Supporting Information

Rational Entry to Cyclic Polymers via Thermally Induced Radical Ring-Expansion Polymerization of Macrocycles with one Bis(hindered amino)disulfide Linkage

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General information

^{1}H spectra were recorded on a Bruker AVANCE III HD500 spectrometer. The LED method for DOSY measurement was used. Pulse program: ledbpgp2s, Diffusion time: 40 ms, Diffusion gradient length: 2000 μs, Maximum gradient strength: 51 g/cm.[1] Analytical size exclusion chromatography (SEC) measurements were carried out at 40 °C on TOSOH HLC-8320 SEC system equipped with a guard column (TOSOH TSK guard column Super H-L), three columns (TOSOH TSK gel SuperH 6000, 4000, and 2500), a differential refractive index detector, and a UV-vis detector. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.6 mL/min. Polystyrene (PS) standards (M_n = 4430–3142000; M_w/M_n = 1.03–1.08) were used to calibrate the SEC system. For some of polymers, absolute molecular weights were measured via multi-angle laser light scattering size exclusion chromatography (SEC-MALS) in THF at 20 °C and a flowrate of 0.6 mL/min on JASCO ChromNAV Lite system equipped a guard column (TOSOH TSK guard column Super H-L), three columns (TOSOH TSK gel SuperH 6000, 4000, and 2500), a differential refractive index detector, and a UV-vis detector. MALS detection consisted of a Wyatt DOWN EOS LASER PHOTOMETER operating at 658 nm and refractive index increment dn/dc of each samples were measured by OTSUKA ELECTRONICS DRM-3000 at 20 °C. Absolute molecular weights were calculated using the Wyatt ASTRA software. MALDI-TOF MS spectra were determined on a Shimadzu AXIMA-CFR mass spectrometer. The spectrometer was equipped with a nitrogen laser (λ = 337 nm) and with pulsed ion extraction. Electrospray ionization mass spectrometry (ESI-TOF-MS) measurements were carried out on Bruker micrOTOF II. DSC was carried out using a Shimadzu DSC-60A DSC at a heating rate of 10 °C min^{-1} under N_2 flow.

Spectral data of macrocyclic monomers (MCMs)

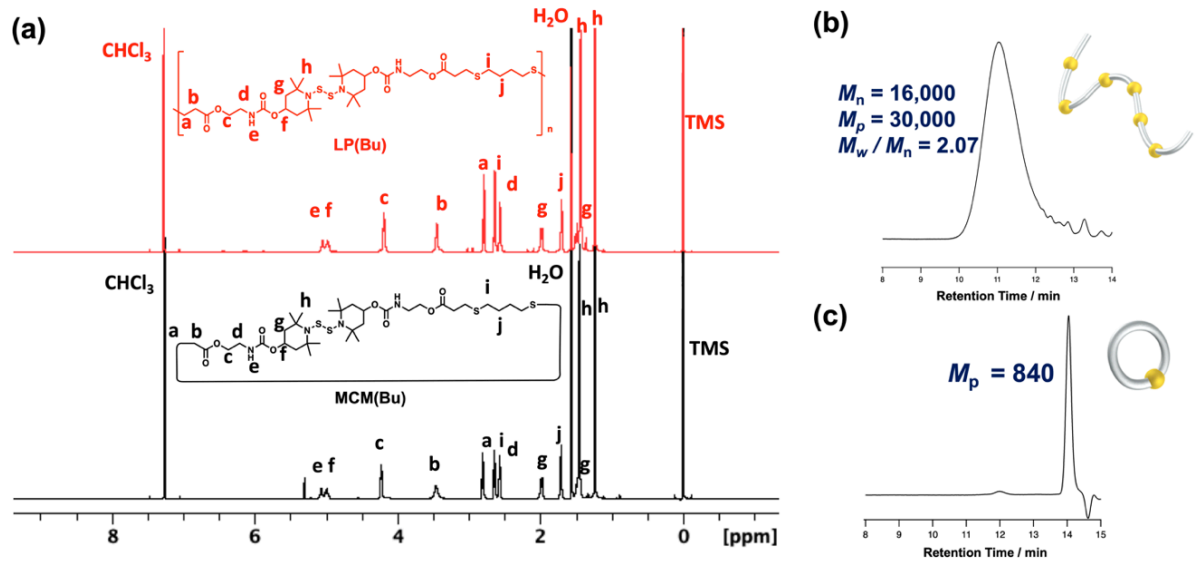


Figure S1. (a) ^{1}H NMR spectrum of **MCM(Bu)** (500 MHz, 25 °C, $CDCl_3$). **(b)** SEC chart of **LP(Bu)** and **(c)** SEC chart of **MCM(Bu)** (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by RI).

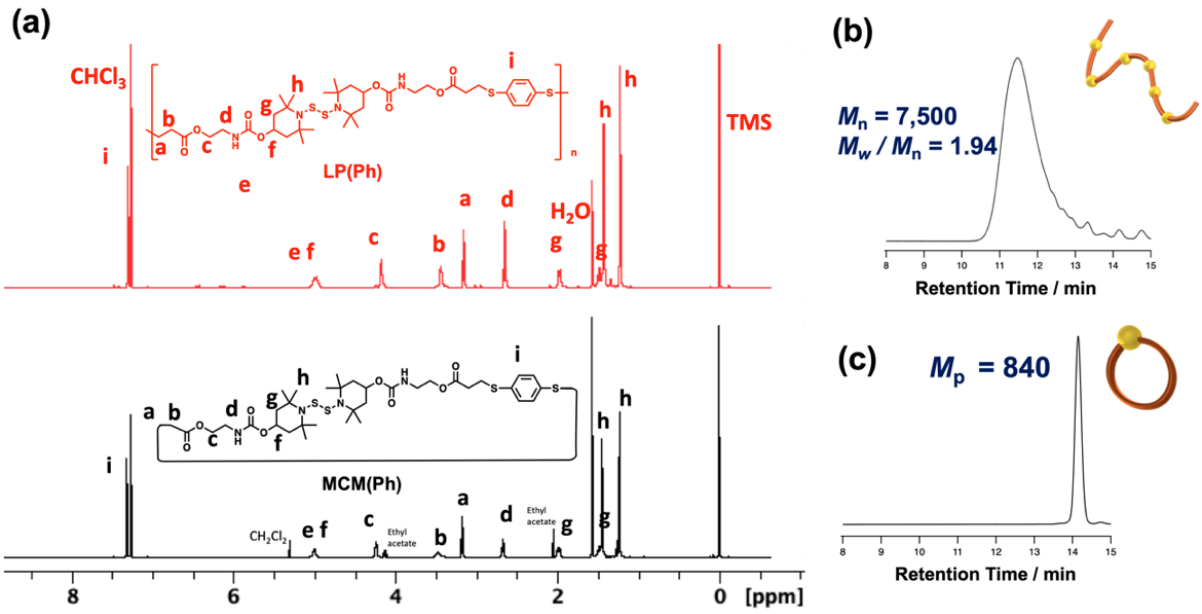


Figure S2. (a) ^{1}H NMR spectrum of **MCM(Ph)** (500 MHz, 25 °C, $CDCl_3$). **(b)** SEC chart of **LP(Ph)** and **(c)** SEC chart of **MCM(Ph)** (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by RI).

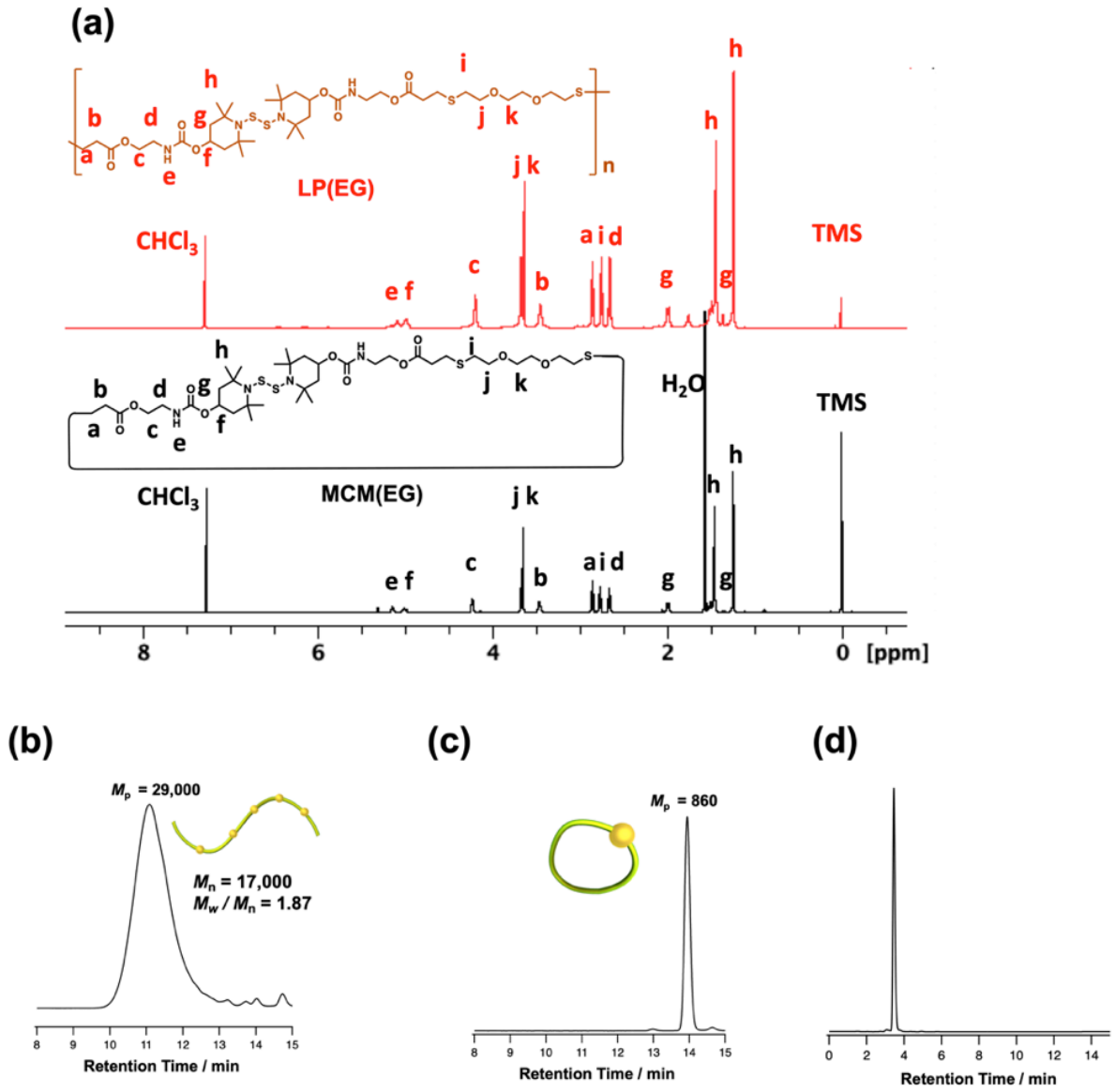


Figure S3. (a) ^{1}H NMR spectrum of **MCM(EG)** (500 MHz, 25 °C, $CDCl_3$). **(b)** SEC chart of **LP(EG)** and **(c)** SEC chart of **MCM(EG)** (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by RI). **(d)** HPLC profile of **MCM(EG)** (eluent, acetonitrile; flow rate, 1.0 mL/min, monitored by UV).

