Supplementary information for

Cyclic poly(methyl acrylate) derived from [1]rotaxane terminated linear polymer via topological transformation

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Experimental section

1. General methods

$^1$H (300 MHz) NMR spectra were recorded on a Bruker Biospin AVANCE DPX-300 spectrometer using CDCl$_3$ as the solvent, and tetramethylsilane was used as the internal standard. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. The size exclusion chromatography (SEC) in CHCl$_3$ (0.85 mL/min) was performed using a JASCO HSS-1500 system equipped with consecutive linear polystyrene gel columns (Shodex GPC K-804 and GPC K-805) at 30 °C. The number of average molecular weight ($M_n$), weight average molecular weight ($M_w$), and polydispersity ($M_w/M_n$) of the polymers were calculated on the basis of a polystyrene calibration. MALDI–TOF MS spectra were measured by a Shimadzu AXIMA–CFR mass spectrometer.

Materials

All solvents were distilled or dried before use according to the general purification procedure.[1] Commercially available reagents were used without further purification unless otherwise noted. All reactions were carried out under inert atmosphere of argon. Silica gel column chromatography was performed using silica gel N 60 (grain size 40–50 µm) (Kanto Chemical Co. Inc., Tokyo, Japan). GPC (Gel permeation liquid column chromatography) was performed by LC-9204 system with JAIGEL 1H-40 (Japan Analytical Industry) with CHCl$_3$ eluent.

2. Chemical synthesis

2.1 Synthesis of semi[2]rotaxane 4

Axle 1 and ring 2 were synthesized by using previously reported methods.[1, 2]

Preparation of end-cap agent 3

To a mixture of 3,3-dimethylglutaric anhydride (5.0 g, 0.035 mol), $N$-hydroxysuccinimide (1.2 g, 0.011 mol) and DMAP (0.43 g, 0.0035 mol) in toluene (36 mL) were added propargyl alcohol (2.6 g, 0.046 mol) and triethylamine (1.1 g, 0.011 mol). The suspension was stirred for 1 h at room temperature and then diluted with EtOAc, washed with cold dil. HCl, dried over Na$_2$SO$_4$, and concentrated. The end cap 3 (5.9 g, 0.030 mol) was obtained in 85% yield as a colorless oil.

$^1$H NMR (300 MHz, CDCl$_3$, 298 K) $\delta$ 4.70 (d, $J = 2$ Hz, 2H), 2.52 (s, 2H), 2.51 (s, 2H), 2.49 (t, $J = 2$ Hz, 1H), 1.18 (s, 6H) ppm.

Preparation of semi[2]rotaxane 4

To a solution of sec-ammonium salt 1 (0.50 g, 0.91 mmol), crown ether 2 (0.65 g, 1.2 mmol), and end cap 3 (0.72 g, 3.6 mmol) in CH$_2$Cl$_2$ (3.8 mL) was added PBu$_3$ (0.18 g, 0.91 mmol) and $N,N'$-disopropylcarbodiimide (0.57 g, 4.6 mmol) at room temperature, and the solution was
stirred for 12 h. The reaction mixture was then poured into n-hexane (200 mL), and the precipitate was collected by decantation. The residue was purified by silica gel column chromatography (eluent: CHCl₃ / EtOAc = 1 / 1) and recycling preparative GPC to give semi[2]rotaxane 4 (0.87 g, 75 %) as a yellow foam.

¹H NMR (300 MHz, CDCl₃, 298 K) δ 7.10 (br, 2H), 7.00 (s, 2H), 6.97 - 6.80 (m, 7H), 5.96 - 5.76 (m, 2H), 5.14 - 4.95 (m, 4H), 4.67 (d, J = 2 Hz, 2H), 4.50 - 4.45 (m, 2H), 4.43 (s, 2H), 4.30 - 4.04 (m, 10H), 3.96 - 3.75 (m, 8H), 3.73 - 3.41 (m, 12H), 3.10 (br, 2H), 2.47 (s, 2H), 2.46 (t, J = 2 Hz, 1H), 2.42 (s, 2H), 2.30 (q, 2H, J = 6 Hz), 2.19 - 2.10 (m, 8H), 1.90 (quint., 2H, J = 6 Hz), 1.77 - 1.57 (m, 4H), 1.49 - 0.96 (m, 26H) ppm.

