

Increasingly threaded polypseudorotaxanes with reduced enthalpies of melting

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A. Materials and Methods

Materials

All chemicals were used as received unless otherwise noted.

Solvents were dried over 4Å sieves unless specified otherwise.

Tert-butyl carbamate was purchased from Ambeed. Sodium hydride (60%, dispersion in Paraffin Liquid) was purchased from TCI Chemicals. 6-Bromo-1-hexene, ammonium hexafluorophosphate, dibenzo-24-crown-8 (DB24C8) was purchased from AAblocks. *N,N*-dimethylformamide (DMF, anhydrous, 99.8%), trifluoroacetic acid (TFA, 99%), and dichloromethane (DCM, ACS Grade, Liquid, ≥99.5%) was purchased from Sigma-Aldrich. Anhydrous magnesium sulfate was purchased from Fisher. Grubbs catalyst M102 (1st generation, G1) and M204 (2nd generation, G2) were obtained from Umicore AG & Co. KG. Deuterated chloroform (CDCl₃, 99.8% with 0.05% v/v TMS) was purchased from Cambridge Isotope Laboratories, Inc.

Methods and Instrumentation

Nuclear Magnetic Resonance (NMR) Spectroscopy. All ¹H NMR and ¹⁹F NMR spectra spectroscopy were collected on Bruker 400 MHz spectrometer. NMR spectra were collected in CDCl₃ and ¹H signals were referenced to the residual CHCl₃ feature (7.26 ppm).

Gel Permeation Chromatograms (GPC). Gel permeation chromatography (GPC) was performed using tetrahydrofuran (THF) as the mobile phase with a flow rate of 1 mL min⁻¹. The setup uses an Agilent 1260 Infinity II pump, Tosoh TSKGel guard and TSKGel GMHHR-M columns, and an Agilent Infinity II differential refractive index (dRI) detector. Polymer molecular weights were determined using conventional calibration analysis with polystyrene standards.

Thermogravimetric Analysis (TGA). All TGAs were measured by TGA Discovery 5500 (MKS is RGA Cirrus 3). These experiments were performed by heating from 30 °C to 600 °C under an atmosphere of nitrogen with a heating rate of 10 °C min⁻¹.

Differential Scanning Calorimetry (DSC). All DSC measurements were performed with a Discovery 2500 in standard aluminum pans. We measured the thermal behavior between -90 °C to 200 °C at a heating and cooling rate of 10 °C min⁻¹ under a nitrogen atmosphere.

Fourier-Transform Infrared Spectroscopy. Fourier-transform infrared spectroscopy (FT-IR) was performed using an Agilent Cary 630 FT-IR instrument with an attenuated total reflection (ATR) attachment with 2 cm⁻¹ resolution in ambient atmosphere on neat samples. All spectra are shown with atmospheric background subtracted.

B. Synthetic Procedures

Synthesis and Characterization of Monomer

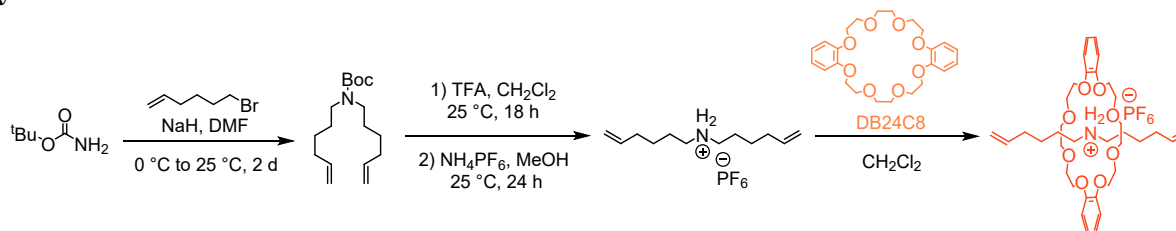


Figure S1. Synthesis of pseudorotaxane diene monomer

A flame-dried 500 mL round bottom flask was evacuated and backfilled with dry nitrogen gas. A stir bar, sodium hydride (1.73 g, 43.3 mmol, 2.1 eq), 6-bromo-1-hexene (6.7 g, 41 mmol, 2.0 eq), and dry DMF (150 mL) were then added to the flask under flowing nitrogen. This mixture was then cooled and stirred in an ice bath. To this cooled mixture, a solution of tertbutyl carbamate (2.41 g, 20.6 mmol, 1.0 eq) in dry DMF (10 mL) was added dropwise over 30 min. The ice bath was then removed and the mixture was allowed to warm to room temperature and stir for 2 days. The reaction mixture was then poured onto 200 g of ice and extracted with diethyl ether (150 mL, 3×). The ether fractions were then combined and washed with water (200 mL, 5×), washed with brine (200 mL, 1×), and dried over anhydrous MgSO₄. The ether solution was then concentrated by rotary evaporation to yield the boc-protected aminodiene as a light-yellow liquid (3.51 g, 62% yield). This material was used without further purification.

¹H NMR (CDCl₃, 400 MHz): 5.80–5.73 (m, 2H), 5.00–4.90 (m, 4H), 3.14–3.11 (m, 4H), δ 2.07–2.02 (m, 4H), δ 1.42 (s, 9H), δ 1.51–1.32 (m, 8H).

To a round bottom flask equipped with a stir bar was added boc-protected amino diene (3.47 g, 12 mmol, 1.0 eq), DCM (100 mL), and TFA (14.19 g, 120 mmol, 10.0 eq). The mixture was stirred for 18 h and then the solvent was removed by rotary evaporation. The obtained solid was then redissolved in DCM (50 mL) and then concentrated by rotary evaporation and further dried under high vacuum. Next, the solid was dissolved in MeOH (100 mL), and ammonium hexafluorophosphate (19.5 g, 120 mmol, 10.0 eq) was added. The mixture was stirred for 24 h, then poured into 500 mL of H₂O. The resulting suspension stood for 24 h at RT, then at -20 °C for 24 hours. The mixture was then vacuum filtered and the solid was washed extensively with H₂O, yielding light tan crystals of the ammonium hexafluorophosphate salt of the amino diene (2.68 g, 77% yield). This material was used without further purification.

¹H NMR (CDCl₃, 400 MHz): 5.77–5.75 (m, 2H), 5.06–4.98 (m, 4H), 3.42–3.09 (m, 4H), δ 2.11–2.06 (m, 4H), δ 1.74–1.44 (m, 8H).

To a flame-dried 20 mL septa vial under inert atmosphere, a stir bar, the pseudorotaxane diene monomer (1.64 g, 1.0 eq), DB24C8 (2.24 g, 1.0 eq), and DCM (5 mL) were added and allowed to stir for 30 min under nitrogen. The solvent was then removed to yield the pseudorotaxane diene monomer as a white solid (3.88 g, 100% yield). The material was dried under high vacuum and used without further purification.

^1H NMR (CDCl_3 , 400 MHz): δ 6.93 – 6.88 (m, 8H), 5.76 – 5.54 (m, 2H), 5.03 – 4.83 (m, 4H), 4.19 – 4.16 (m, 8H), δ 3.90 (s, 8H), δ 3.79 – 3.75 (m, 8H), δ 3.29 – 3.05 (m, 4H), δ 2.08 (m, 8H), δ 1.81 – 1.45 (m, 12H).

^{19}F NMR (CDCl_3 , 400 MHz): δ 72.04, 73.72.

FT-IR (Diamond-ATR, cm^{-1}): 3187, 3075, 2927, 2879, 1694, 1590, 1506, 1457, 1252, 1217, 1093, 1047, 956, 920, 835, 751

Melting Point: $-14\text{ }^\circ\text{C}$

Synthesis and Characterization of Variably Threaded Linear Polyrotaxanes

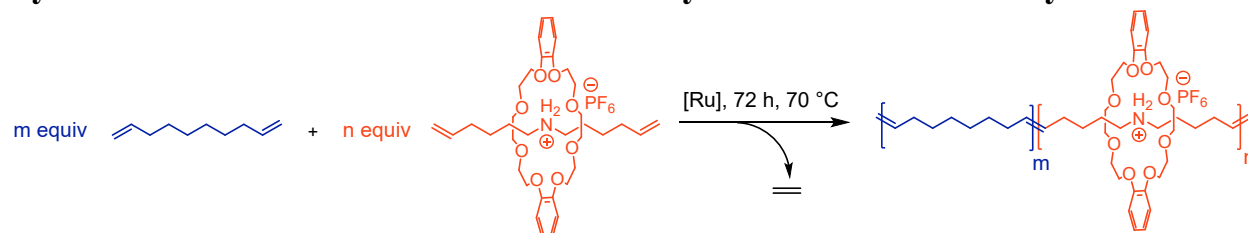


Figure S2. Synthesis of variably threaded Linear Polyrotaxanes

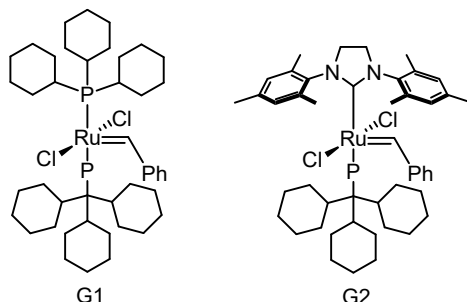


Figure S3. Structure of G1 and G2

General Synthesis of PR-n: To a flame-dried 20 mL septa vial under inert atmosphere, a stir bar, pseudorotaxane diene monomer (n equiv.), 1,9-decadiene (m equiv.), and dichlorobenzene were added to establish a solution where the total monomer concentration was 1 M. This mixture was then stirred for 10 minutes at room temperature after which time a [Ru] catalyst was added at 1 mol % relative to total monomer concentration. This reaction was stirred at $70\text{ }^\circ\text{C}$ under high vacuum for 3 days. If the reaction mixture was observed to solidify, a small amount of additional dichlorobenzene was added.

