Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Arm-Degradable Star Polymers with Crosslinked Ladder-Motif Cores as a Route to Soluble Microporous Nanoparticles

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Table of Contents

1. General Information 2
2. Synthetic Procedures 3
3. Supporting Figures and Tables 5
  3.1. GPC Traces 5
  3.2. Sorption isotherms 6
  3.3. NMR spectra 7
4. References 11

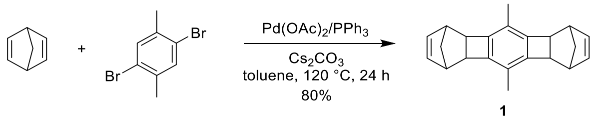
1. General Information

Materials. All chemicals were obtained from commercial sources and used as received unless otherwise noted. Dry toluene and THF were obtained from solvent purification columns. $(H_2IMes)(pyr)_2(Cl)_2RuCHPh$ (**G3**)[1] and compound **2**[2] were prepared according to literature procedures. All CANAL reactions were performed under nitrogen in flame-dried glassware. Flash chromatography (FC) was carried out with Silica 60 (230-400 mesh; Fisher). Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm silica gel plate (silica gel 60, F254, EMD chemical).

Characterizations. ^1H and ^{13}C NMR spectra were recorded using 300 MHz, 400 MHz, or 500 MHz Varian NMR spectrometers. Chemical shifts are reported in ppm using the residual protiated solvent as an internal standard ($CDCl_3$ ^1H: 7.26 ppm and ^{13}C: 77.16 ppm). Gel permeation chromatography (GPC) was carried out in THF on two PolyPore columns (Agilent) connected in series with a DAWN multiangle laser light scattering (MALLS) detector and an Optilab T-rEX differential refractometer (both from Wyatt Technology). No calibration standards were used, and d*n*/d*c* values were obtained for each injection by assuming 100% mass elution from the columns. Dynamic light scattering (DLS) experiments were performed using a Malvern Zetasizer Nano ZS90 instrument. Samples were prepared by dilution to 1 mg/mL in THF. Gas adsorption was performed on a Micromeritics ASAP 2020. Samples were degassed in high vacuum (< 4 μbar) at 120 °C for 2 h before each measurement. Data points in the range of $p/p_0 = 0.01\text{-}0.3$ from CO_2 isotherms at 195 K were selected for BET analysis based on the Rouquerol criteria. Cross sectional areas 0.170 nm^2 was used for CO_2. P_0 of 1880 mbar was used for CO_2 at 195 K.

2. Synthetic Procedures

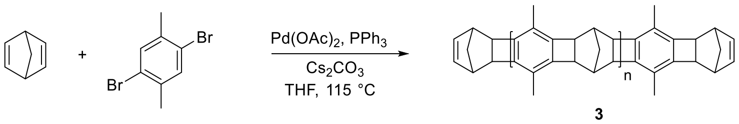
Procedure for bis-norbornene synthesis via CANAL



1

To a flame-dried 50 mL glass pressure tube were added 2,5-dibromo-*p*-xylene (2.65 g, 10 mmol), $Pd(OAc)_2$ (45 mg, 0.20 mmol), and PPh_3 (52 mg, 0.40 mmol). The tube was transferred into a nitrogen-filled glovebox, and Cs_2CO_3 (6.52 g, 20 mmol), norbornadiene (5.0 mL, 50 mmol) and 17 mL toluene were added. The tube was then sealed with a Teflon valve and taken out of the glovebox. The mixture was heated to 120 °C for 24 h. The reaction was cooled to room temperature and was passed through a thin layer of Celite to remove the inorganic salt. CH_2Cl_2 (2×5 mL) was then used to wash the residue on Celite. The solution was concentrated *in vacuo* and the residue was purified by column chromatography (hexanes) to yield **1** as a white solid (mixture of syn/anti isomers, 2.30 g, 80 %). ^{1}H NMR (300 MHz, Chloroform-*d*) ^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.20 (s, 4H), 2.98 (s, 4H), 2.73 (d, *J* = 1.9 Hz, 4H), 2.07 (s, 6H), 1.25 (d, *J* = 8.8 Hz, 2H), 0.85 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.21, 143.04, 136.65, 136.59, 123.98, 123.73, 45.23, 45.13, 41.66, 40.93, 12.36. δ 143.21, 143.04, 136.65, 136.59, 123.98, 45.23, 45.13, 41.66, 40.93, 12.36. EI-MS m/z Calc'd for $C_{22}H_{22}^+$ [M^+]: 286.17, found 286.0.

