Supporting Information

Cross-linking Polymerization-induced Self-assembly to Branched

Core Cross-linked Star Block Polymer Micelles

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Materials and Methods

Materials. Unless noted otherwise, the chemicals were used as purchased. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) and acetonitrile (MeCN) were purchased from Sigma-Aldrich (St. Louis, MO, USA). d,1-Lactide was kindly provided by Corbion Purac (Amsterdam, Netherlands) and stored in a glovebox after recrystallization from toluene. Benzoic acid was purchased from Daejung chemicals (Siheung, Korea). Styrene (S, 99%) and divinylbenzene (DVB) (technical grade, 80%) were filtered through basic alumina prior to use. HPLC grade toluene was purchased from Burdick & Jackson (Morristown, NJ, USA) and purified using a solvent purification system (C&T International, Suwon, Korea). Azobisiobutyronitrile (AIBN, 98%) was purchased from Junsei (Tokyo, Japan) and purified by recrystallization in methanol. 1,2-Bis(2-maleimidoethoxy)ethane (BMI) was synthesized following a literature procedure.¹

S-Dodecyl-S'-(R,R'-dimethyl-R"-acetic acid) trithiocarbonate (CTA) ² and 2hydroxylethyl 2-(((dodecylthio)carbonothioyl)-thio)-2-methylpropanoate) (CTA-OH)³ were prepared by following literature procedure. Polylactide macro-chain transfer agent (PLA-CTA) was synthesized by ring opening transesterification polymerization (ROTEP) using CTA-OH as initiator and DBU as catalyst.³ The PLA-CTAs were denoted as PLA-CTA-xx where xx represents the number averaged molar mass of the PLA-CTA (kg mol⁻¹) that was determined by end group analysis using ¹H nuclear magnetic resonance (NMR) spectroscopy. The molar mass distribution of PLA-CTA was determined by size exclusion chromatography (SEC) using chloroform as elution solvent. PLA-CTA-19.6 (19.6 kg mol⁻¹, D = 1.11) and PLA-CTA-19.8 (19.8 kg mol⁻¹, D = 1.07) were used in this study (Figure S1).

Methods. ¹H nuclear magnetic resonance (NMR) signal was obtained using a Bruker Advance 400 MHz spectrometer (Bilerica, MA, USA) using the residual NMR solvent signal as an internal reference. Size exclusion chromatography (SEC) was performed in chloroform at 40 °C with a flow rate of 1 mL min⁻¹ on an Agilent 1260 infinity system (Santa Clara, CA, 2 USA). The instrument is equipped with an Optilab T-rEX refractive index detector purchased from Wyatt technology and three PLgel 10 µm Mixed-B columns in series with a molar mass range 500 - 10,000,000 g mol⁻¹ (corresponding to 50 nm - 10 μ m in pore size). The molar masses and dispersities (D) of the polymers were calculated relative to linear polystyrene standards (Easivial) purchased from Agilent Technologies. Dynamic light scattering (DLS) measurements were performed on a Brookhaven 90Plus/BI-MAS particle size analyzer (Holtsville, NY) at wavelength of 658 nm with scattering angle of 90°. Samples were prepared at a concentration of 2 mg mL⁻¹ and Filtered through 0.2 mm PTFE syringe filters prior to the measurements. Scanning electron microscope (SEM) images were obtained on a Hitachi S-4900 FE-SEM (Schaumburg, IL, USA) with a 5 kV accelerating voltage and an upper secondary electron detector. Samples were treated with 0.5 M NaOH solution in water/methanol mixture (6/4) at 70 °C to degrade PLA and also remove the residual monomers and solvent, and then coated with Os prior to imaging. Transmission electron microscopy (TEM) was performed on a Jeol JEM-2100F field-emission transmission electron microscope (Tokyo, Japan) with acceleration voltage of 200 kV. Samples were prepared on 300 mesh carbon-coated copper grids by dropping solution (2 mg mL⁻¹).