PR-00: Following the general synthesis outlined above, without adding dichlorobenzene, 1,9-decadiene (0.69 g, 1.0 eq) was polymerized using G1 as the catalyst.

^1H NMR (CDCl_3 , 400 MHz): δ 5.38 – 5.34 (m, 1H), 1.95 (m, 2H), 1.28 – 1.32 (s, 4H).

FT-IR (Diamond-ATR, cm^{-1}): 2919, 2850, 1466, 965, 721

Melting Point: $22\text{ }^\circ\text{C}$

PR-04: Following the general synthesis outlined above, without adding dichlorobenzene, pseudorotaxane diene monomer (0.16 g, 1.0 eq) and 1,9-decadiene (0.69 g, 24.0 eq) was polymerized using G1 as the catalyst.

¹H NMR (CDCl₃, 400 MHz): δ 6.90 (m, 0.21H), 5.43 – 5.33 (m, 1H), δ 4.17 – 4.15 (m, 0.21H), 3.90 (s, 0.21H), 3.80 (s, 0.21H), 3.04 (s, 0.11H), 2.02 – 1.94 (m, 2H), 1.86 – 1.73 (m, 0.37H), 1.34 – 1.25 (m, 4H).

FT-IR (Diamond-ATR, cm⁻¹): 2920, 2850, 1724, 1504, 1459, 1250, 1051, 965, 841, 729

Melting Point: 22 °C

PR-10: Following the general synthesis outlined above, adding dichlorobenzene (1M), pseudorotaxane diene monomer (0.11 g, 1.0 eq) and 1,9-decadiene (0.17 g, 9.0 eq) was polymerized by using G2 as the catalyst.

¹H NMR (CDCl₃, 400 MHz): δ 6.90 (m, 0.53H), 5.39 – 5.33 (m, 1H), δ 4.16 (m, 0.53H), 3.90 (s, 0.53H), 3.80 (s, 0.53H), 3.02 (s, 0.27H), 2.02 – 1.96 (m, 1.72H), 1.84 – 1.64 (m, 0.77H), 1.33 – 1.27 (m, 3.62H).

FT-IR (Diamond-ATR, cm⁻¹): 3176, 2926, 2853, 1724, 1593, 1502, 1454, 1251, 1210, 1122, 1049, 960, 831, 757

Melting Point: 22 °C

PR-20: Following the general synthesis outlined above, adding dichlorobenzene (1M), pseudorotaxane diene monomer (0.24 g, 1.0 eq) and 1,9-decadiene (0.17 g, 4.0 eq) was polymerized using G2 as the catalyst.

¹H NMR (CDCl₃, 400 MHz): δ 6.90 (m, 0.83H), 5.38 – 5.34 (m, 1H), δ 4.16 (m, 0.83H), 3.90 (s, 0.83H), 3.80 (s, 0.83H), 3.05 (s, 0.41H), 1.96 (m, 1.66H), 1.84 – 1.64 (m, 1.20H), 1.29 (m, 3.31H).

FT-IR (Diamond-ATR, cm⁻¹): 3177, 2920, 2851, 1724, 1593, 1504, 1455, 1249, 1211, 1118, 1049, 962, 833, 753

Melting Point: 9 °C

PR-30: Following the general synthesis outlined above, adding dichlorobenzene (1M), pseudorotaxane diene monomer (0.26 g, 3.0 eq) and 1,9-decadiene (0.11 g, 7.0 eq) was polymerized using G2 as the catalyst.

¹H NMR (CDCl₃, 400 MHz): δ 6.89 (m, 1.19H), 5.37 (m, 1H), δ 4.15 (m, 1.19H), 3.89 (s, 1.19H), 3.80 (s, 1.19H), 3.04 (s, 0.65H), 1.95 (m, 1.40H), 1.84 – 1.64 (m, 1.31H), 1.29 (m, 2.70H).

FT-IR (Diamond-ATR, cm⁻¹): 3176, 2920, 2855, 1724, 1593, 1502, 1457, 1250, 1213, 1116, 1053, 952, 835, 746

Melting Point: 12 °C

PR-40: Following the general synthesis outlined above, adding dichlorobenzene (1M), pseudorotaxane diene monomer (0.26 g, 4.0 eq) and 1,9-decadiene (0.07 g, 6.0 eq) was polymerized using G2 as the catalyst.

¹H NMR (CDCl₃, 400 MHz): δ 6.89 (m, 1.48H), 5.37 (m, 1H), δ 4.15 (m, 1.48H), 3.89 (s, 1.48H), 3.80 (s, 1.48H), 3.03 (s, 0.75H), 1.96 (m, 1.25H), 1.84 – 1.64 (m, 1.75H), 1.29 (m, 2.41H).

¹⁹F NMR (CDCl₃, 400 MHz): δ 71.82, 73.77.

FT-IR (Diamond-ATR, cm⁻¹): 3183, 2922, 2857, 1725, 1594, 1504, 1457, 1254, 1213, 1118, 1055, 952, 835, 747

Melting Point: 17 °C

C. Nuclear Magnetic Resonance Spectroscopy

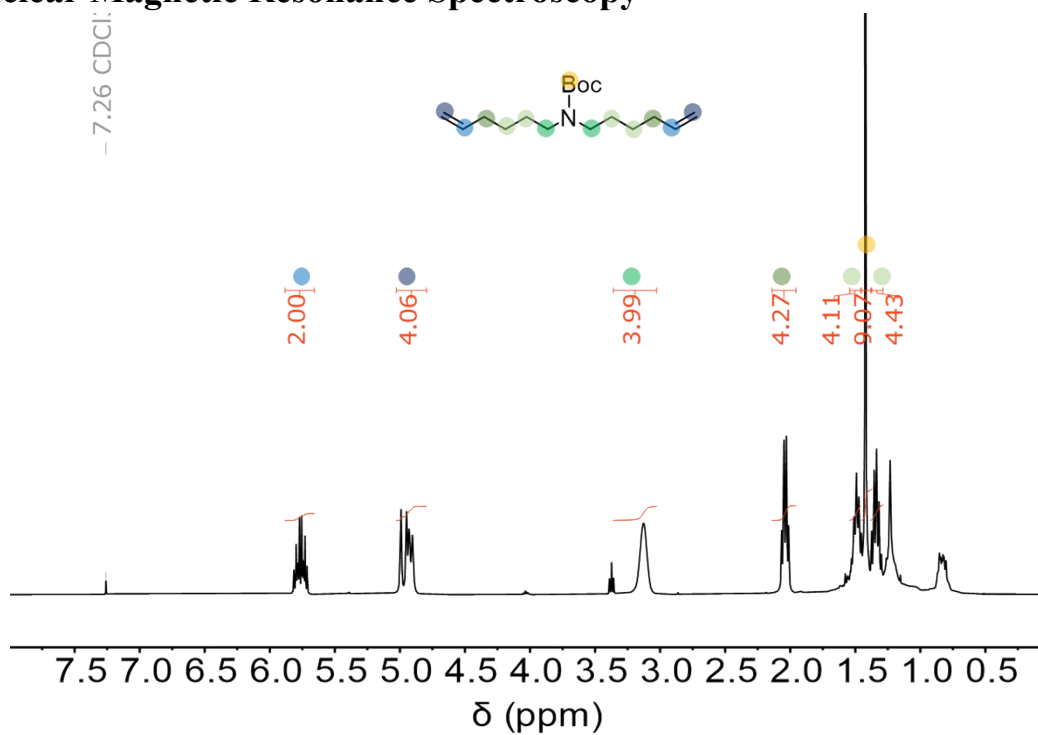


Figure S4. ¹H NMR spectrum of boc-protected amino diene.