Procedure for norbornene-terminated ladder polymer synthesis via CANAL



3

To a flame-dried 50 mL glass pressure tube were added 2,5-dibromo-*p*-xylene (1.32 g, 5.0 mmol), $Pd(OAc)_2$ (22 mg, 0.10 mmol), and PPh_3 (52 mg, 0.20 mmol). The tube was transferred into a nitrogen-filled glovebox, and Cs_2CO_3 (3.26 g, 10 mmol), norbornadiene (0.59 mL, 6.0 mmol) and 10 mL THF were added. The tube was then sealed with a Teflon valve and taken out of the glovebox. The mixture was heated to 115 °C for 16 h. The reaction was cooled to room temperature and was passed through a thin layer of Celite to remove the inorganic salt. $CHCl_3$ was then used to wash the residue on Celite. The solution was concentrated *in vacuo* and the crude polymer was dissolved in $CHCl_3$, precipitated into acetone and washed with acetone.

General procedure for star polymer formation via ROMP

Star polymer syntheses were performed in a glovebox. In a typical experiment, a small vial was charged with PLA macromonomer and a stir bar. The desired amount of anhydrous THF was added to dissolve the macromonomer. A stock solution of catalyst **G3** in degassed, anhydrous THF was prepared in a separate vial. The desired amount of catalyst was injected into the macromonomer solution to initiate the polymerization ($[MM]_0 = 0.05$ M). After 5 minutes of stirring at 25 °C, aliquots of the polymerization mixture were transferred to the vials containing the desired amount of cross-linker dissolved in THF ([PLA oligoMM]$_0$ = 0.30 mM). The resulting mixtures were stirred at 25 °C for 3 h, at which point a few drops of ethyl vinyl ether were added to quench the reactions. The reaction mixtures were concentrated and precipitated into MeOH.

General procedure for arm cleavage of star polymer for isolation of cores

In a 20 mL vial, the star polymer (70 mg) was dissolved in 4M HCl in dioxane (3 mL) and H_2O (20 µL). The reaction mixture was heated to 80 °C and stirred for 2 h. The reaction mixture was cooled to room temperature, concentrated in *vacuo* and the crude polymer was dissolved in THF, precipitated into and washed with methanol.

3. Supporting Figures and Tables

3.1. GPC traces

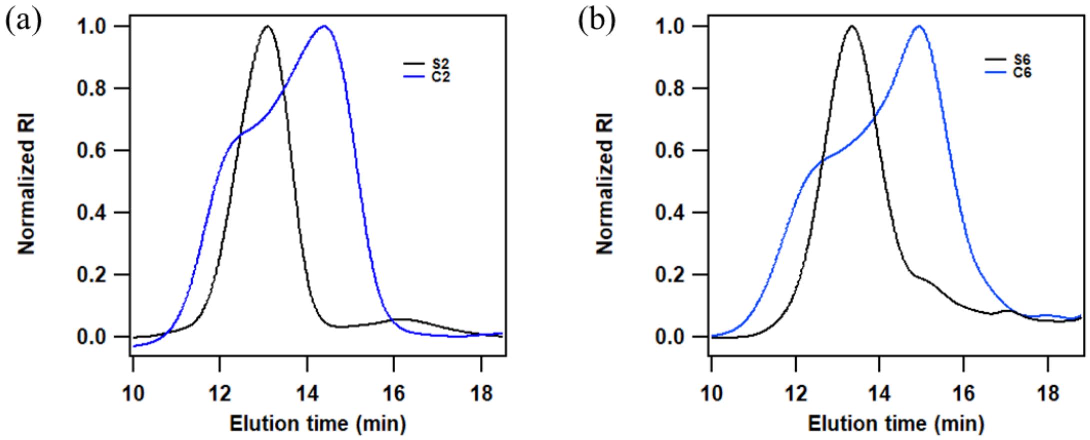


Figure S1. GPC traces of star polymers (**S**, black traces) and their corresponding cores after arm degradation (**C**, blue traces) for (a) **S2** and (b) **S6**. The high MW shoulder for the arm-removed cores suggests their microscopic aggregation.

