(\text{PDMA}_{20}\text{-PSt}_{148}\text{-PNIPAM}_{177}\text{-TTC-Z})_4$.

Table S1. GPC data of macro-RAFT agents used in the present study.

Macro-RAFT agent	M_n (kg/mol) ^a	M_w/M_n ^a
(TTC-PDMA ₂₀ -R) ₄	7.4	1.03
(PDMA ₂₀ -TTC-Z) ₄	7.2	1.05
(PDMA ₁₃ -TTC-Z) ₄	5.2	1.07
(PDMA ₂₇ -TTC-Z) ₄	8.2	1.06
PDMA ₂₁ -TTC-Z	2.5	1.09
(PDMA ₂₂ -TTC-Z) ₂	4.7	1.07
(PDMA ₂₁ -TTC-Z) ₃	6.5	1.04

^a Based on the GPC measurement against polystyrene standards.

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