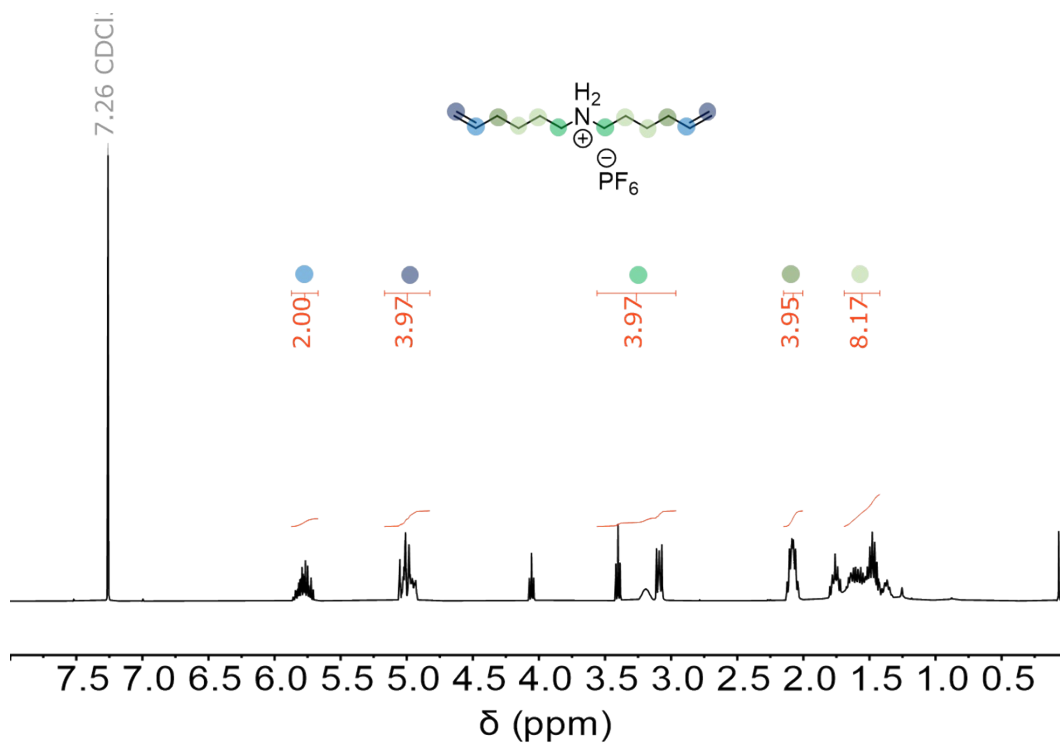


Figure S5. ¹H NMR spectrum of ammonium diene.

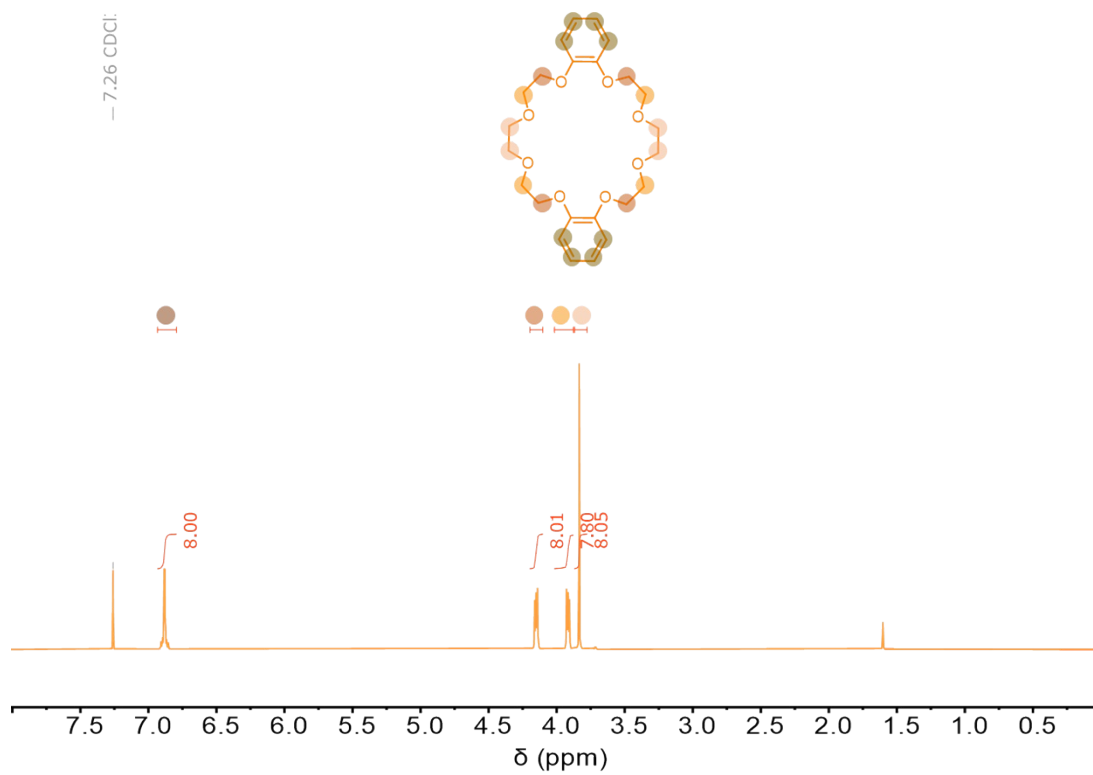


Figure S6. ¹H NMR spectrum of macrocycle.

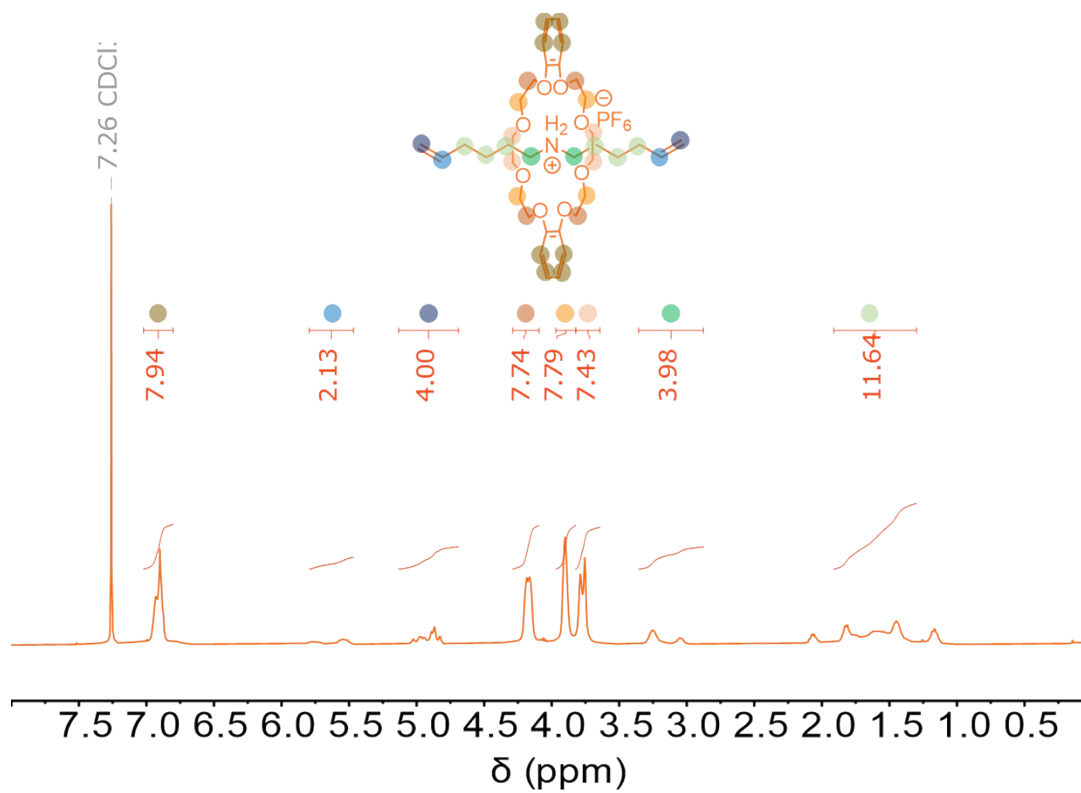


Figure S7. ¹H NMR spectrum of pseudorotaxane diene monomer.

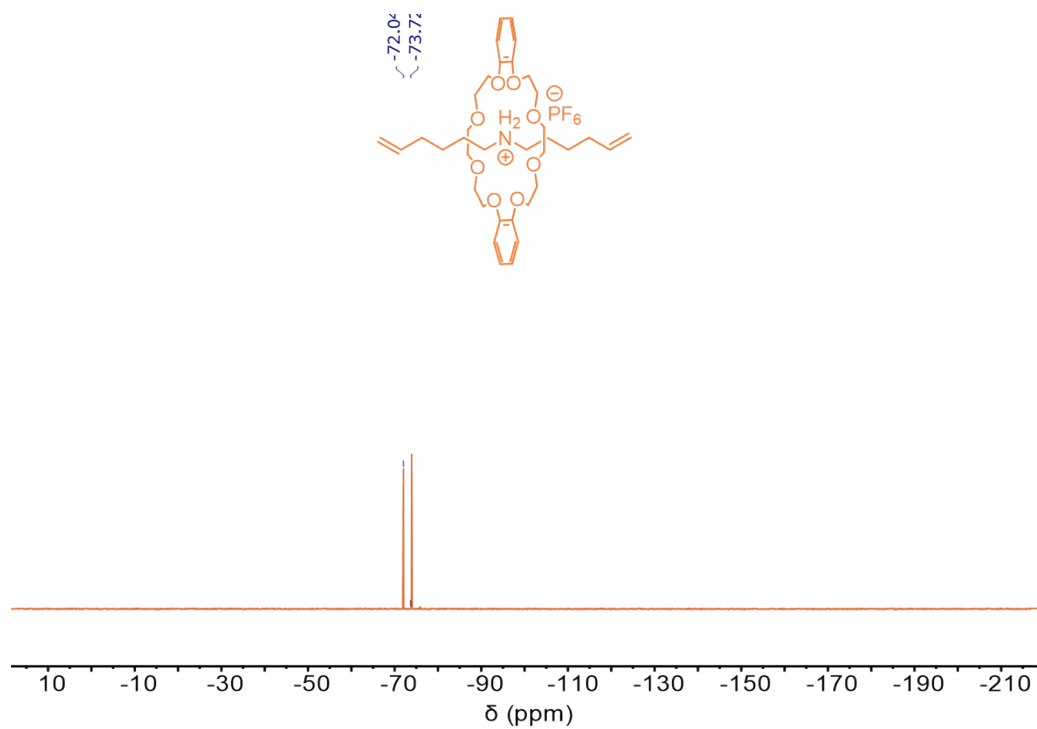


Figure S8. ¹⁹F NMR spectrum of pseudorotaxane diene monomer.