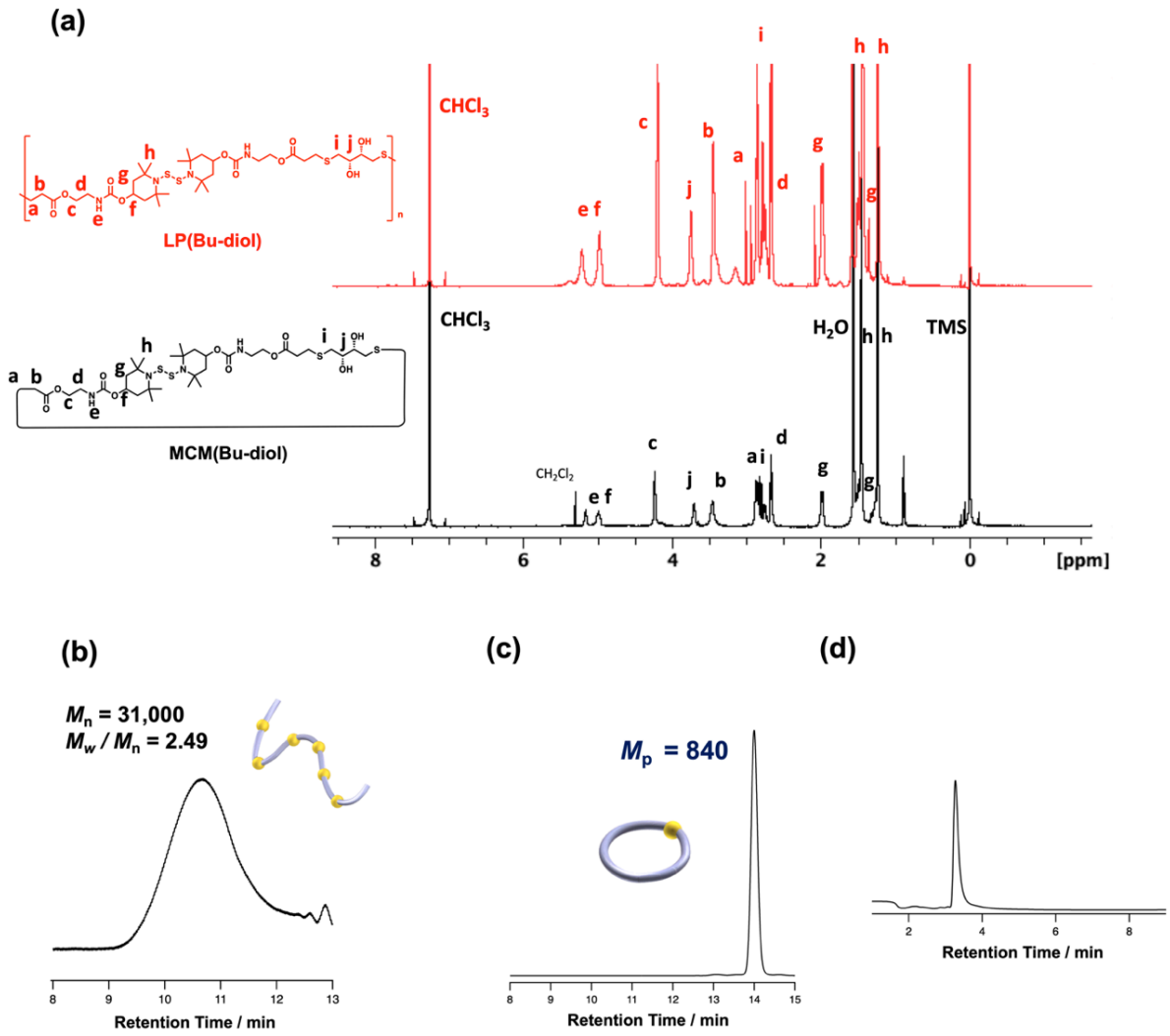


Figure S4. (a) ^{1}H NMR spectrum of **MCM(Bu-diol)** (500 MHz, 25 °C, $CDCl_3$). **(b)** SEC chart of **LP(Bu-diol)** and **(c)** SEC chart of **MCM(Bu-diol)** (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by RI). **(d)** HPLC profile of **MCM(Bu-diol)** (eluent, acetonitrile; flow rate, 1.0 mL/min, monitored by UV).

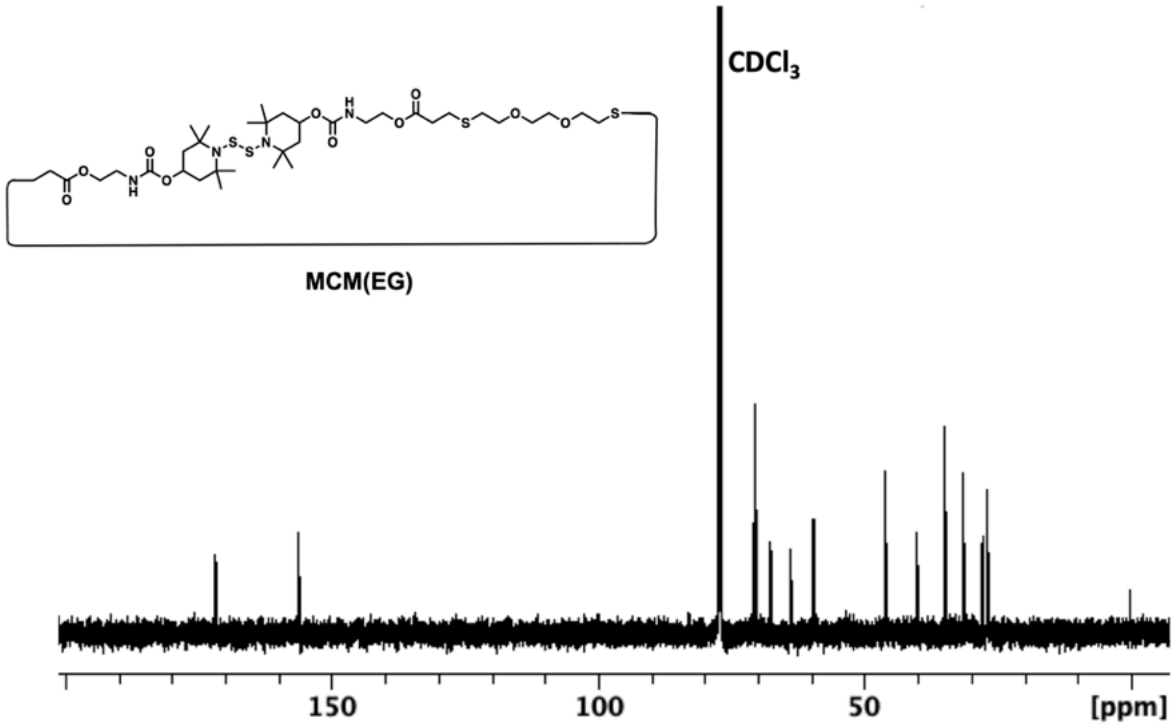


Figure S5. ^{13}C NMR spectrum of **MCM(EG)** (125 MHz, 25 °C, $CDCl_3$).