3.2. Sorption isotherms of isolated arm-removed cores

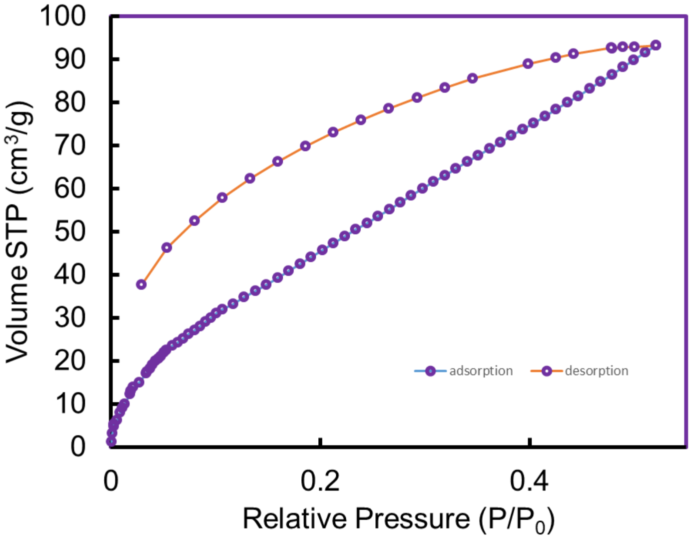


Figure S2. CO_2 adsorption and desorption isotherms for arm-removed core of **S2** at 195 K. The surface area determined by BET analysis is 213 m^2/g.

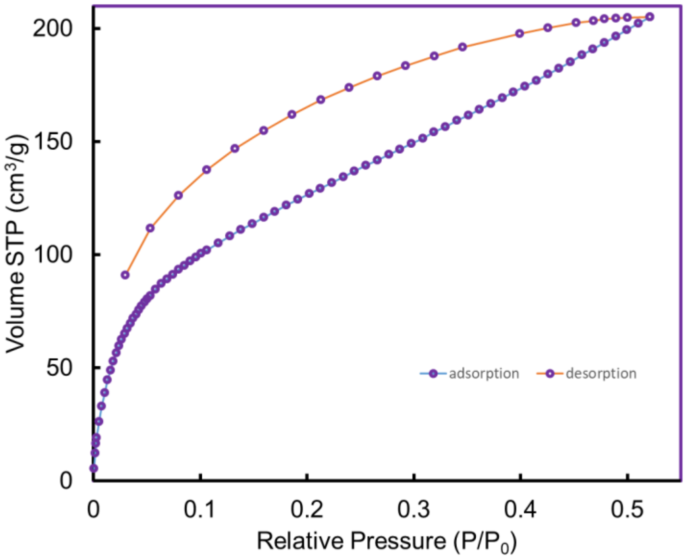
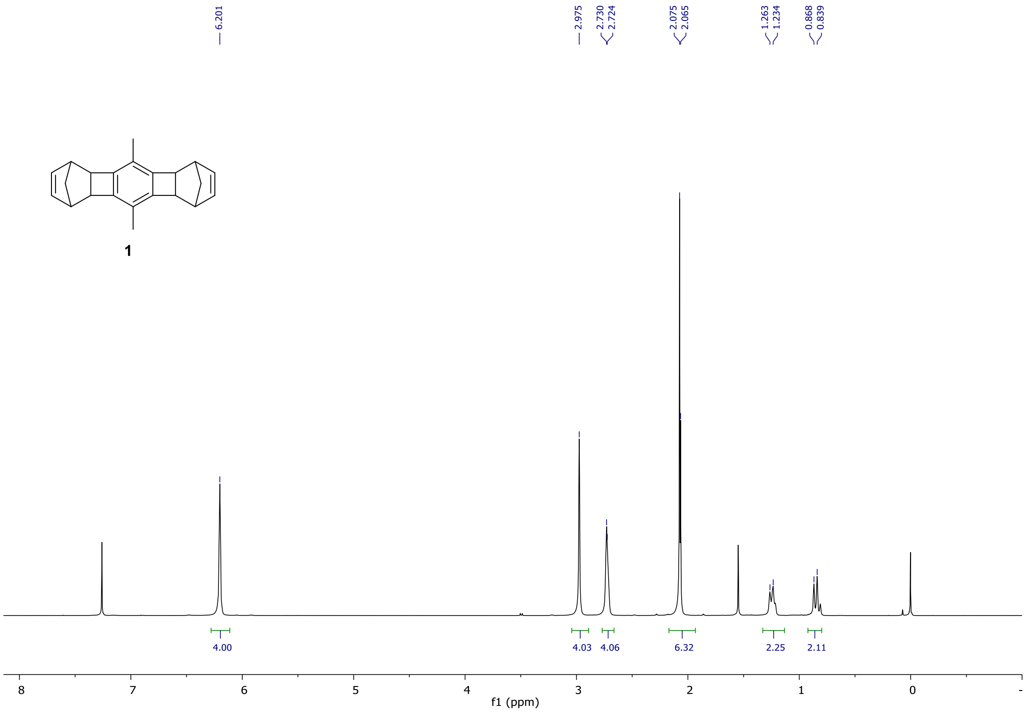