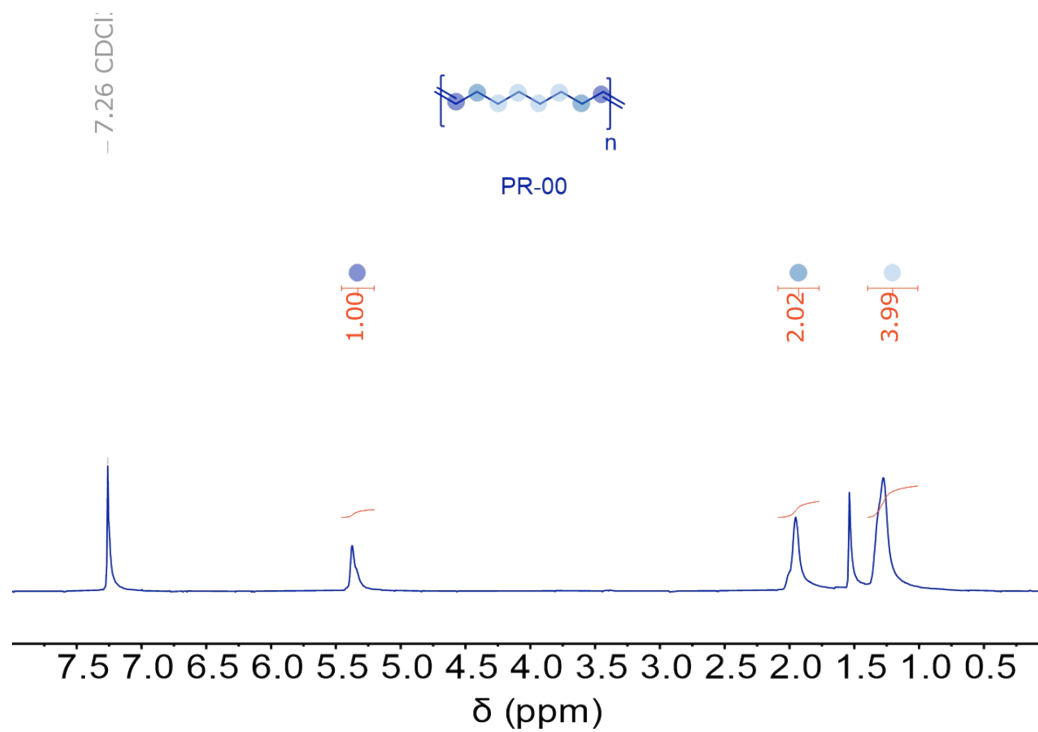


Figure S9. ¹H NMR spectrum of PR-00.

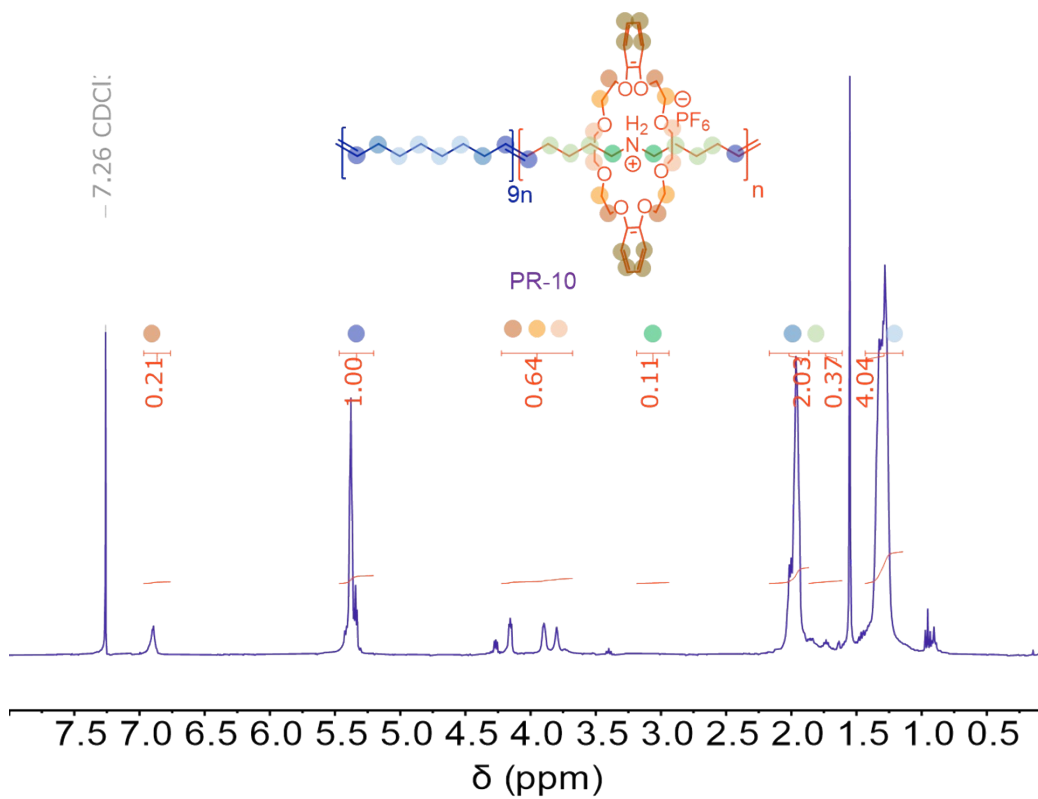


Figure S10. ¹H NMR spectrum of PR-04.

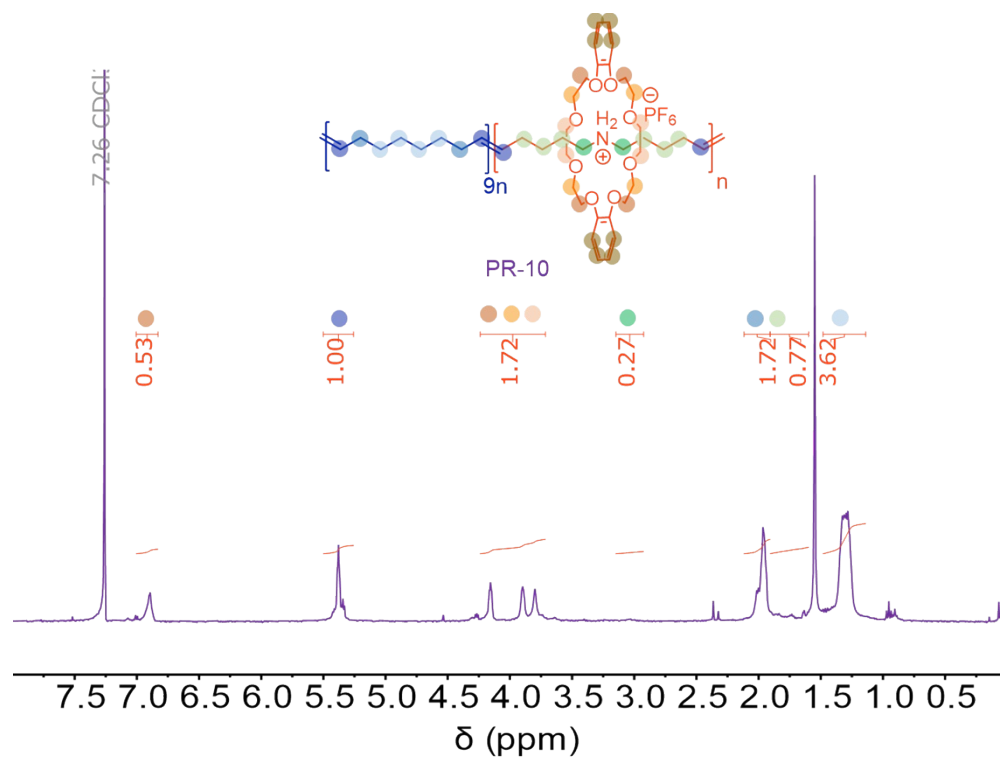


Figure S11. ¹H NMR spectrum of PR-10.