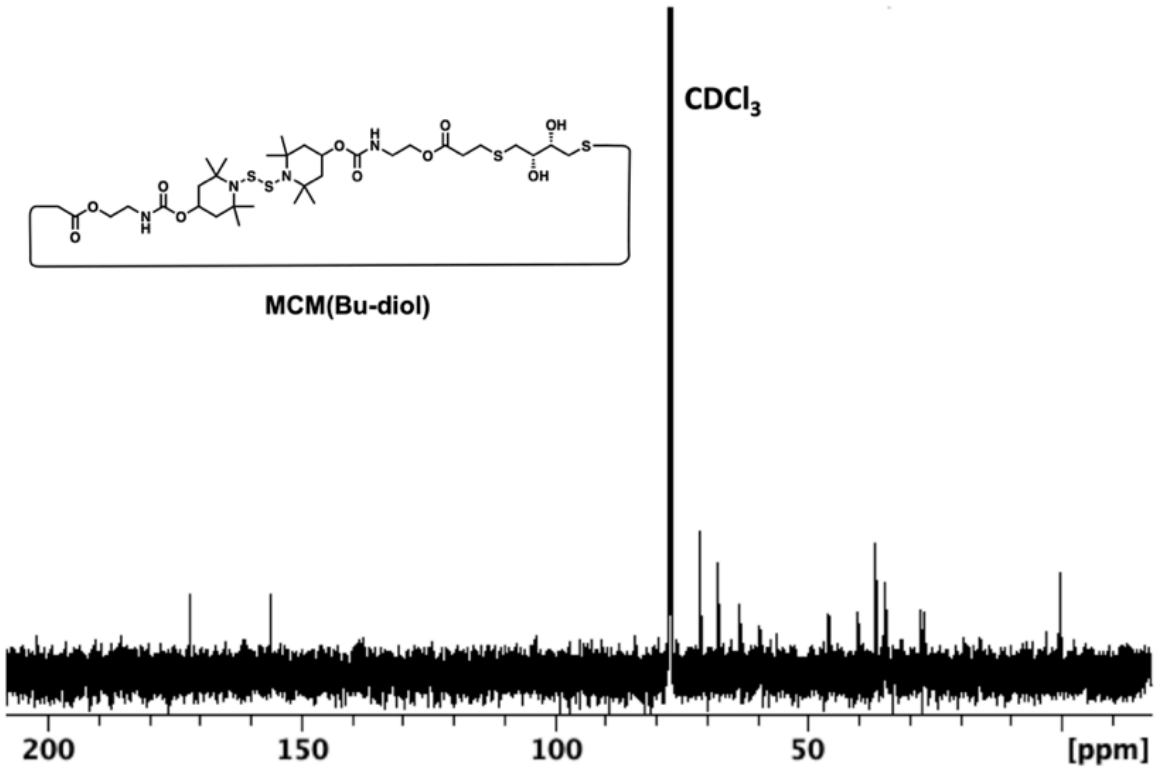


Figure S6. ^{13}C NMR spectrum of **MCM(Bu-diol)** (125 MHz, 25 °C, $CDCl_3$).

Spectral data of CP(Bu)

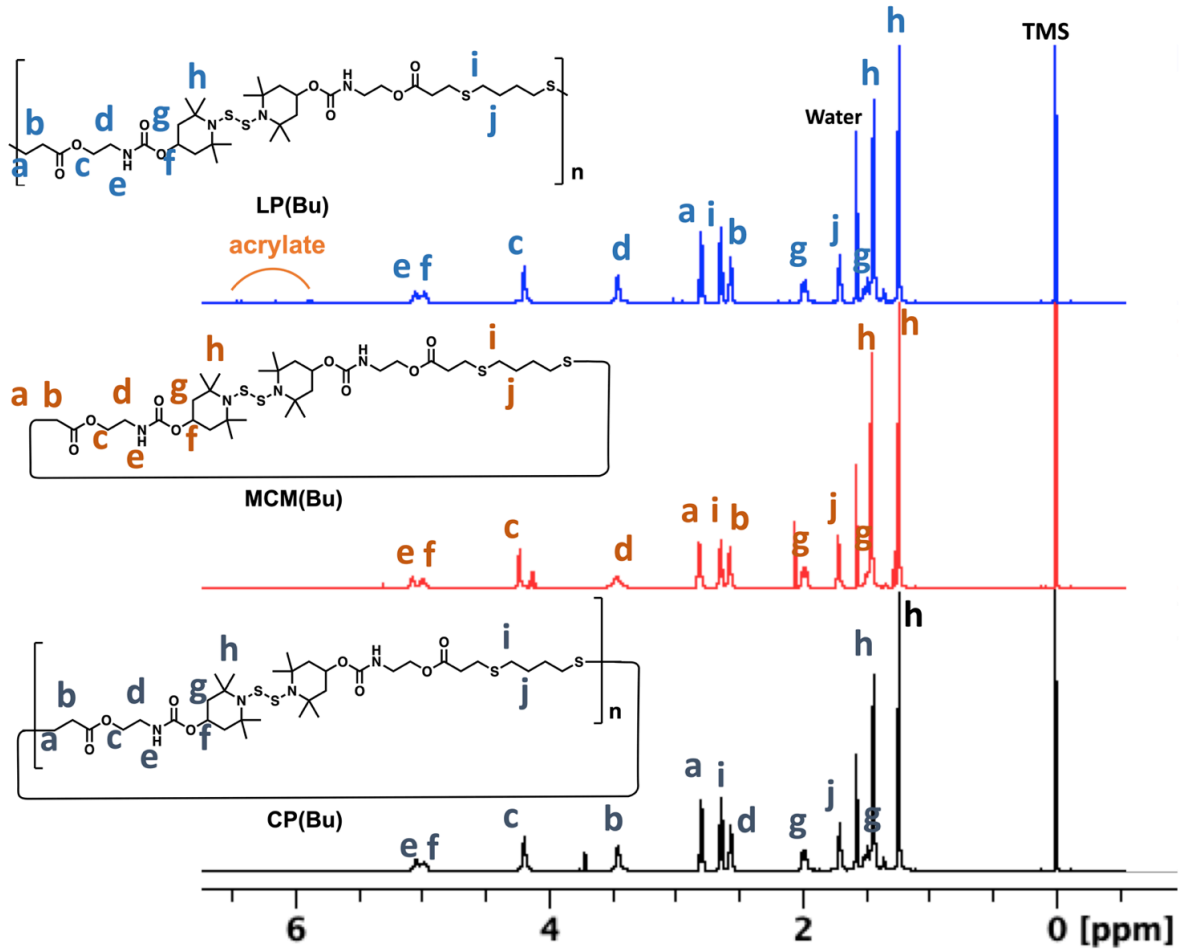
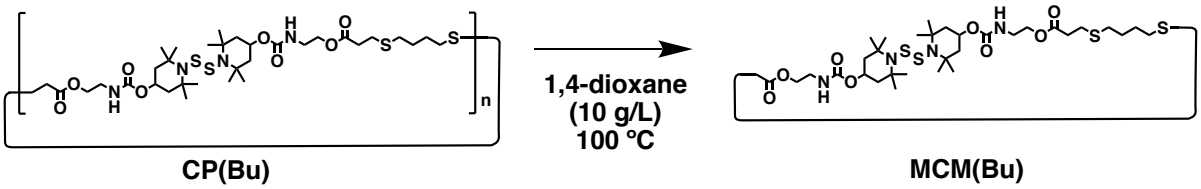


Figure S7. (a) ^{1}H NMR spectra of **CP(Bu)** [blue; **LP(Bu)**, red; **MCM(Bu)**, black; **CP(Bu)**] (500 MHz, 25 °C, $CDCl_3$).

Depolymerization behavior



CP(Bu) **MCM(Bu)**

(Experiment)

In a 20 mL test tube, 1,4-dioxane (2.0 mL) was added to **CP(Bu)** (20 mg) and stirred at 100 °C for 24 hours.

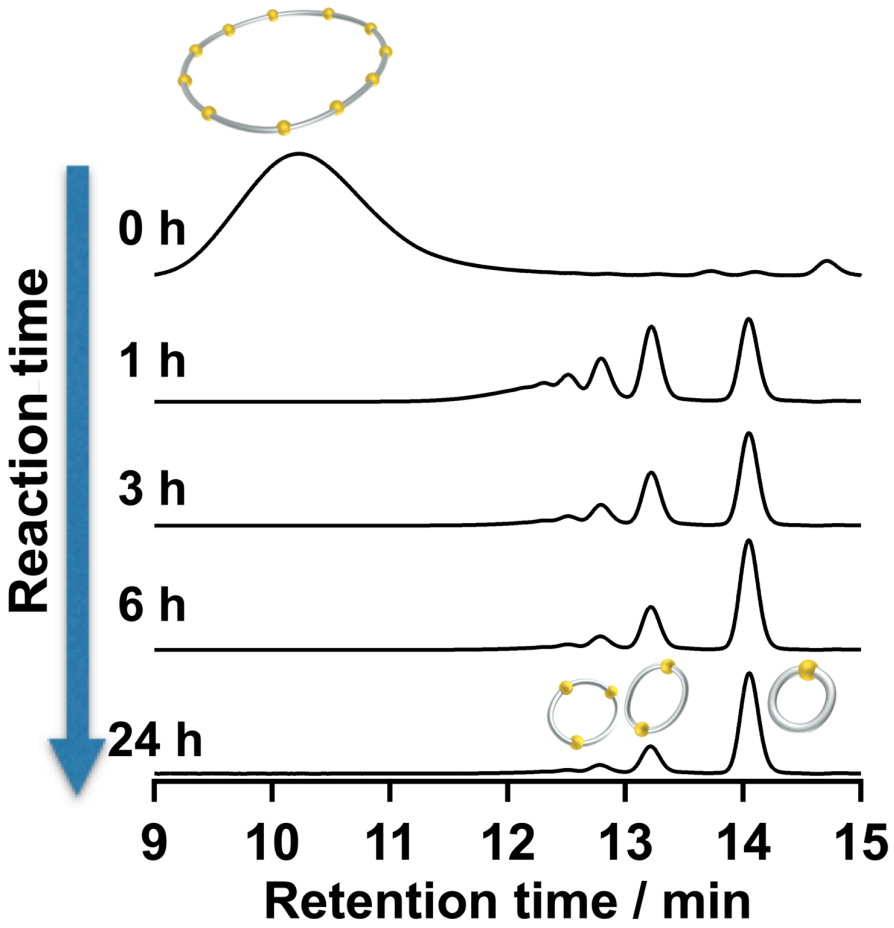


Figure S8. Change in SEC charts in ring-contraction depolymerization of **CP(Bu)** (10 g/L) at 100 °C in dioxane (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by UV).