Figure S3. CO_2 adsorption and desorption isotherms for arm-removed core of **S6** at 195 K. The surface area determined by BET analysis is 504 m^2/g.

3.3. NMR spectra

(a)



(b)

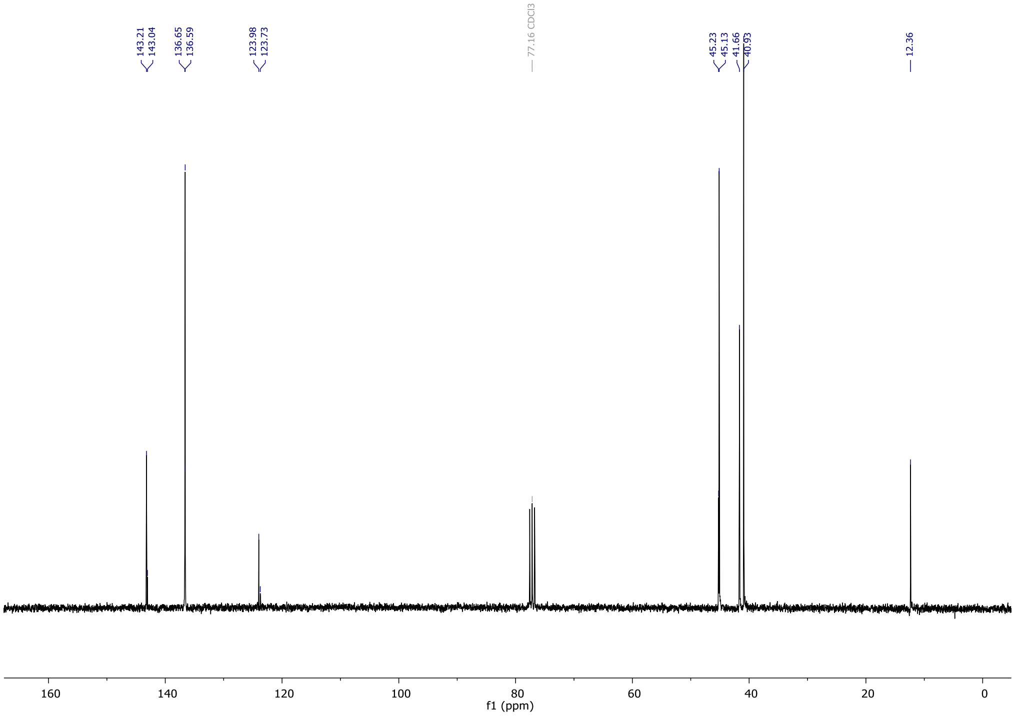


Figure S4. (a) ^{1}H NMR and (b) ^{13}C NMR spectrum of **1**.