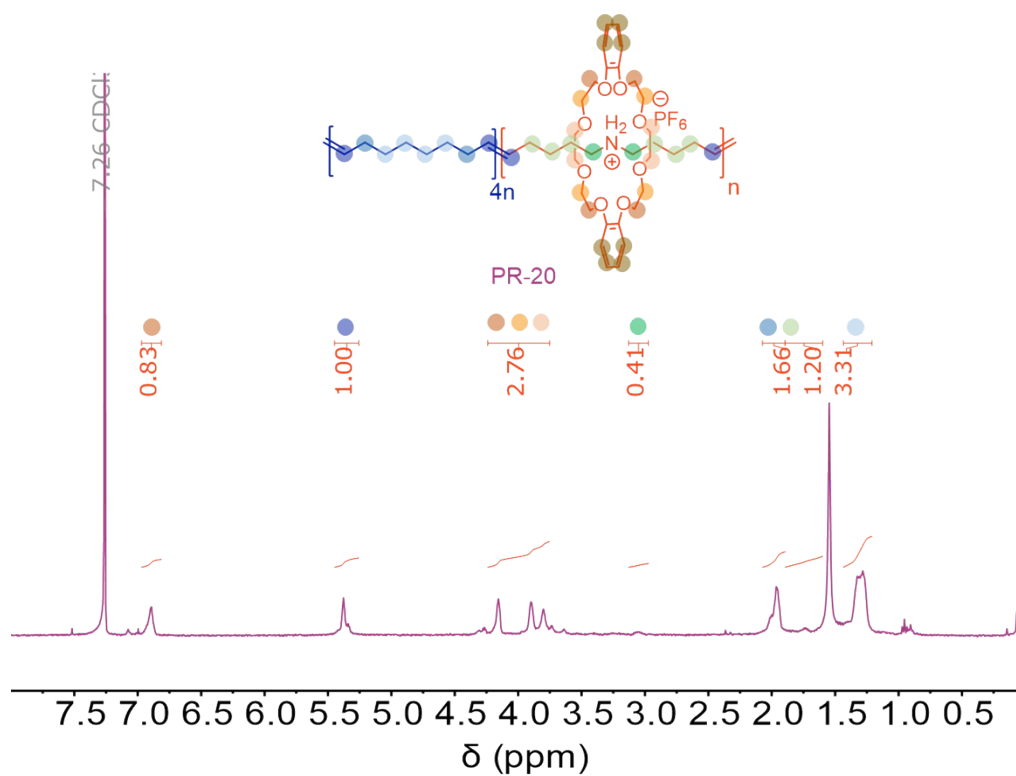


Figure S12. ¹H NMR spectrum of PR-20.

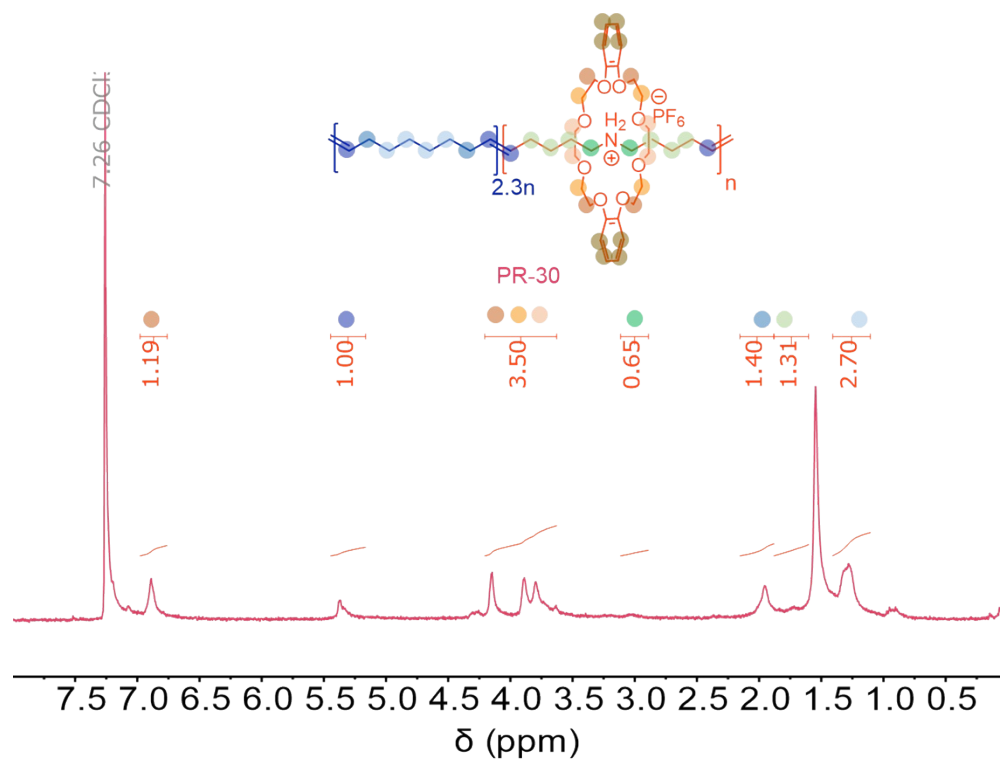


Figure S13. ¹H NMR spectrum of PR-30.

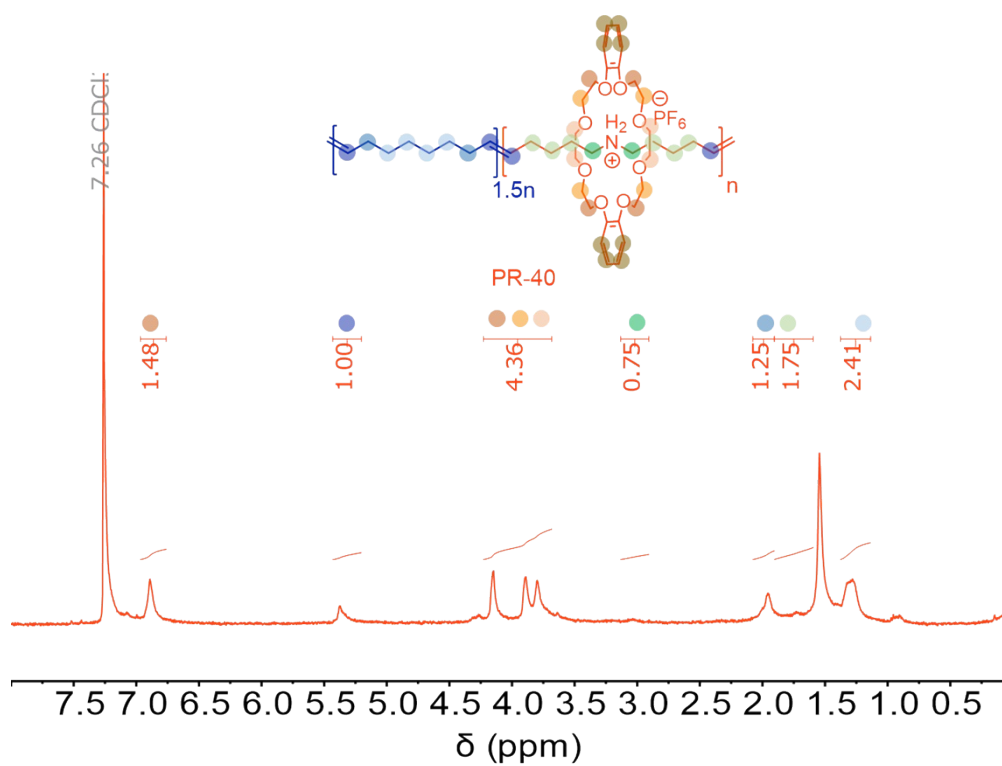


Figure S14. ¹H NMR spectrum of PR-40.

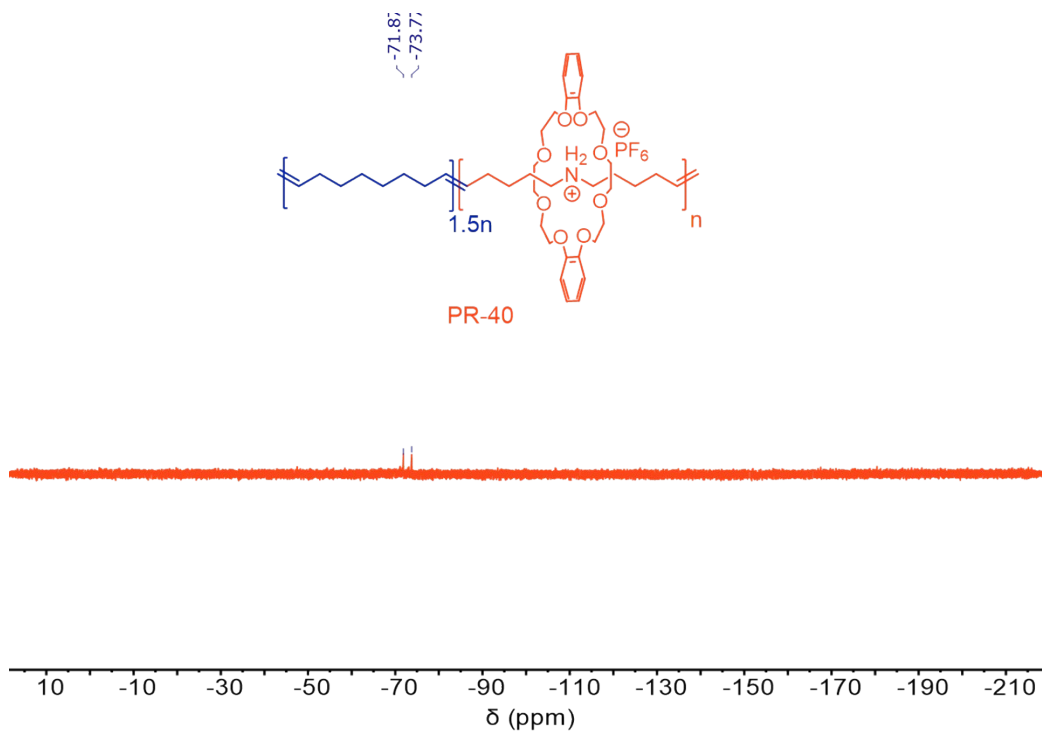


Figure S15. ^{19}F NMR spectrum of PR-40.