Polymerization. Polymerization of DVB(0.2) is given as an example. A polymerization mixture containing S (1.7941 g, 17.2261 mmol), DVB (0.5543 g, 4.2576 mmol), PLA-CTA ($M_{n, NMR} = 19.6 \text{ kg mol}^{-1}$, 1.0007 g, 0.0511 mmol), AIBN (0.0008 g, 0.0049 mmol) and MeCN (28.7961 g, 36.64 ml) was prepared and participated in 9 ampoules. After three cycles of freeze-pump-thaw, the ampoule was flame-sealed under vacuum and then immersed in an oil bath preset to 70 °C. After stirring for certain reaction time, the ampoule was cooled to RT and then opened to stop the polymerization. A portion of the sample was taken from the polymerization mixture for the ¹H NMR (conversion) and DLS (hydrodynamic size) analyses. The rest was

precipitated in methanol to recover the polymer product by filtration. The resulting polymer was collected and dried under vacuum at 40 °C overnight prior to ¹H NMR and SEC analyses.

The identical protocol was used for the polymerization of DVB(0), DVB(0.5), and BMI(0.2) with different amounts of the cross-linker.



Figure S1. (A) Chemical structure and representative ¹H NMR spectra of PLA-CTA (400 MHz, CDCl₃, 20 °C). (B) SEC traces of PLA-CTAs used in this study (1 mL min⁻¹, chloroform, 40 °C).



Figure S2. Representative of SEM images as a function of MeCN wt%, which were obtained after basic treatment and followed by OsO4 coating.



Figure S3. ¹H NMR spectra of the polymerization mixtures after the designated time (400 MHz, CDCl₃, 20 °C). (A) DVB(0). (B) DVB(0.2). (C) DVB(0.5). (D) BMI(0.2).



Figure S4. SEC traces of DVB(0.2) obtained after 192 h after filtering through 0.2 and 0.45 μ m syringe filters.



Figure S5. Conversion of styrene and the cross-linker as a function of reaction time. (A) DVB(0). (B) DVB(0.2). (C) DVB(0.5). (D) BMI(0.2).



Figure S6. First-order kinetic plots. (A) DVB(0). (B) DVB(0.2). (C) DVB(0.5). (D) BMI(0.2).



Figure S7. ¹H NMR spectra of the synthesized polymers obtained by precipitation in methanol (400 MHz, CDCl₃, 20 °C). (A) DVB(0). (B) DVB(0.2). (C) DVB(0.5). (D) BMI(0.2).



Figure S8. DLS correlation curve of the polymerization mixtures. The samples were prepared by diluting the copolymerization mixture in MeCN. (A) DVB(0). (B) DVB(0.2). (C) DVB(0.5).(D) BMI(0.2).



Figure S9. Hydrodynamic diameter (D_h) estimated from the DLS correlation curves shown in Figure S8. (A) DVB(0). (B) DVB(0.2). (C) DVB(0.5). (D) BMI(0.2).



Figure S10. (A, C, E) DLS correlation curve of the synthesized polymers in toluene. The samples were prepared by dissolving the purified polymer in toluene. (A) DVB(0.2). (C) DVB(0.5). (E) BMI(0.2). (B, D, F) D_h estimated from the DLS correlation curves (blue). The D_h values from MeCN (orange) are shown as a reference. (B) DVB(0.2). (D) DVB(0.5). (F) BMI(0.2).



Figure S11. D_h of DVB(0.2) in MeCN (as-synthesized and re-dissolved) and toluene (redissolved) as a function of polymerization time.



Figure S12. TEM images of DVB(0) obtained after different reaction time intervals. B is identical to Figure 5D in the manuscript.



Figure S13. TEM images of DVB(0.2) obtained after different reaction time intervals. A, B, and D are identical to Figures 5A, 5B and 5C in the manuscript, respectively.



Figure S14. TEM images of DVB(0.5) obtained after different reaction time intervals. D is identical to Figure 5E in the manuscript.



Figure S15. TEM images of BMI(0.2) obtained after different reaction time intervals. D is identical to Figure 5F in the manuscript.



Figure S16. TEM images of DVB(0.2) from toluene solution. The samples were prepared by dissolving the purified polymer in toluene.



Figure S17. Representative TEM images of re-dissolved DVB(0.2) after 48 and 192 h, which were prepared from the solutions by dissolving the purified polymer in MeCN.

References

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