SEC data of LP(Bu)

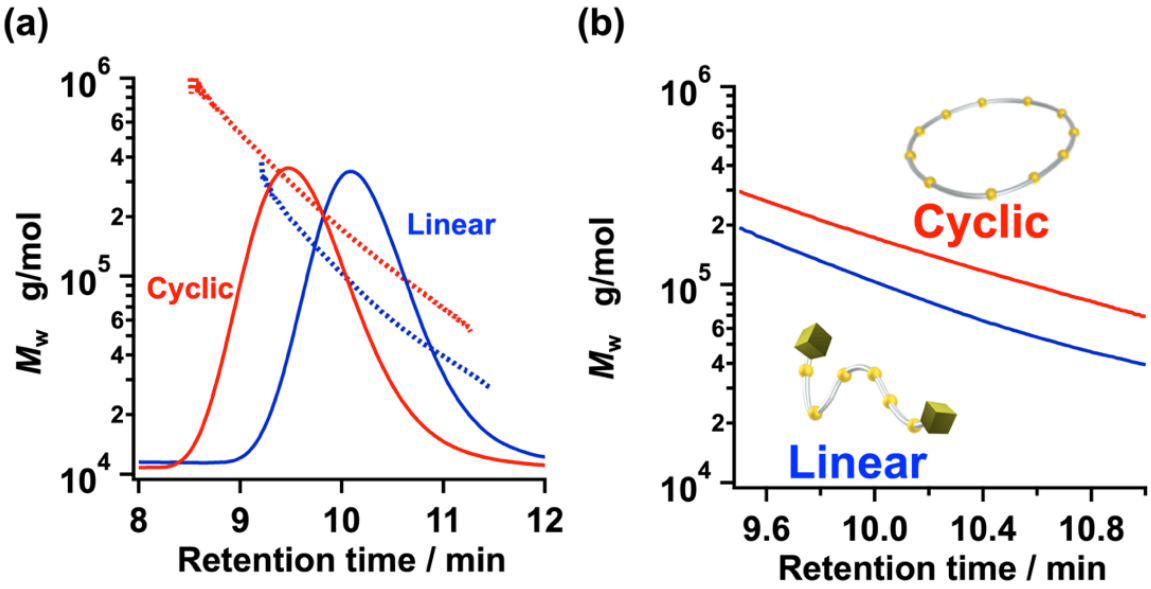


Figure S9. (a) SEC-MALS charts of **CP(Bu)** (Cyclic) and **LP(Bu)-dianthracene** synthesized by ring-opening polymerization (Linear) (eluent, THF; flow rate, 0.6 mL/min, detected by RI). **(b)** Plot of logarithm of absolute molecular weight versus retention time. [red; **CP(Bu)**, blue; **LP(Bu)-dianthracene**].

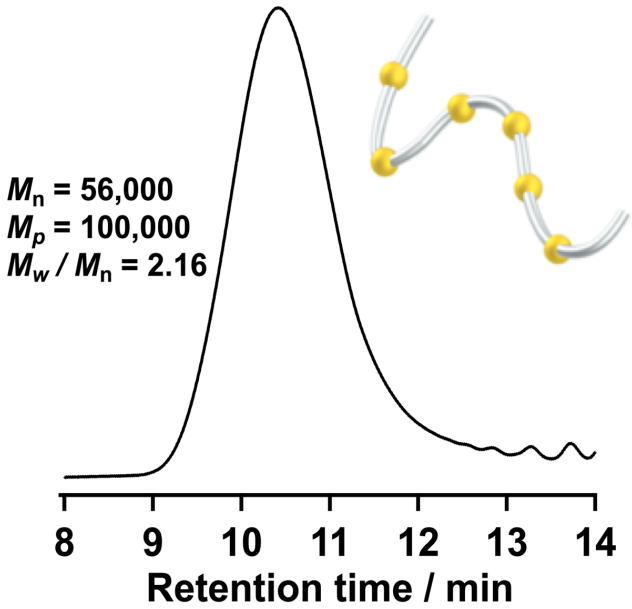
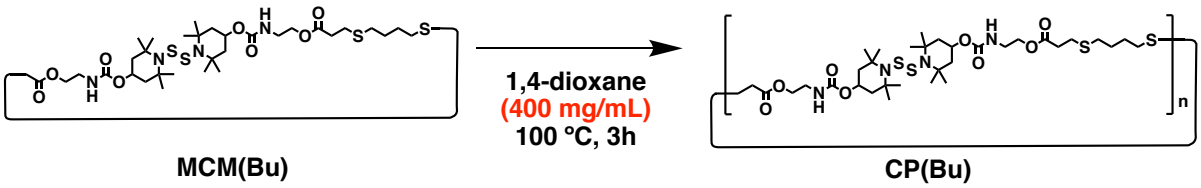


Figure S10. SEC charts of **LP(Bu)** synthesized by polyaddition for DSC analysis (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by RI).

DSC data of small size CP(Bu).



The synthesis of cyclic polymers was carried out in 1,4-dioxane (400 g/L) at 100 °C. In a 20 mL test tube, 1,4-dioxane (250 μL) was added to **MCM(Bu)** (100 mg) and stirred at 100 °C for 3 h. Then, the mixture was poured into hexane/ethanol (30 mL, 8/2, v/v). The obtained precipitate was separated by filtration and dried under reduced pressure to obtain **CP(Bu)** as a white solid.

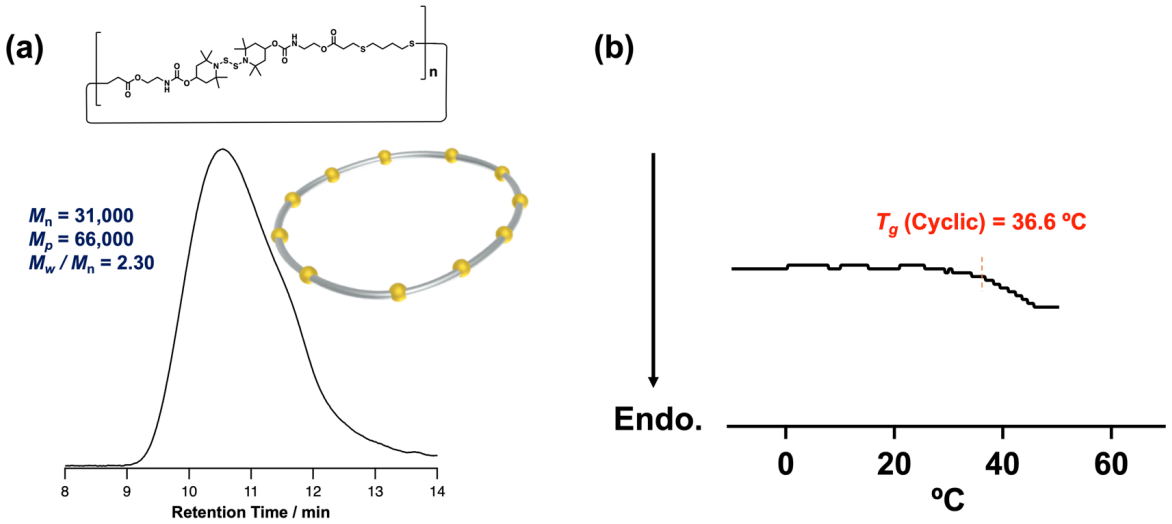
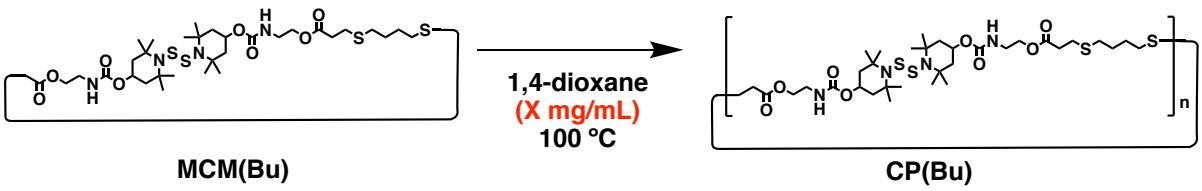


Figure S11. (a) SEC elution curve for small size **CP(Bu)** (polystyrene (PS) standards; eluent: THF; flow rate: 0.6 mL/min; detected by RI). (b) DSC curves for small size **CP(Bu)**.

Polymerization behavior of MCM(Bu).



In a 20 mL test tube, 1,4-dioxane (1 mL) was added to **MCM(Bu)** [(a) 20 mg, (b) 30 mg, (c) 50 mg, (d) 100 mg, (e) 200 mg, and (f) 400 mg] and stirred at 100 °C for 24 hours. (g) 50 mg of **MCM(Bu)** was heated without any solvent.