D. Gel Permeation Chromatograms

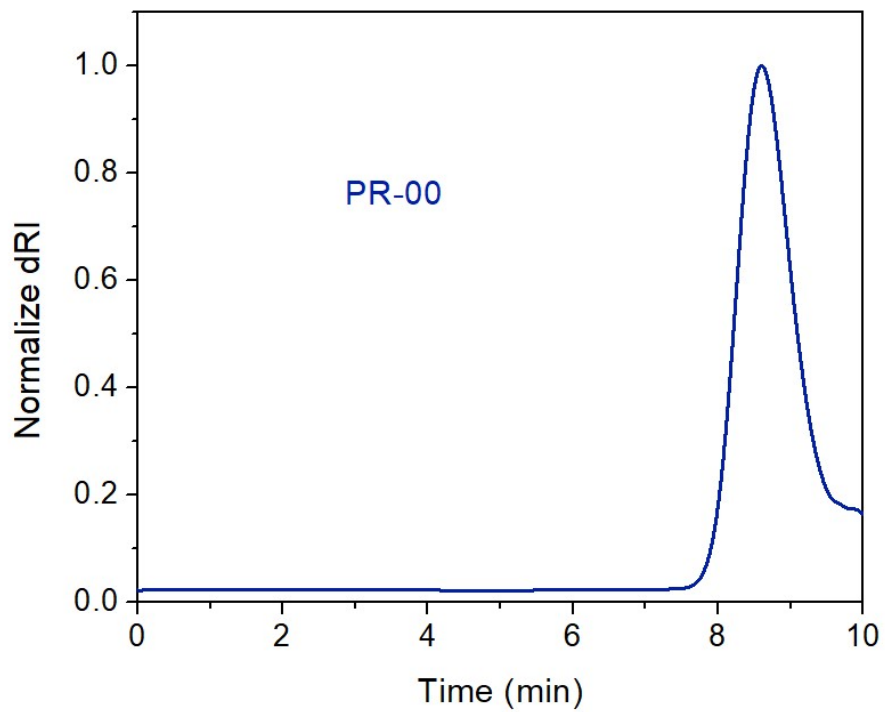


Figure S16. Gel permeation chromatograms (GPC) of PR-00.

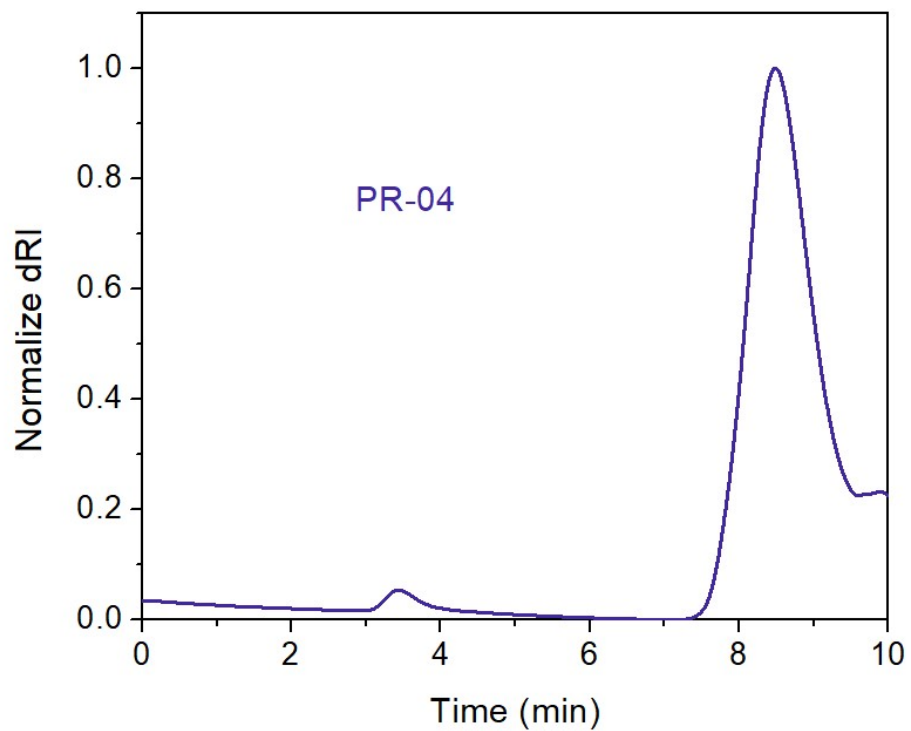


Figure S17. Gel permeation chromatograms (GPC) of PR-04.

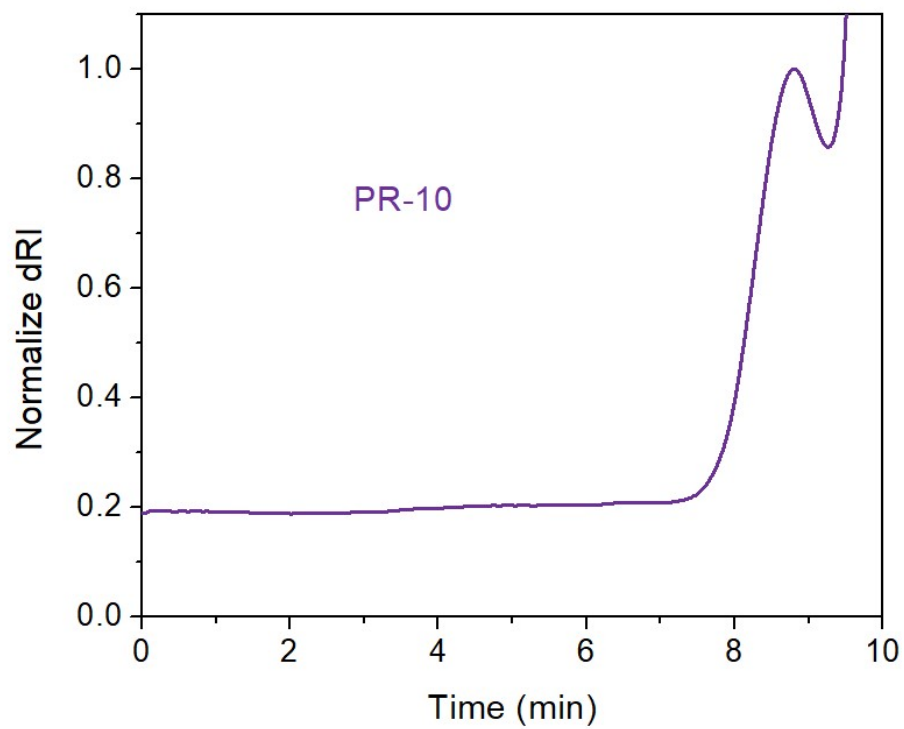


Figure S18. Gel permeation chromatograms (GPC) of PR-10.

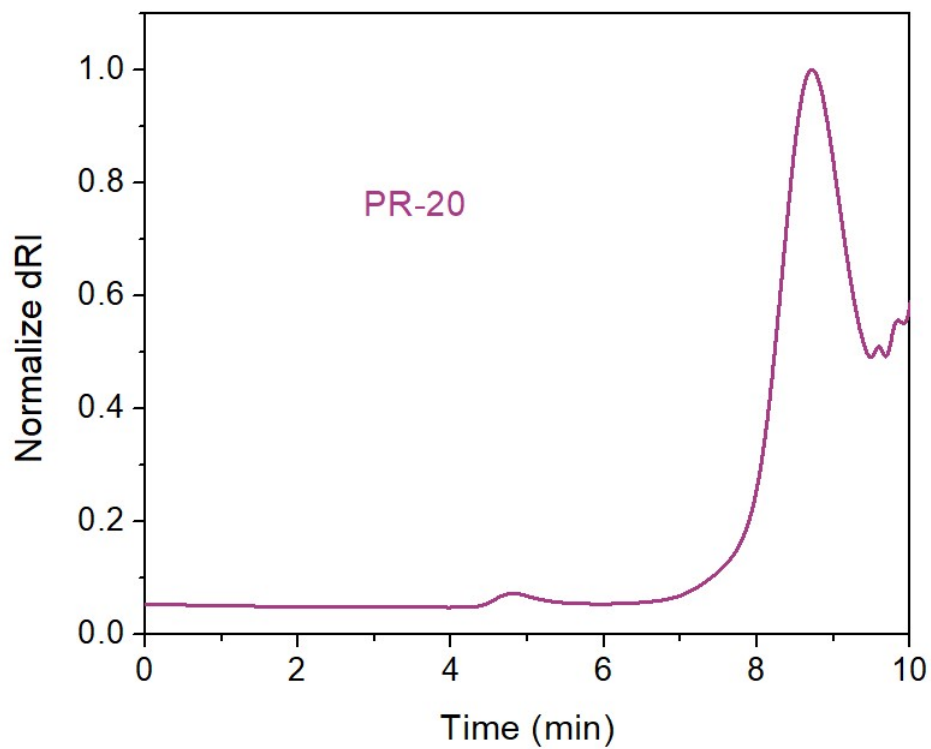


Figure S19. Gel permeation chromatograms (GPC) of PR-20.