Synthesis of PMA building blocks

**Preparation of PMA 6**

A dry flask, charged with CuBr (0.020 g, 0.14 mmol), methyl 2-bromo-2-methylpropionate (0.11 g, 0.62 mmol), PMDETA (0.025 g, 0.14 mmol) and MA (1.3 g, 15 mmol) was sealed with a rubber septum and cycled three times between vacuum and argon to remove oxygen. The mixture was heated at 80 ºC and reacted for 1h. After heating stopped, the reaction mixture was cooled to room temperature and diluted with THF. The solution was passed through a short alumina column and the solvent was evaporated. The product was purified by reprecipitation into n-hexane, 5 (1.23 g, 55 %) as a sticky solid.

To a solution of 5 (0.74 g, 0.21 mmol) in DMF (5 mL), NaN₃ (0.069 g, 1.1 mmol) was added and stirred at r.t. for 12 h. The reaction mixture was poured into water and extracted with CH₂Cl₂. The polymer was isolated by reprecipitation from CH₂Cl₂ into n-hexane to obtain polymer 6 quantitatively.

**Preparation of PMA 10**

A dry flask, charged with CuBr (0.020 g, 0.14 mmol), 2-hydroxyethyl 2-bromoisobutyrate 7 (0.060 g, 0.62 mmol), PMDETA (0.025 g, 0.14 mmol) and MA (1.3 g, 15 mmol) was sealed with a rubber septum and cycled three times between vacuum and argon to remove oxygen. The mixture was heated at 80 ºC and reacted for 1h. After heating stopped, the reaction mixture was cooled to room temperature and diluted with THF. The solution was passed through a short alumina column and the solvent was evaporated. The product was purified by reprecipitation into n-hexane, 8 (1.21 g, 61 %) as a sticky solid.

The polymer 8 (0.73 g, 0.23 mmol), 3,5-bistrifluoromethylphenylisocyanate (0.087 g, 3.5 mmol) and cat. DBTDL (1 drop) were dissolved in CH₂Cl₂ (5 mL) and reacted 12 h at r.t. The
polymer was isolated by reprecipitation from CH₂Cl₂ in n-hexane to obtain polymer 9 (0.74 g, yielded 92%).

To a solution of 9 (0.74 g, 0.21 mmol) in DMF (5 mL), NaN₃ (0.069 g, 1.1 mmol) was added and stirred at r.t. for 12 h. The reaction mixture was poured into water and extracted with CH₂Cl₂. The polymer was isolated by reprecipitation from CH₂Cl₂ into n-hexane to obtain polymer 10 quantitatively.

2.2 Synthesis of macromolecular semi[2]rotaxane 11

To a solution of rotaxane 4 (0.45 g, 0.35 mmol) and PMA 6 (0.74 g, 0.21 mmol) in CH₂Cl₂ (1.0 mL), [Cu(CH₃CN)₄]PF₆ (0.086 g, 0.23 mmol) was added and evacuated three times and filled with argon. Then the mixture was stirred at r.t. for 48 h. After dilution of the reaction mixture with CH₂Cl₂, it was passed through a short aluminum column and the solvent was evaporated. The crude product was purified by recycling preparative GPC to remove the residual 4 to give 11 (0.82 g) in 78 % yield.