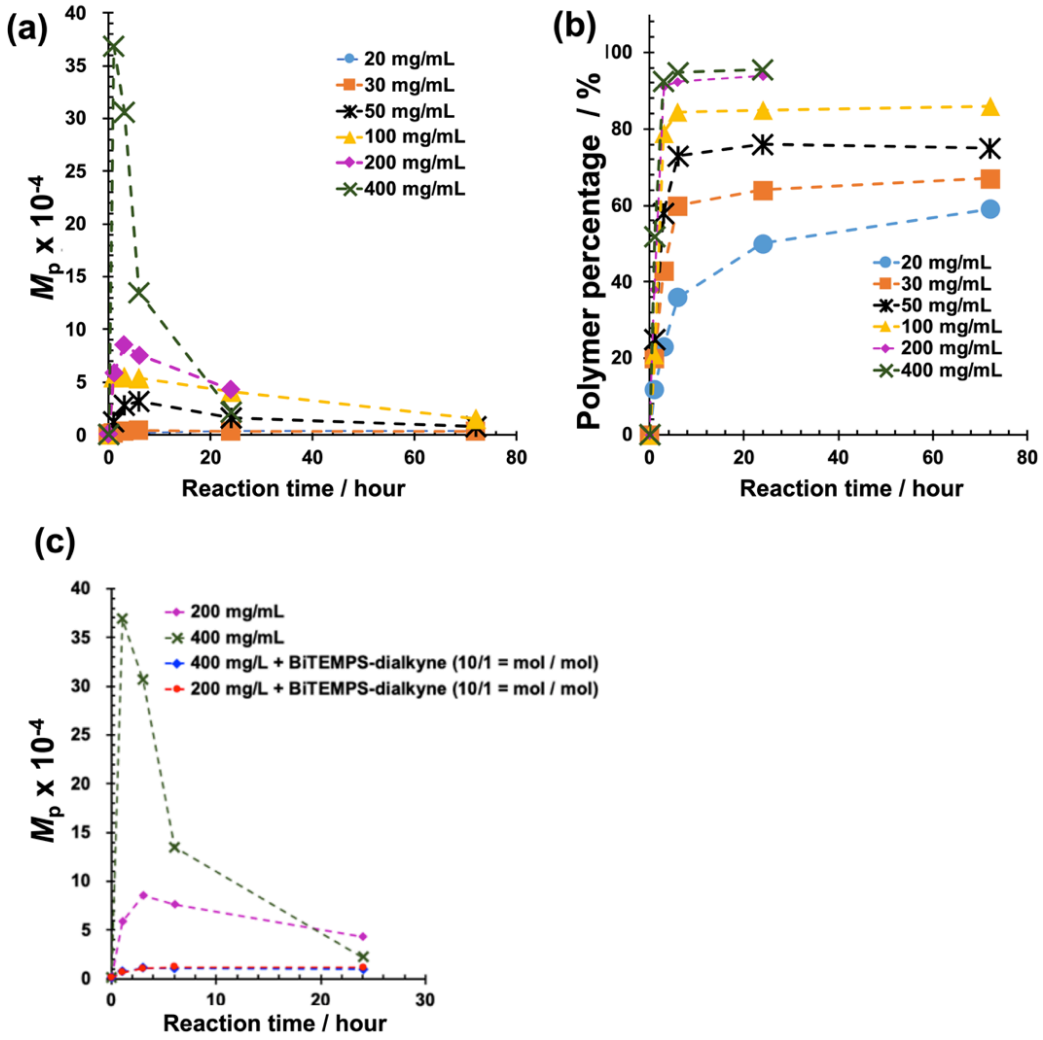


Figure S12. (a) Peak top molecular weight from SEC vs. Time (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by UV). (b) Conversion estimated by SEC vs. time (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by UV). (c) Peak top molecular weight from SEC vs. Reaction Time (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by UV) compared with ring-opening polymerization we previously reported.

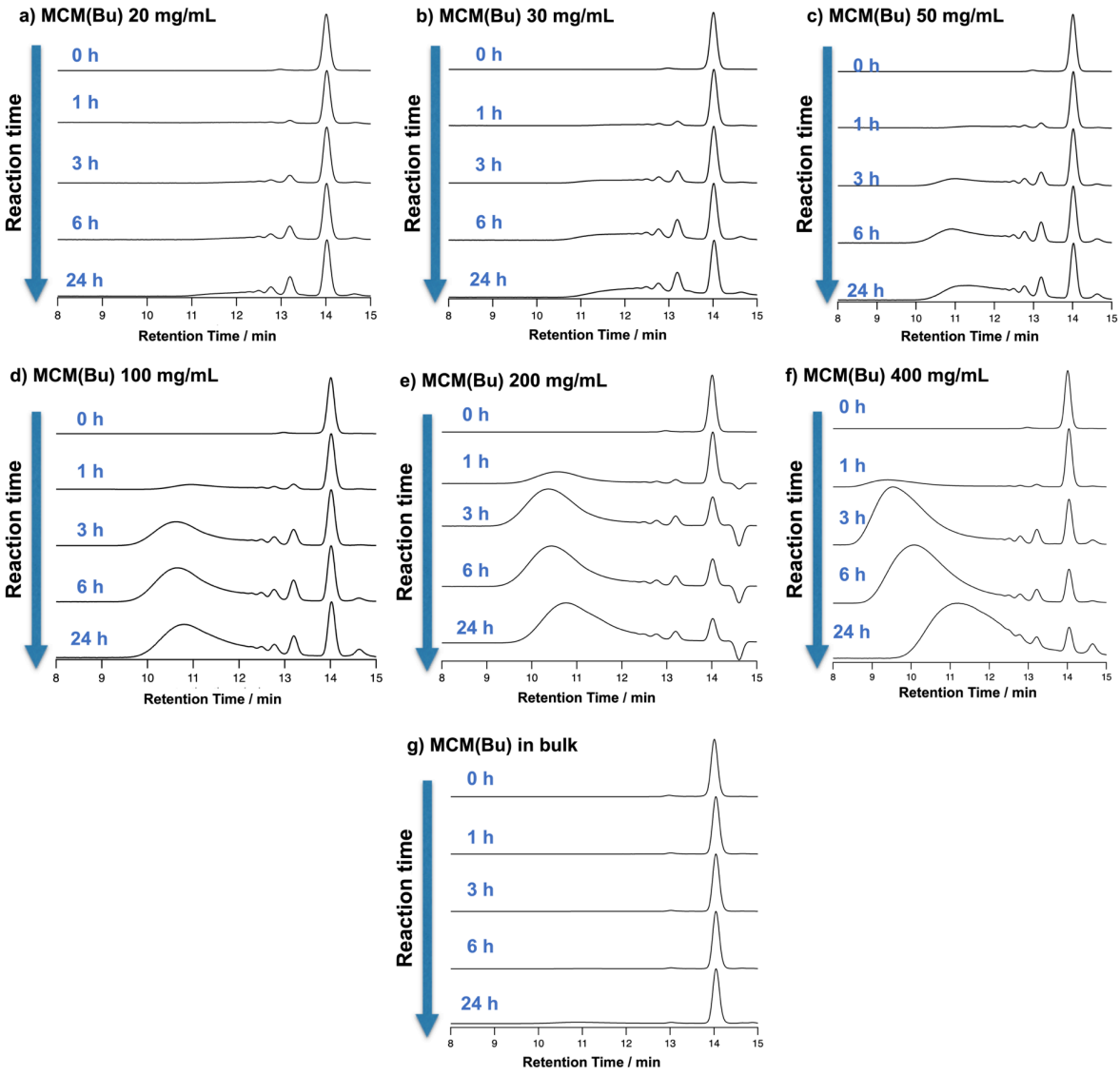


Figure S13. Change in SEC charts in polymerization reaction of **MCM(Bu)** at 100 °C in 1,4-dioxane. **(a)** 20 mg/mL, **(b)** 30 mg/mL, **(c)** 50 mg/mL, **(d)** 100 mg/mL, **(e)** 200 mg/mL, **(f)** 400 mg/mL, and **(g)** bulk (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by UV).

Data of Cyclic oligomers

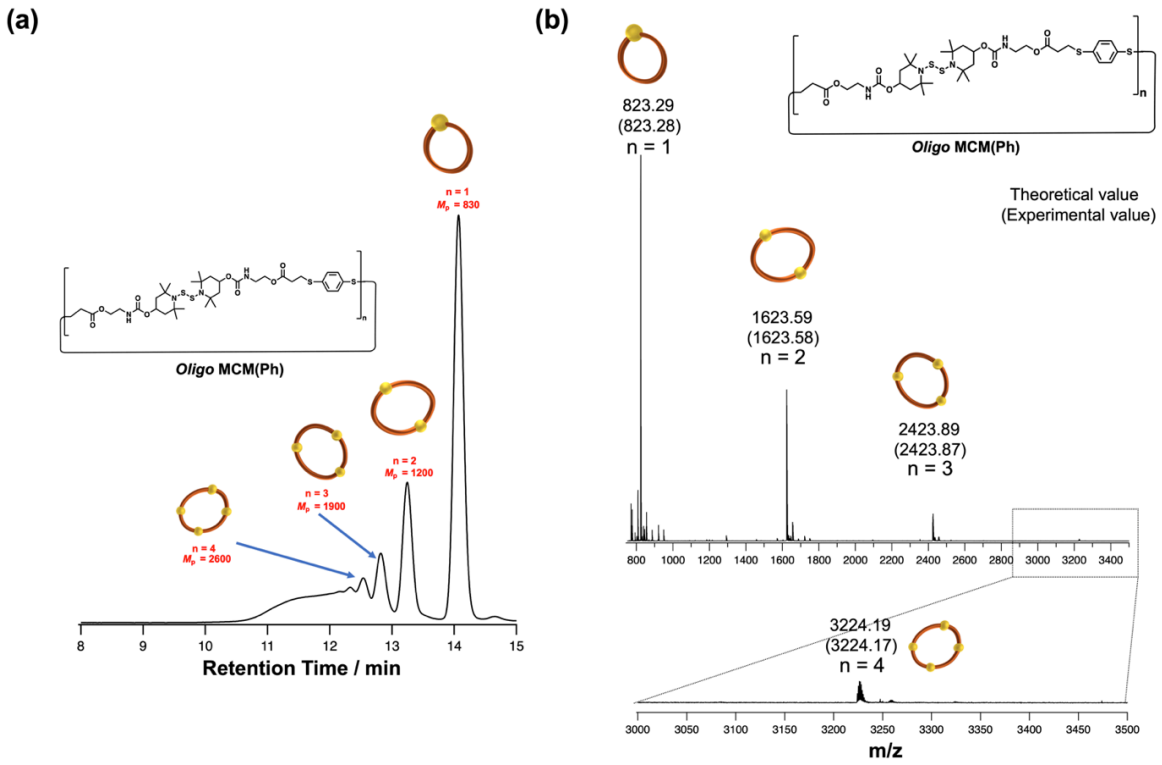


Figure S14. (a) SEC chart of obtained ***Oligo* MCM(Ph)** (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by UV). **(b)** ESI-TOF MS spectrum of obtained ***Oligo* MCM(Ph)** (M_n < 3500, all peaks were detected as $[M+Na]^+$).