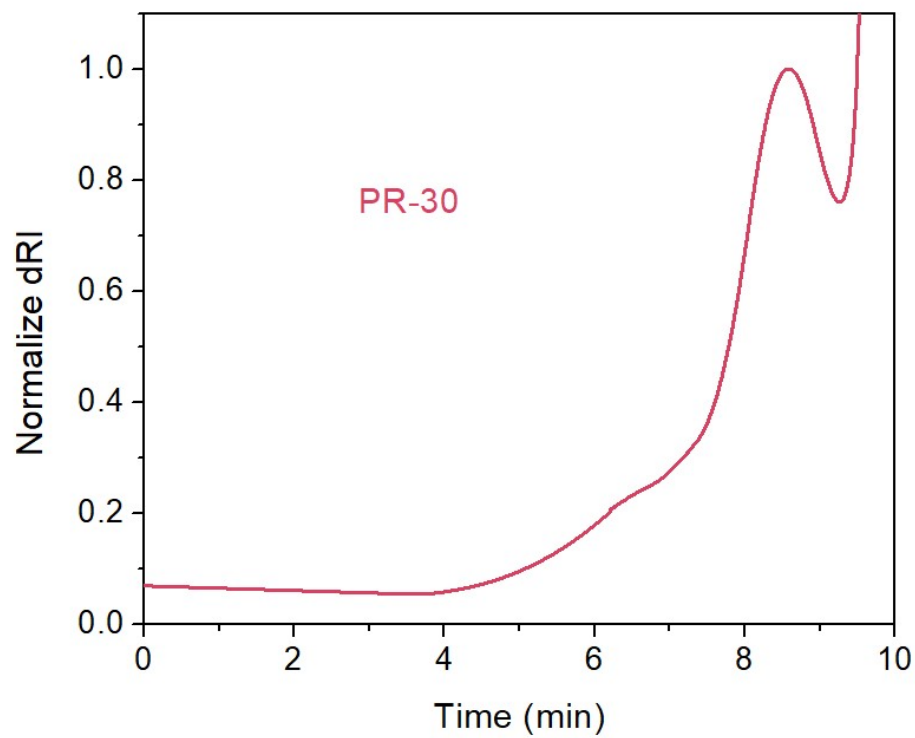


Figure S20. Gel permeation chromatograms (GPC) of PR-30.

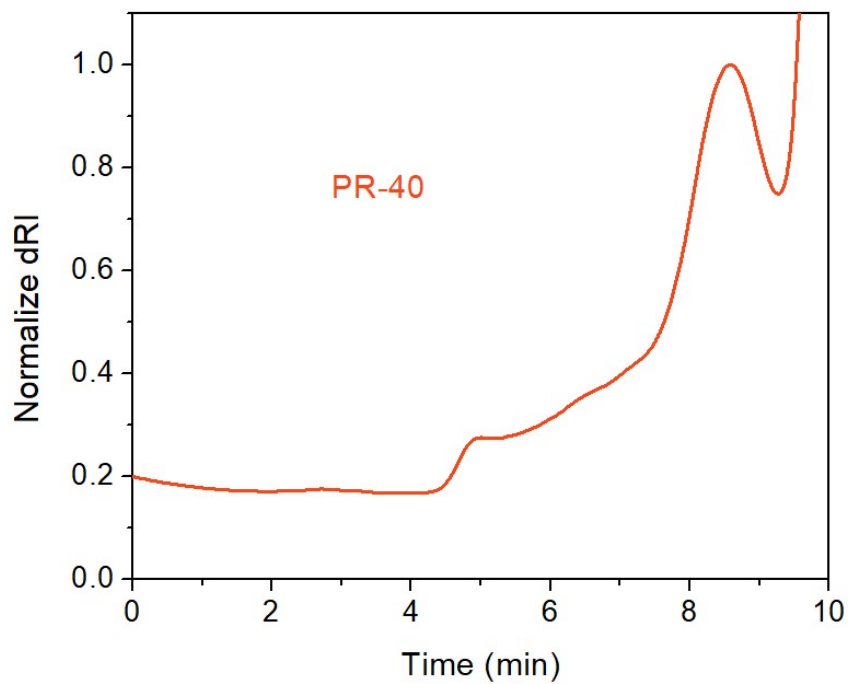


Figure S21. Gel permeation chromatograms (GPC) of PR-40.

E. Fourier-Transform Infrared Spectroscopy

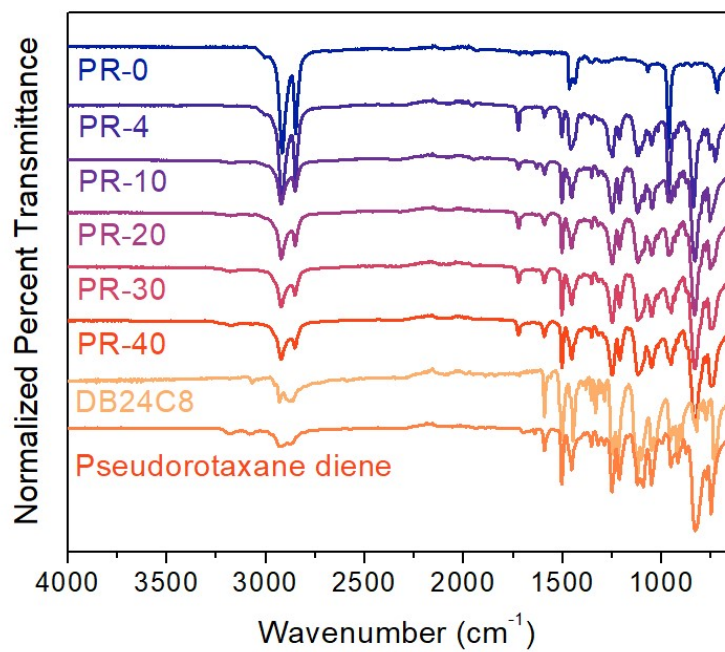


Figure S22. Fourier-transform infrared spectra of the variably threaded polyrotaxanes, DB24C8, and pseudorotaxane diene monomer (4000-650 cm⁻¹)

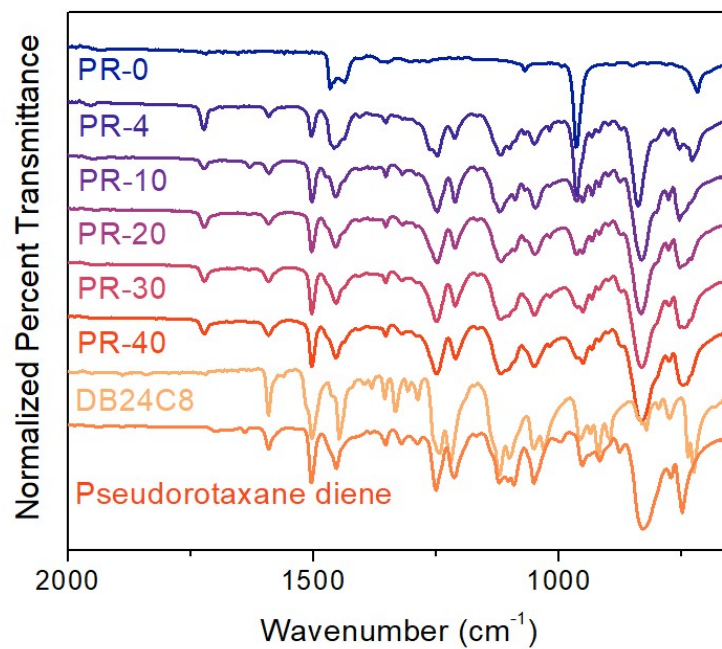


Figure S23. Fourier-transform infrared spectra of the variably threaded polyrotaxanes, DB24C8, and pseudorotaxane diene monomer (2000-650 cm⁻¹)