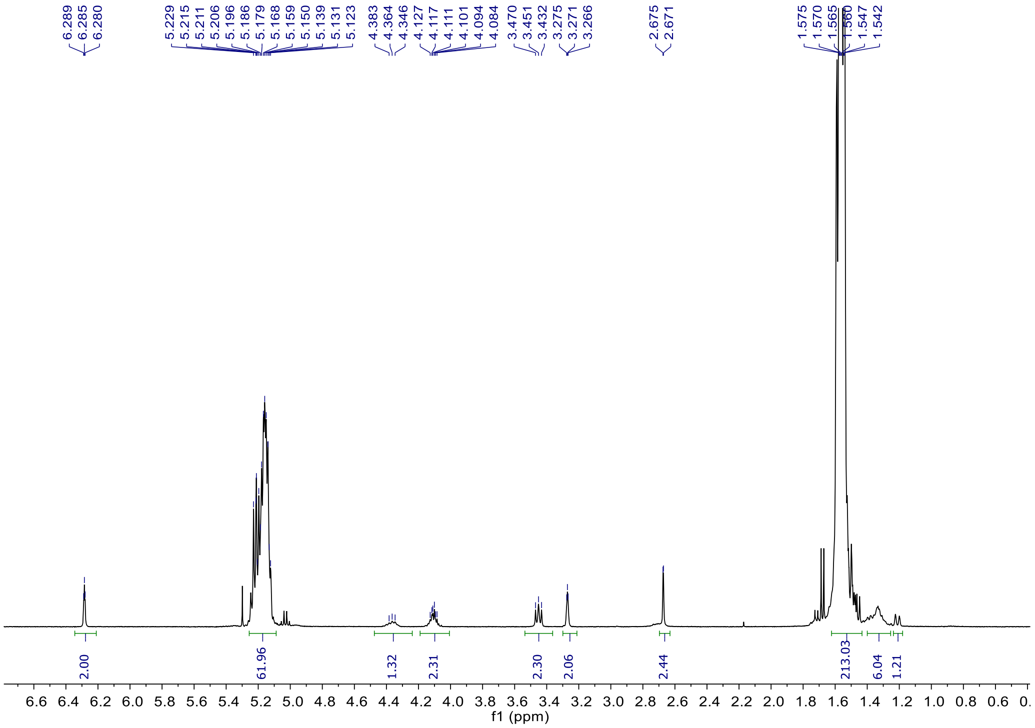


Figure S5. ^{1}H NMR spectrum of PLA-MM.

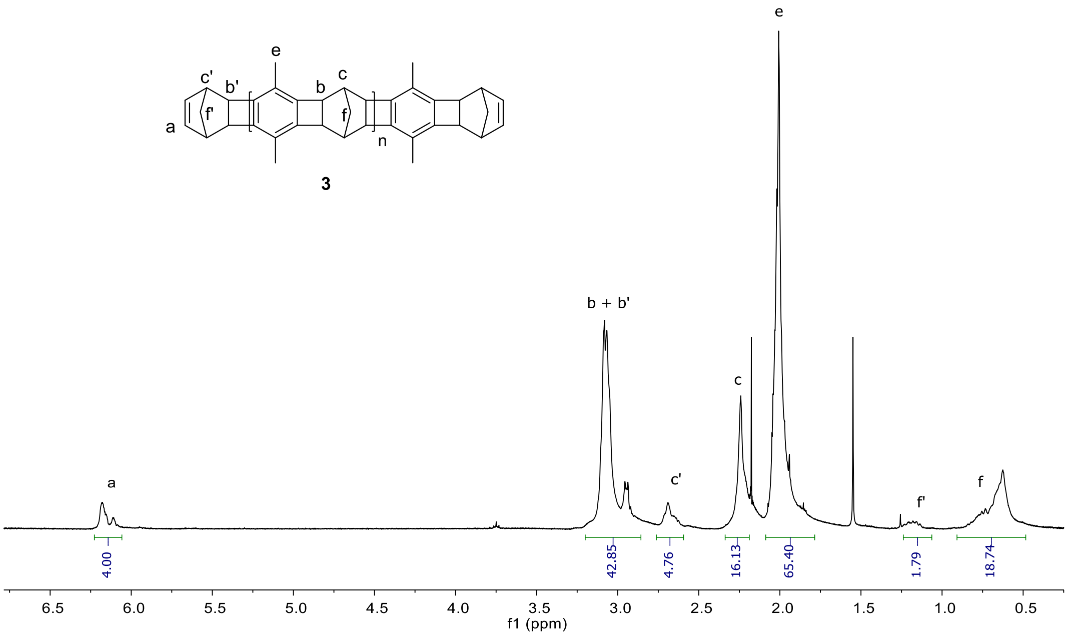


Figure S6. ^{1}H NMR spectrum of **3**.

