Electronic supplementary information

Reversible Cyclic-Linear Topological Transformation using a Long-Range Rotaxane Switch

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1. Experimental Materials

Dichloromethane was purchased from ASAHI GLASS CO., LTD., and distilled over CaH₂ under a nitrogen atmosphere after being washed with water. *ɛ*-Caprolactone (99%, Tokyo Kasei Kogyo Co., Ltd. (TCI)) was distilled over CaH₂ under reduced pressure. Diphenyl phosphate (99%, TCI), 3,5-bis(trifluoromethyl)phenyl isocyanate (98%, TCI), acetic anhydride (98%, SIGMA-ALDRICH), paraformaldehyde (95%, MERCK), sodium triacetoxyborohydride (>80%, TCI), triethylamine (99%, FUJIFILM Wako Pure Chemical Corporation), ammonium hexafluorophosphate (95%, FUJIFILM Wako Pure Chemical Corporation), and sodium carbonate (99%, FUJIFILM Wako Pure Chemical Corporation), and sodium carbonate (99%, FUJIFILM Wako Pure Chemical Corporation), and sodium carbonate (99%, FUJIFILM Wako Pure Chemical Corporation), and sodium carbonate solution was used for conversion of linear polymer to cyclic one.

2. Instruments

¹H and ¹³C NMR 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 R_H (nm) was calculated using the Stokes-Einstein equation : $R_H = k_B T/6\pi \eta D_{diff}$ ($k_B = 1.38 \times 10^{-23} m^2 kg s^{-2} K^{-1}$, T=298 k, $\eta = 0.57 \times 10^{-3}$ Pa×s). IR spectra were recorded on a JASCO FT/IR-230 spectrometer. Melting points were measured on a MELTING POINT APPARATUS SMP3 (Stuart Scientific) instrument. FAB and ESI HR-MS spectra were obtained at the Center for Advanced Material Analysis, Tokyo Institute of Technology on request. The size exclusion chromatography (GPC) was performed at 30 °C in CHCl₃ (0.85 mL / min) using a JASCO PU-2080 system equipped with a set of a Shodex K-804 and a Shodex K-805 columns. The number average molecular weight (M_n) , weight average molecular weight (M_w), and polydispersity index (M_w/M_n) of the polymers were calculated on the basis of a polystyrene calibration. MALDI-TOF-MS were taken on a Shimadzu AXIMA-CFR mass spectrometer. The spectrometer was equipped with a nitrogen laser (I = 337 nm) and with pulsed ion extraction. The operation was performed at an accelerating potential of 20 kV by a linear-positive ion mode. The sample polymer solution (1 mg / mL) was prepared in CHCl₃, and the matrix, dithranol, and cationizing agent, sodium trifluoroacetate, were dissolved in CHCl₃ or THF (10 and 1 mg / mL, respectively). The polymer solution and the matrix solution were mixed, and 1 µL portion of the mixed solution was deposited onto a sample target plate and allowed to dry in the air at room temperature. Mass values

were calibrated by the two-point method with insulin β plus H⁺ at 3497.96 and *R*-cyanohydroxycinnamic acid dimer plus H⁺ at 379.35 Da.

3. Synthetic procedure

Synthesis of PCL_S²

PCL_S was synthesized by using previously reported techniques.² DPP (23.2 mg, 92.8 µmol) was added to a solution of initiator **1** (300 mg, 185.6 µmol) in CH₂Cl₂ (1.5 mL) after sonication for 20 sec. ϵ -CL (1.06 g, 9.28 mmol) was then added to the solution to initiate the polymerization at 10 °C. After 6 h, excess 3,5-bis(trifluoromethyl)phenyl isocyanate (474 mg, 1.86 mmol) was added to the solution and stirred for 24 h to introduce bulky end-cap groups at the termini of the polymer. The polymer was isolated by reprecipitation from CH₂Cl₂ into ethanol / hexane = 1/9 (v/v) two times and into hexane once to obtain **PCL_S** (isolated: 828 mg, 84% calculated by DP_{NMR} =28, n = 14) as a white solid. M_n _{NMR} = 5320 Da. Polymerization degree of the PCL was calculated by ¹H NMR using the integrals of signal f and A in Figure 3.

Synthesis of PCL_U

Paraformaldehyde (130 mg, 4.33 mmol), sodium triacetoxyborohydride (458 mg, 2.16 mmol) and triethylamine (438 mg, 4.33 mmol) were added to a solution of **PCL_S** (500 mg, 94.0 µmol) dissolved in 4 mL of NMP and the mixture was allowed to stir at 70°C for 2 d. The mixture was then filtered to remove excess paraformaldehyde, and the polymer was isolated from NMP by reprecipitation in water. The precipitate was dissolved in CHCl₃ and dried over magnesium sulfate and then washed with sodium carbonate three times, dried over sodium sulfate, evaporated in vacuo to give **PCL_U** (289 mg, 57.1 µmol, 61%) as a white solid. DP _{NMR} = 28, n = 14, $M_{n NMR}$ = 5060 Da. Polymerization degree of the PCL was calculated by ¹H NMR using the integrals of signal f and A in Figure 3.

Conversion of *N*-methylated PCL_U to linear polymer PCL_T

Cyclic polymer **PCL_U** (200 mg, 39.5 μ mol) and ammonium hexafluorophosphate (128.9 mg, 0.791 mmol) were dissolved in THF (4 mL) and the solution was bubbled with argon for 5 h at room temperature. After 5 h, THF was removed under reduced pressure and the obtained solid mixture was dissolved in CHCl₃. The mixture was then filtered to remove excess salt and

was concentrated to obtain PCL_T (206 mg, 38.5 μ mol, 97%) as a white solid. The same procedure was applied to acid-base cycle tests.

Conversion of linear polymer PCL_T to PCL_U₂

PCL_T(137 mg, 25.6 μmol) was dissolved in CHCl₃, washed with saturated sodium carbonate aq. three times, dried over sodium sulfate, and evaporated in vacuo to give **PCL_U₂** (135 mg, 25.6 μmol, qunat.) as a white solid. The same procedure was applied to acid-base cycle tests. The subscript number in **PCL_U₂** denotes the number of neutralization/acidification processes.



4. Cyclic/linear Topology Transformation

Figure S1. DOSY NMR spectrum of PCL_U (500 MHz, 25 °C, CDCl₃).



Figure S3. DOSY NMR spectrum of PCL_U₂ (500 MHz, 25 °C, CDCl₃).



Figure S4. ¹⁹F NMR spectra of PCL_U, PCL_T, and PCL_U₂



Figure S5. GPC charts of **PCL_U**_n via cycle tests (RI, CHCl₃, 30 °C, PSt standard). The subscript number in **PCL_U**_n denotes the number of neutralization/acidification processes.



Figure S6. Hydrodynamic radius in cycle tests of polymer switching calculated by DOSY NMR (500 MHz, CDCl₃, 298 K)



Figure S7.¹⁹F NMR spectra of **PCL_U** and **PCL_U**₅ (471 MHz, CDCl₃, C_6F_6 = -164.9 ppm). The subscript number in **PCL_U**₅ denotes the number of neutralization/acidification processes.



Figure S8. DSC traces in cycle tests of polymer switching (2^{nd} heating, 10 °C). The subscript number in **PCL_T**_n and **PCL_U**_n denotes the number of neutralization/acidification processes.

5. SI references

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