F. Thermogravimetric Analysis

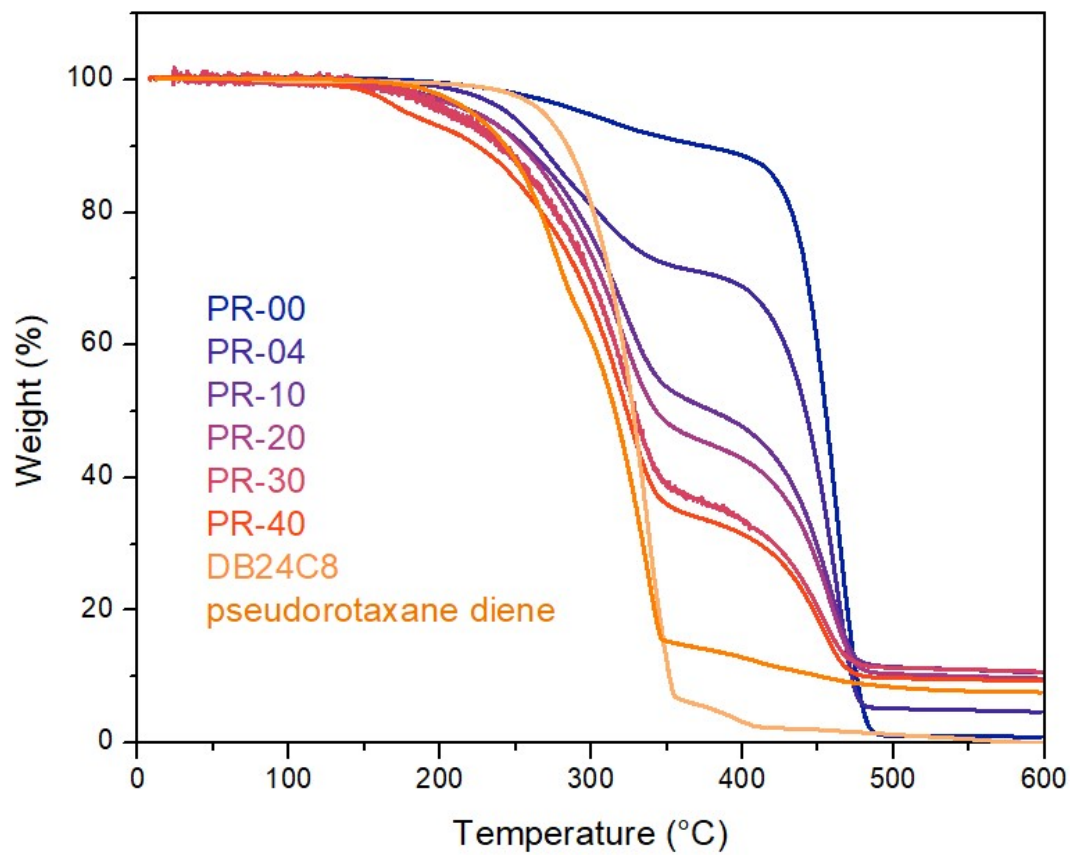


Figure S24. Thermogravimetric analysis (TGA) of the variably threaded polyrotaxanes, DB24C8, and pseudorotaxane diene monomer

G. Differential Scanning Calorimetry

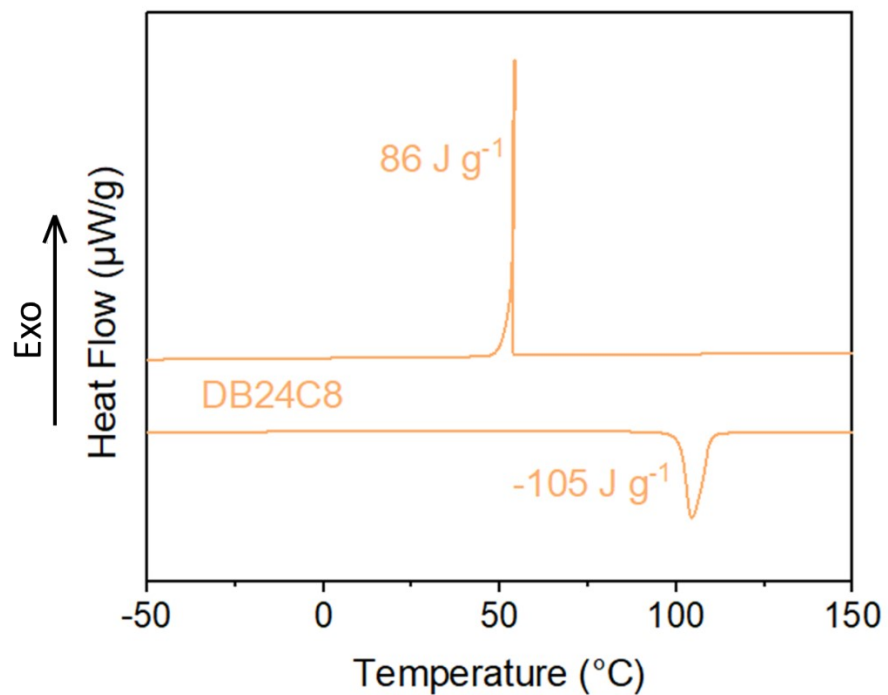


Figure S25. Differential scanning calorimetry (DSC) thermograms of DB24C8

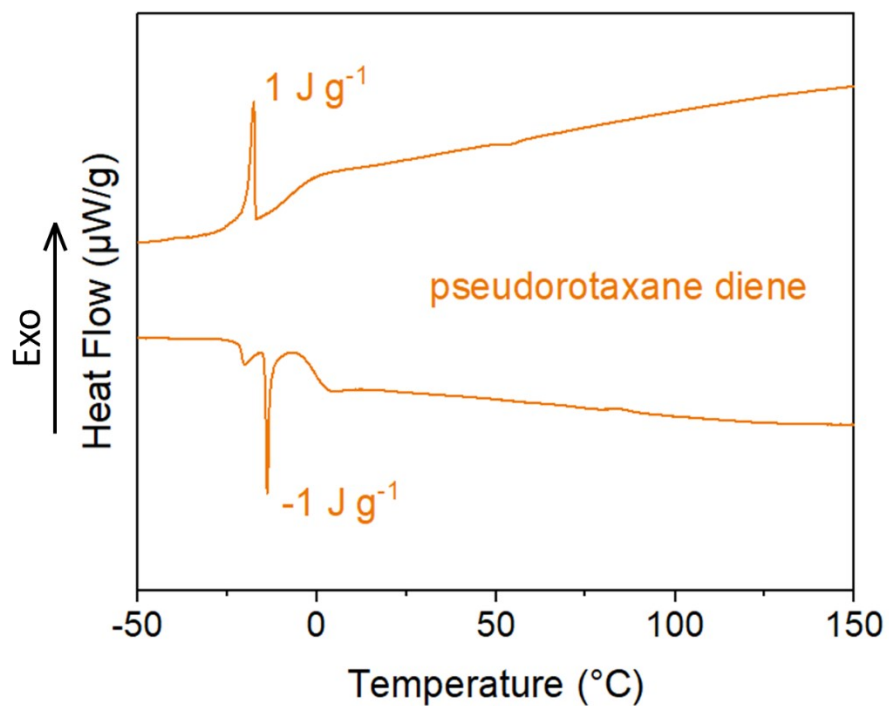


Figure S26. Differential scanning calorimetry (DSC) thermograms of pseudorotaxane diene monomer

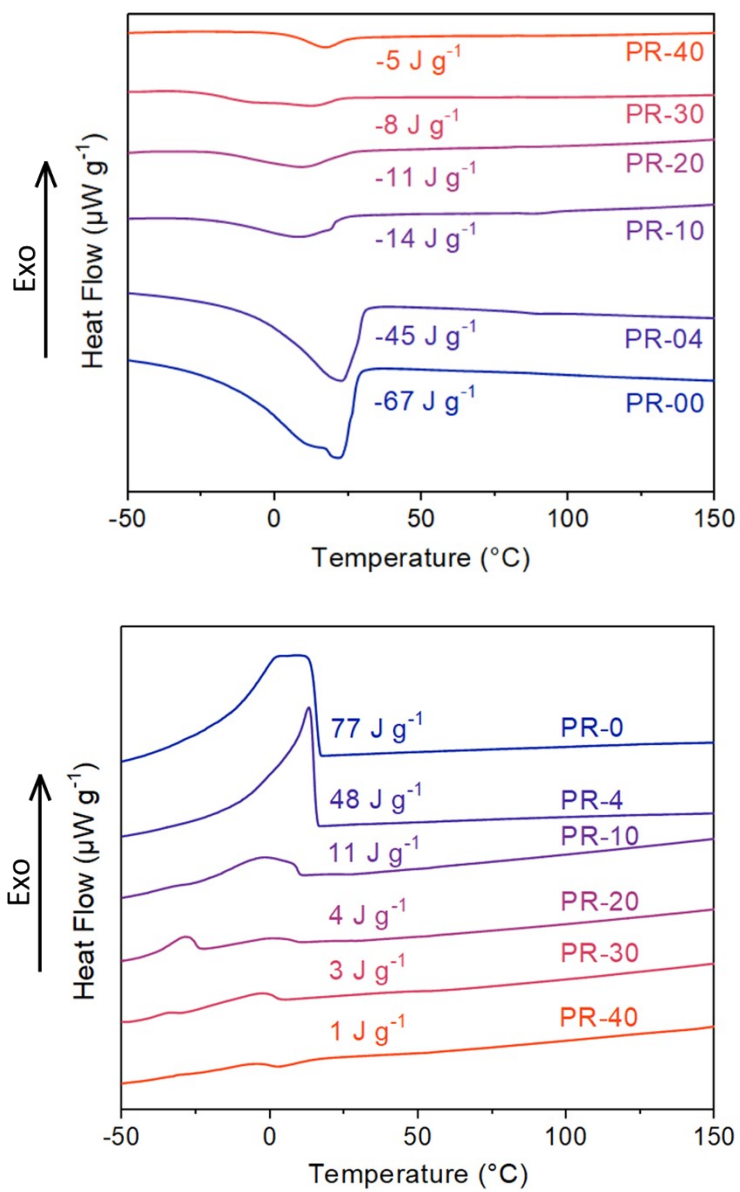


Figure S27. Differential scanning calorimetry (DSC) thermograms of variably threaded polyrotaxanes