Representative ^{1}H NMR of star polymer and its arm-degraded core

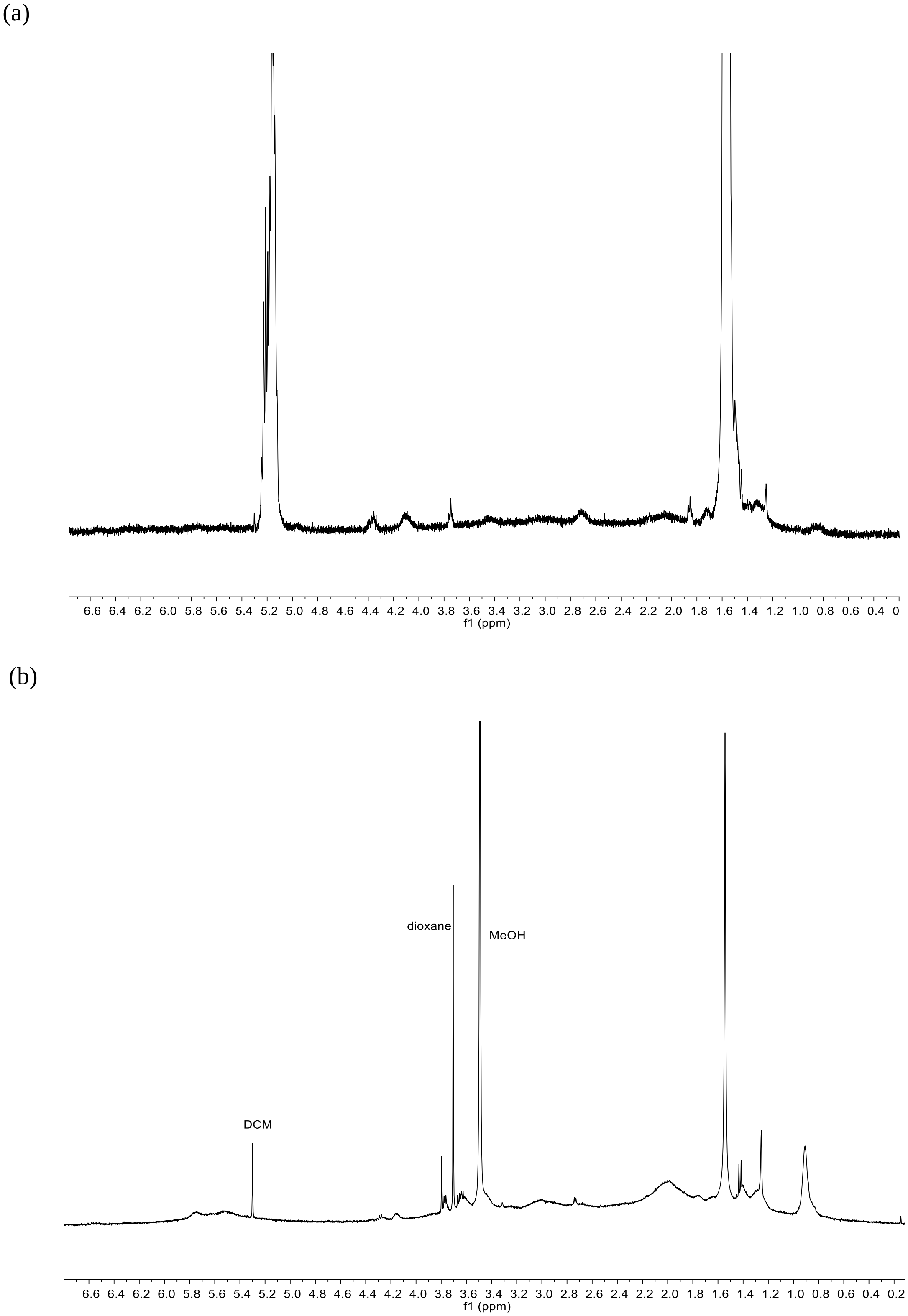


Figure S7. ^{1}H NMR spectra of (a) **S2** and (b) corresponding arm-removed core.