Anion exchange reaction of macromolecular semi[2]rotaxane 11

To a solution of 11 (50 mg, 10 µmol) in THF (2 mL), an excess of tetrabutylammonium chloride (28 mg, 0.10 mmol) was added and reacted at r.t. for 24 h. The solvent was removed by evaporation, and then the residue was dissolved in CH₂Cl₂. The solution was washed with water and dried over MgSO₄, filtered, and concentrated. Purification was performed by preparative GPC, and the high molecular weight region was collected to give 12 (41 mg, 92%).
2.3 Synthesis of macromolecular [1]rotaxane 15

To a solution of semi[2]rotaxane 4 (0.45 g, 0.35 mmol) and PMA 8 (0.74 g, 0.23 mmol) in CH$_2$Cl$_2$ (1.0 mL), [Cu(CH$_3$CN)$_4$]PF$_6$ (0.094 g, 0.25 mmol) was added and evacuated three times and filled with argon. The mixture was stirred at r.t. for 48 h. The solvent was removed by evaporation, and the residue was dissolved into CH$_2$Cl$_2$. The solution was passed through a short aluminum column and the solvent was evaporated. The product was purified by recycling preparative GPC to give macromolecular [2]rotaxane 13 (0.86 g) in 80% yield.

To a solution of macromolecular [2]rotaxane 13 (0.14 g, 0.029 mmol) in CH$_2$Cl$_2$ (40 mL), Grubbs' catalyst 2nd generation (7.3 mg, 0.0086 mmol) was added and degassed by three consecutive freeze pump-thaw cycles, then filled with argon. The solution was heated to reflux and stirred for 15 h. The reaction mixture was cooled to room temperature and the solvent was removed to about half under reduced pressure. The solution was poured into hexane to reprecipitate the polymer, and the formed polymer precipitate was collected by filtration.
Further purification was performed by preparative GPC with CHCl$_3$ as the eluent to obtain macromolecular [1]rotaxane 14 (0.12 g) in 85% yield.

To a solution of 14 (0.10 g, 0.021 mmol), acetic anhydride (0.11 g, 1.1 mmol), and triethylamine (0.21 g, 2.2 mmol) in THF (0.50 mL) was stirred at 40 °C for 20 h. After the solvent was evaporated, the residue was purified by a preparative GPC with CHCl$_3$ as the eluent to obtain N-acetylated macromolecular [1]rotaxane 15 (0.088 g) in 89% yield.

### 2.4 Synthesis of N-acetylated macromolecular [2]rotaxane 16

![Scheme S1](image)

To a solution of macromolecular [2]rotaxane 13 (0.10 g, 0.021 mmol), acetic anhydride (0.11 g, 1.1 mmol), and triethylamine (0.21 g, 2.2 mmol) in THF (0.50 mL) was stirred at 40 °C for 20 h. The solution was purified by a preparative GPC with CHCl$_3$ as the eluent to obtain N-acetylated macromolecular [2]rotaxane 16 (0.094 g) in 92% yield.

### 3. References

4. Spectra of synthesized chemicals

Figure S1. $^1$H NMR spectrum of rotaxane 4 (400 MHz, CDCl$_3$, 298 K)

Figure S2. $^1$H NMR spectra of PMA 5 and PMA 8 (400 MHz, CDCl$_3$, 298 K)
Figure S3. MALDI-TOF mass spectrum of 5

M.W.\textsubscript{calc} \([5 + \text{Na}^+]\)
\[= 182.94 \ \text{(end group)} + 86.04 \times n \ \text{(PMA)} + 22.99 \ \text{(Na})\]

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Figure S4. MALDI-TOF mass spectrum of 8

M.W.\textsubscript{calc} \([8 + \text{Na}^+]\)
\[= 212.95 \ \text{(end group)} + 86.04 \times n \ \text{(PMA)} + 22.99 \ \text{(Na})\]

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3161.1  3247.0  3332.9  3418.8
Figure S5. SEC traces of PMA 5 (a) and PMA 8 (b)
(eluent: CHCl₃, flow rate 0.85 mL/min, detected by UV, PSt standards)

Figure S6. MALDI-TOF mass spectrum of 9
Figure S7. FT-IR spectra of 5, 6, 9, and 10 (NaCl).

Figure S8. FT-IR spectra of 6, 10, 11, 13
Figure S9. MALDI-TOF mass spectrum of 11

Figure S10. MALDI-TOF mass spectrum of 12
Figure S11. MALDI-TOF mass spectrum of 13

Figure S12. MALDI-TOF mass spectrum of 14