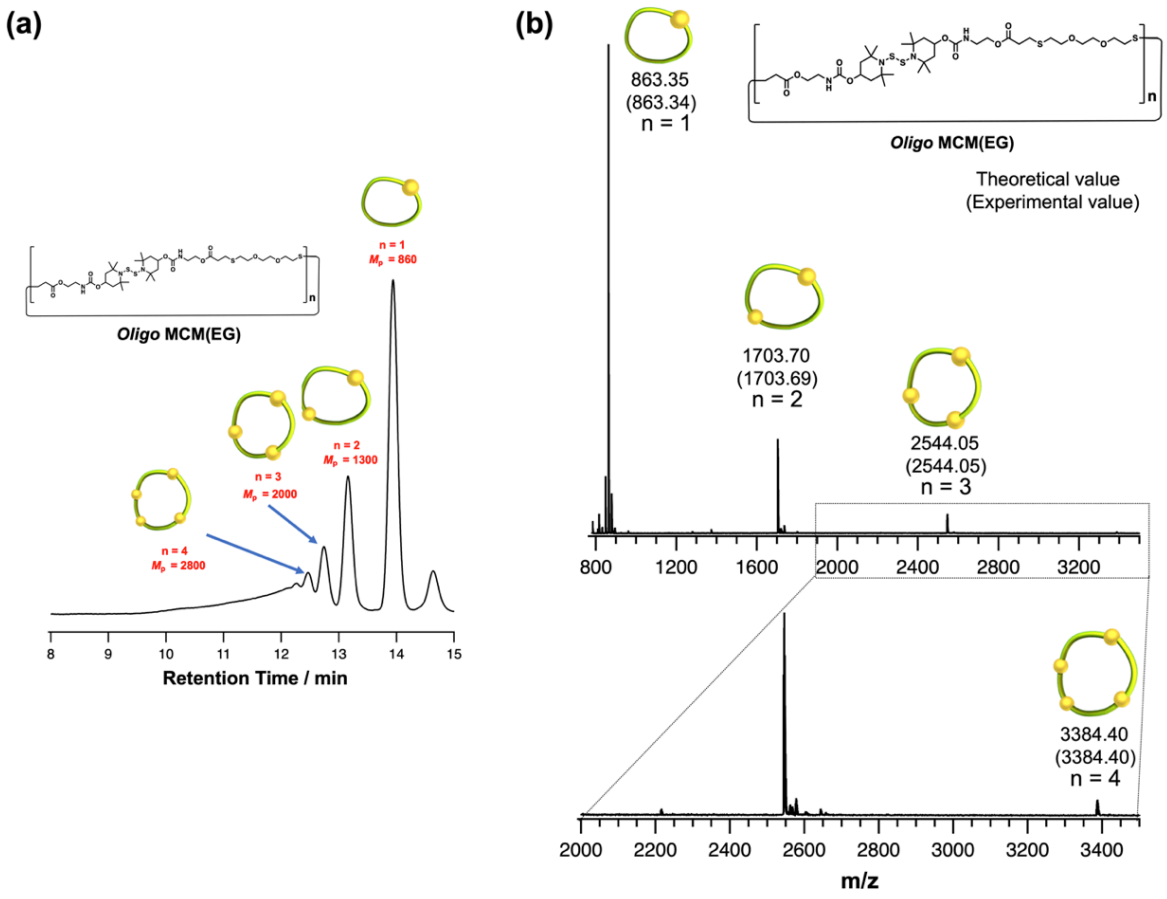


Figure S15. (a) SEC chart of obtained ***Oligo* MCM(EG)** (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by UV). **(b)** ESI-TOF MS spectrum of obtained ***Oligo* MCM(EG)** (M_n < 3500, all peaks were detected as $[M+Na]^+$).

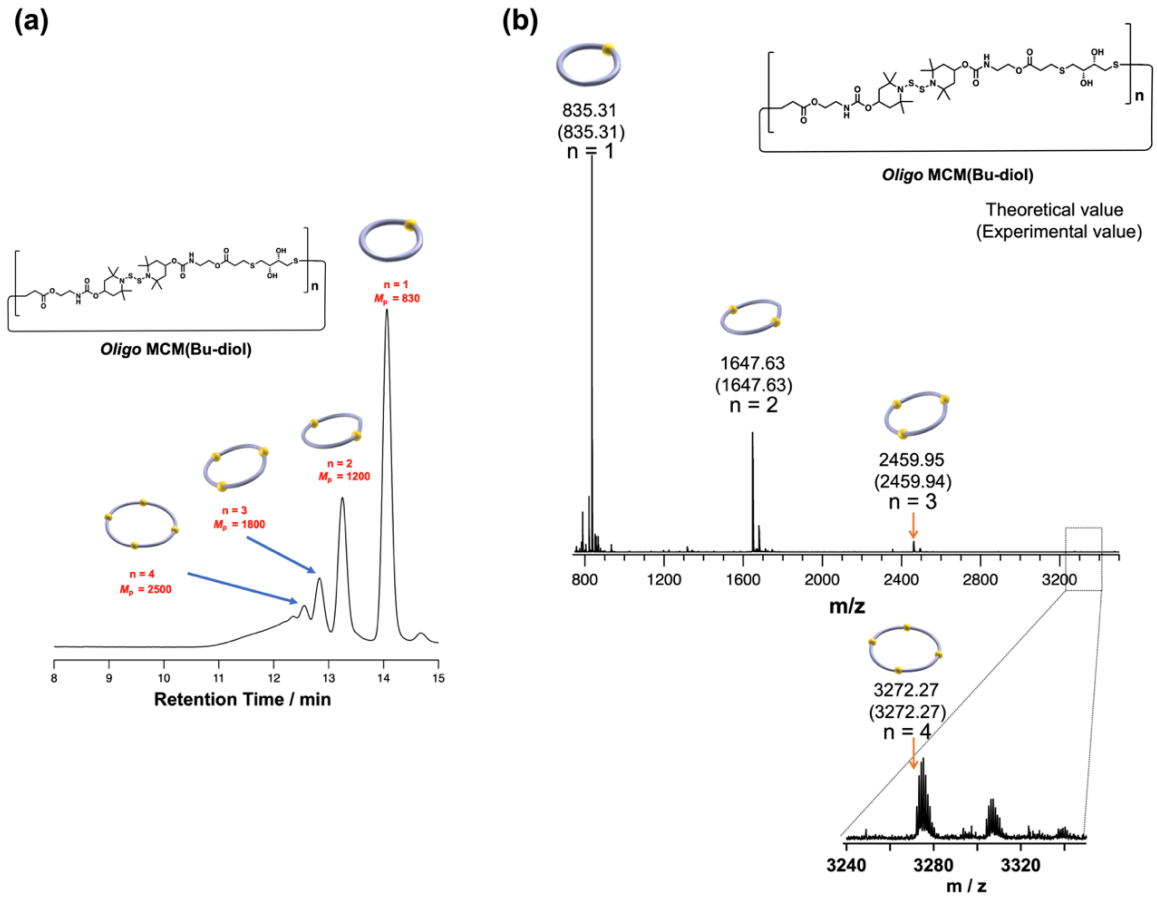


Figure S16. (a) SEC chart of obtained ***Oligo* MCM(Bu-diol)** (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by UV). **(b)** ESI-TOF MS spectrum of obtained ***Oligo* MCM(Bu-diol)** (M_n < 3500, all peaks were detected as $[M+Na]^+$).

Functionalized macro cyclic monomer.

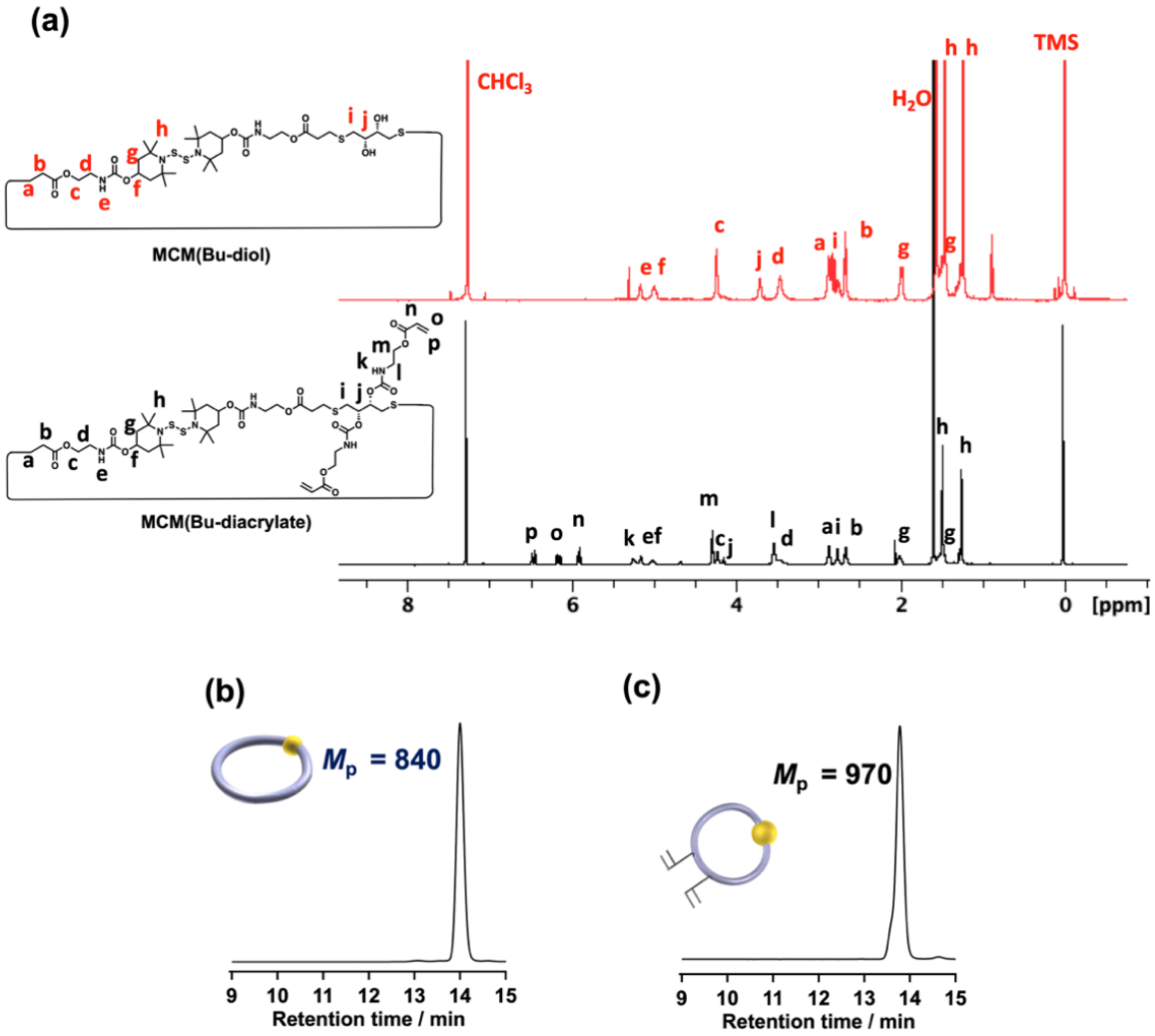


Figure S17. (a) ^{1}H NMR spectrum of **MCM(Bu-diacrylate)** (500 MHz, 25 °C, $CDCl_3$). **(b)** SEC chart of **MCM(Bu-diol)** and **(c)** SEC chart of **MCM(Bu-diacrylate**) (eluent, acetonitrile; flow rate, 1.0 mL/min, monitored by UV).

