A Direct Route to Cyclic Organic Nanostructures via Ring-Expansion Metathesis Polymerization of a Dendronized Macromonomer

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SUPPORTING INFORMATION

General Considerations. Cyclic catalysts **SC-5** and **UC-6** and macromonomer **1** were prepared as previously described and stored in a N_2-filled glove-box.[1,2] C_6D_6 was obtained from a solvent purification column[3] and stored in a N_2-filled glove-box. All polymerization reactions were conducted using dry, degassed solvents under N_2 atmosphere. Gel permeation chromatography (GPC) was carried out in THF on two PLgel 10 µm mixed-B LS columns (Polymer Labs) connected in series with a DAWN EOS multiangle laser light scattering (MALLS) detector and an Optilab DSP differential refractometer (both from Wyatt Technology). Molecular weights were determined from light scattering and considered to be absolute. Atomic force microscopy was performed using a Veeco (Digital Instruments) Multimode microscope with a Nanoscope V controller. Imaging was performed in semi-contact (tapping) mode using Veeco RTESP tips. AFM samples were prepared by spin-coating 300 µL of a solution of **P1** in $CHCl_3$ onto freshly cleaved mica at 1000 rpm for 18 s. Sonicated polymer samples were prepared for imaging by sonicating the same **P1** solution used for cyclic imaging for 30 s, and then following the same protocol for cyclic sample preparation.

Representative Polymerization Procedure. In a N_2-filled glove-box, a screw-cap NMR tube was charged with macromonomer **1** (126 mg, 0.14 mmol) and C_6D_6 (0.65 mL). The NMR tube was sealed with a septum-lined screw cap and placed in an oil bath at 55 °C until complete macromonomer dissolution was achieved. A stock solution of cyclic catalyst **SC-5** (0.06 M in C_6D_6) was prepared and 50 µL of this solution was injected into the NMR tube containing **1**. The reaction solution was maintained at 55 °C and monitored by ^1H NMR spectroscopy. Upon completion, the solution was added dropwise into MeOH (15 mL) causing precipitation of polymer **P1**. The product was isolated via vacuum filtration and dried under high vacuum to provide 122 mg (97% yield) of **P1**.

1) Boydston, A. J.; Xia, Y.; Kornfield, J. A.; Gorodetskaya, I. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2008**, *130*, 12775.

2) Rajaram, S.; Choi, T.-L.; Rolandi, M.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2007**, *129*, 9619.

3) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
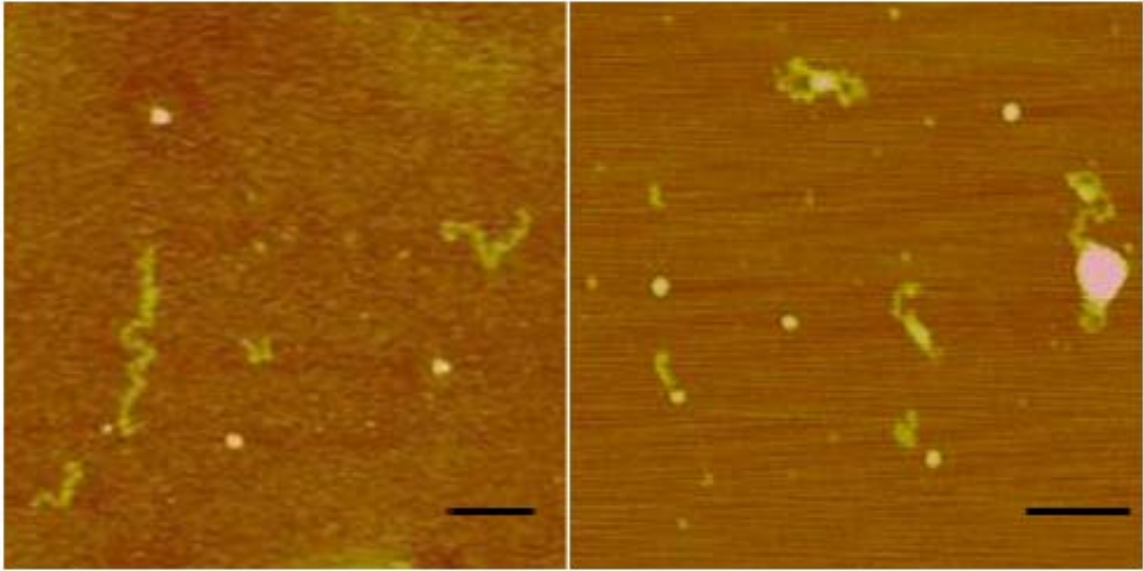
Figure S1. AFM images of **P1**$_{son}$ prepared as described above. Scale bars = 100 nm.