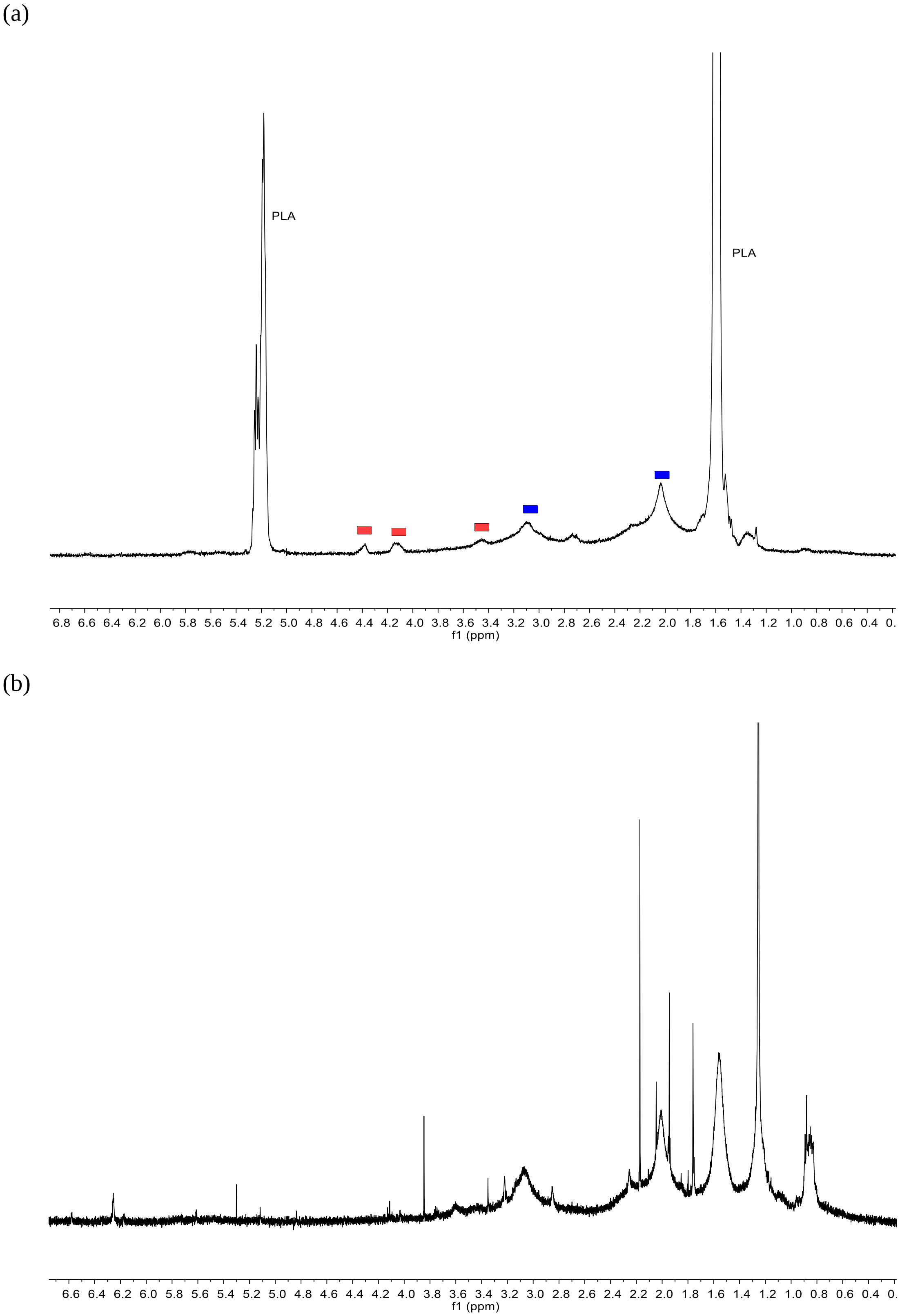


Figure S8. ^{1}H NMR spectra of (a) **S5** showing signals originating from PLA arms (red) and NBE-terminated ladder polymer (blue) and (b) corresponding arm-removed core.

4. References

1. Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H., *Angew. Chem. Int. Ed.* **2002,** *41*, 4035-4037.
2. Teo, Y. C.; Xia, Y., *Macromolecules* **2015,** *48*, 5656-5662.