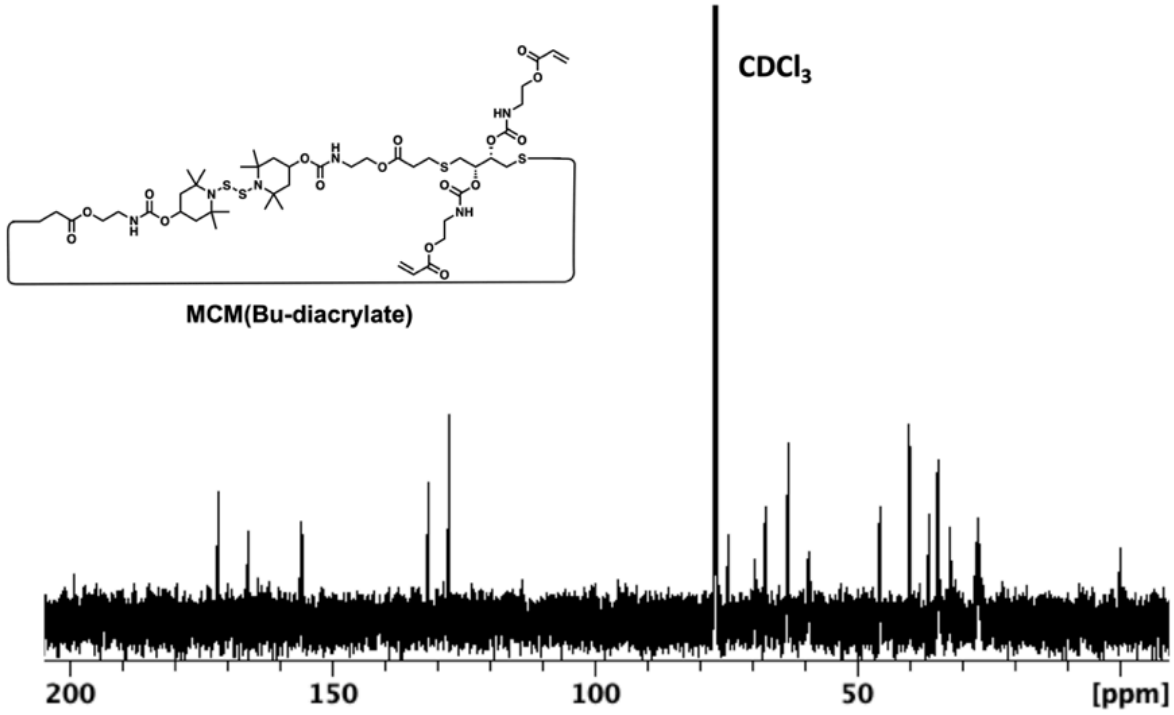


Figure S18. ^{13}C NMR spectrum of **MCM(Bu-dacrylate)** (125 MHz, 25 °C, $CDCl_3$).

Functionalized cyclic oligomer and polymer.

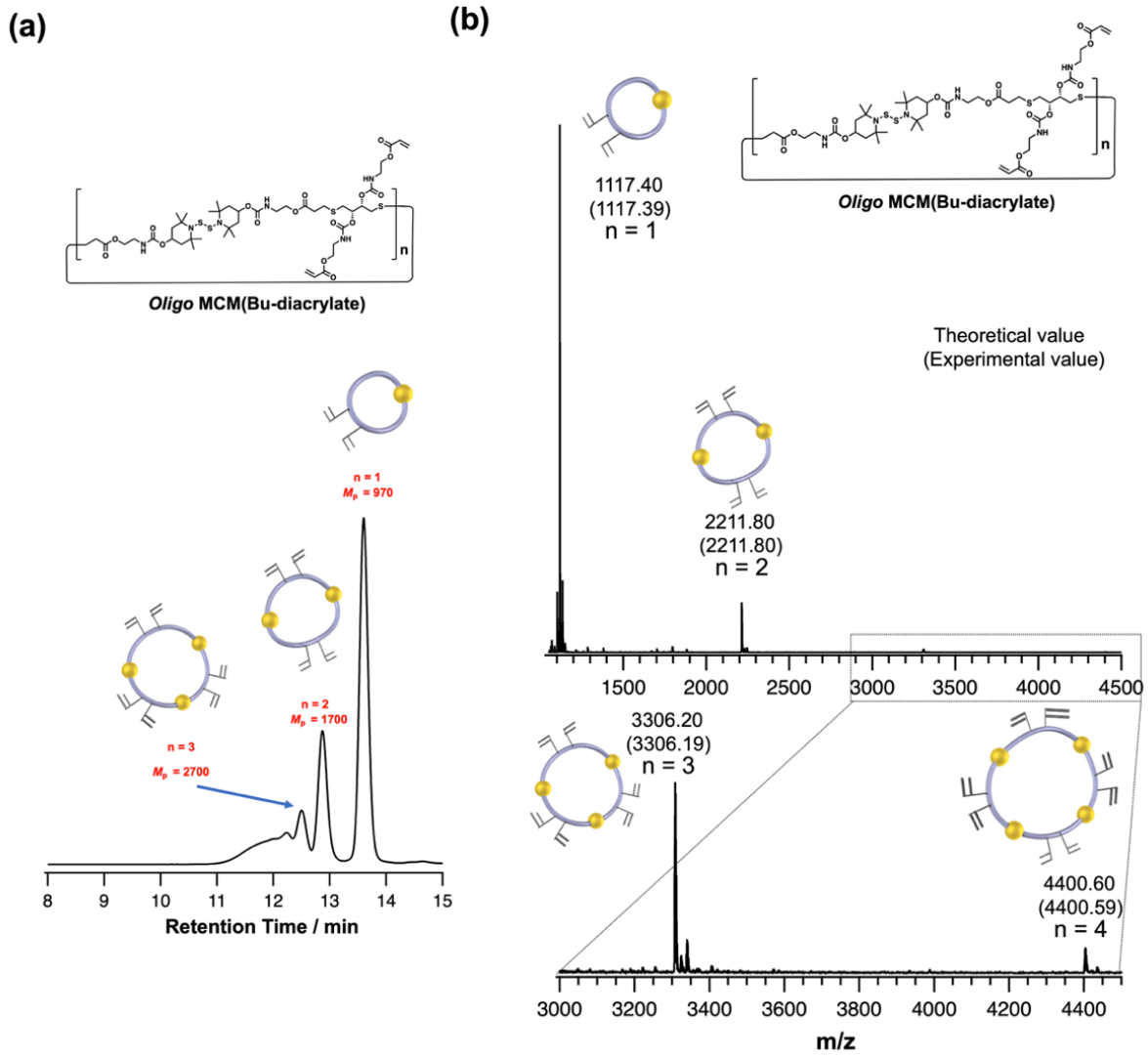


Figure S19. (a) SEC chart of obtained ***Oligo* MCM(Bu-diacrylate)** (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by UV). **(b)** ESI-TOF MS spectrum of obtained ***Oligo* MCM(Bu-diacrylate)** (M_n < 4500, all peaks were detected as $[M+Na]^+$).

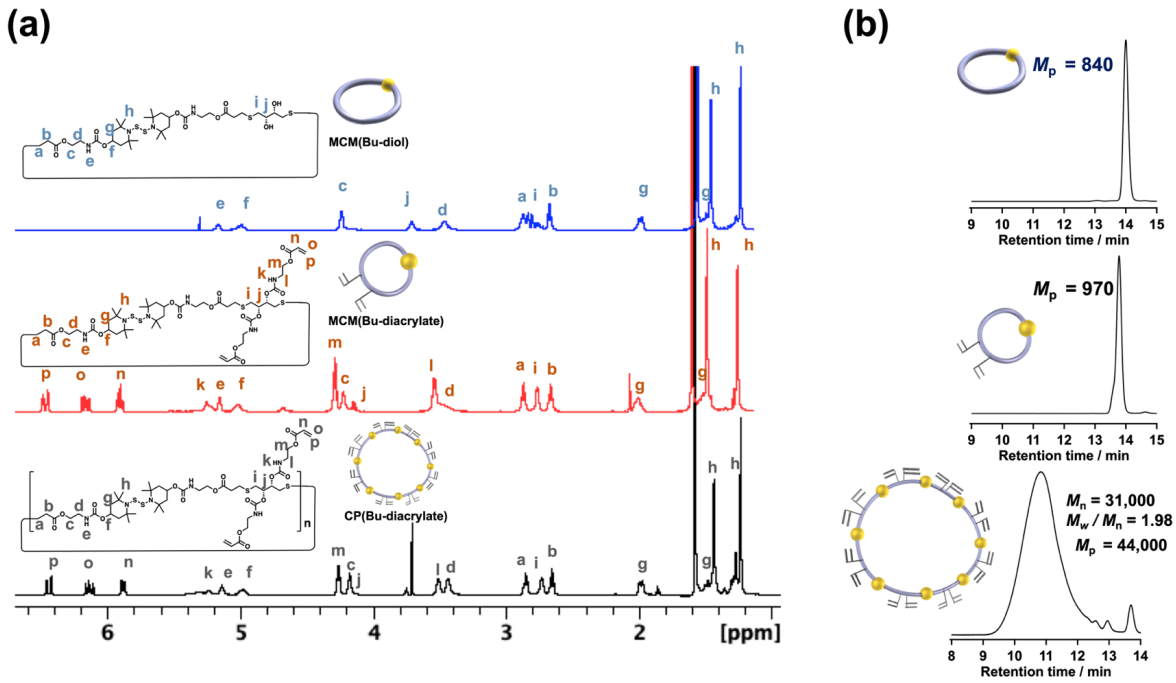


Figure S20. (a) ^{1}H NMR spectrum of **CP(Bu-diacrylate)**, its monomer, and their precursor (500 MHz, 25 °C, $CDCl_3$). **(b)** SEC charts of **CP(Bu-diacrylate)**, its monomer, and their precursor (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by RI).

Cyclic copolymer.

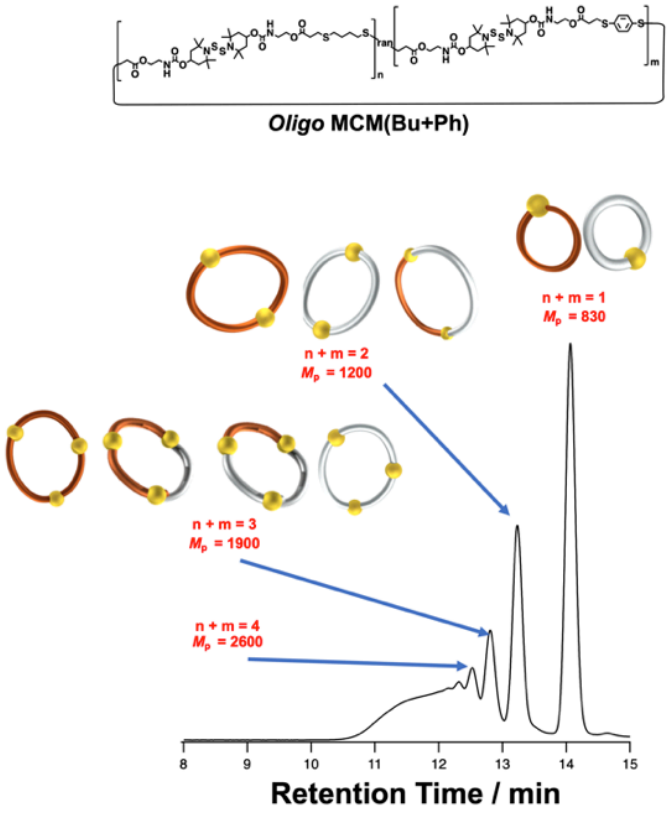


Figure S21. SEC chart of obtained ***Oligo*** **MCM(Bu+Ph)** (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by UV).

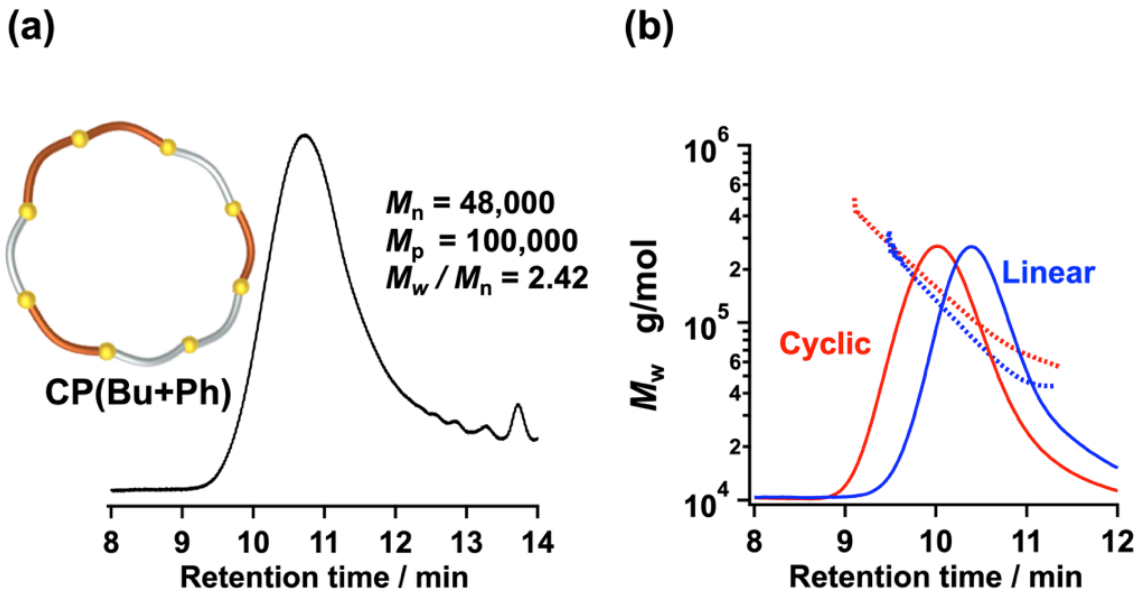
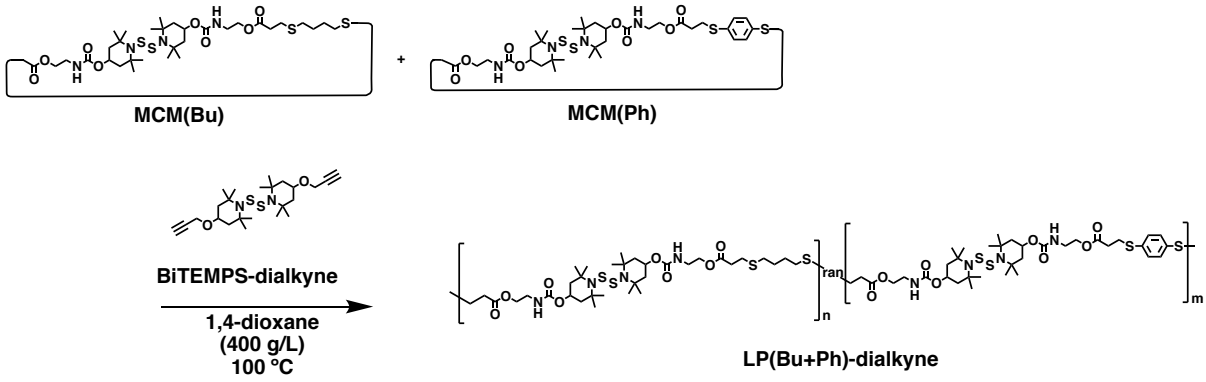


Figure S22. (a) SEC chart of **CP(Bu+Ph)** and **(b)** SEC-MALS charts of **CP(Bu+Ph)** and **LP(Bu+Ph)-dialkyne** synthesized by ring-opening polymerization (PS standard, eluent, THF; flow rate, 0.6 mL/min, detected by RI).



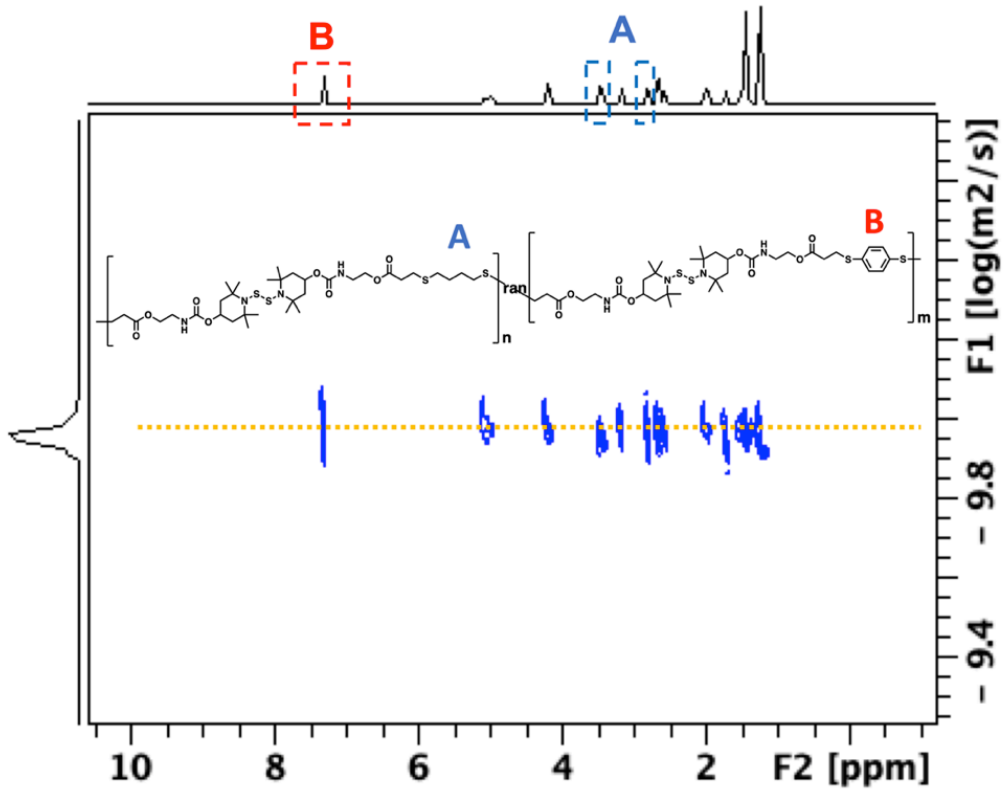


Figure S23. DOSY spectra of **LP(Bu+Ph)-dialkyne** (500 MHz, 25 °C, $CDCl_3$).

SI reference

(1) Wu, D.; Chen, A.; Johnson, C. S. An Improved Diffusion-Ordered Spectroscopy Experiment Incorporating Bipolar-Gradient Pulses. *J. Margn. Reson. A.* **1995**, *115* (2), 260–264.