

# Supporting Information

## Synthesis of “Necklace” Polymers by Chain-Walking Polymerization

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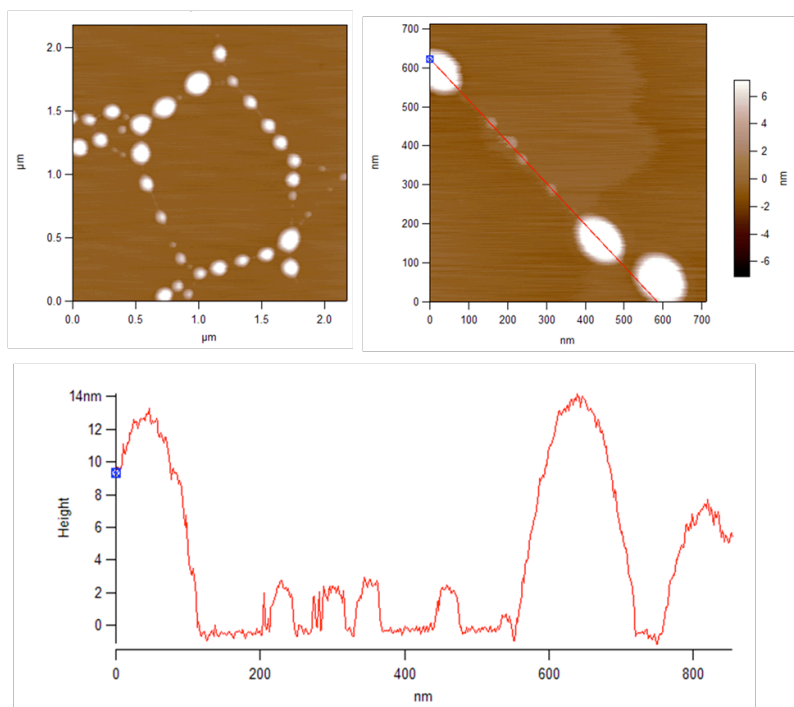
**General Procedure for Synthesis.** NMR spectra were measured on Bruker GN500 and Bruker Cryo500 MHz FT-NMR instruments.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded in ppm and referenced to the indicated deuterium solvents. All NMR data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet), coupling constant(s) in Hertz (Hz) and integration. Multiplets (m) were reported over the range (ppm) where they appeared at the indicated field strength. All the catalyst synthesis and work-up were done in Vacuum Atmosphere glove box charged with nitrogen. All other moisture and air-sensitive reactions were carried out in flame-dried glassware charged with a positive pressure of argon. Removal of all the organic solvents was accomplished by rotary evaporation and is referred to as concentrated *in vacuo*. Chain-walking polymerization follows this procedure: Catalyst was weighed in glove box and added into round-bottom flask, following tight seal by septum before it's taken out from the glove box. Solvent was added using air-tight syringe (chlorobenzene/toluene mixture). The 0.1 atm gas mixture (ethylene / nitrogen = 1/9) was induced into the round-bottom flask and bubbled in the catalyst solution under vigorous stirring at room temperature (20 °C).

**Materials.** All chemicals were purchased from Sigma-Aldrich and used as received. The m-Xylene was degassed by argon bubbling overnight prior to use and sealed under argon. The chlorobenzene was degassed by argon overnight prior to use and stored in glove-box. The anhydrous and oxygen-free toluene and THF was taken from the solvent system before use.

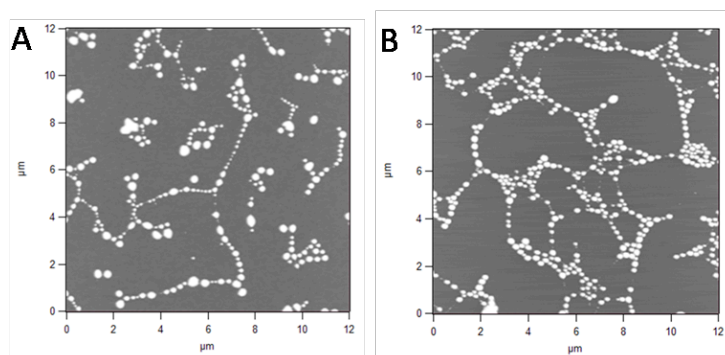
**SEC-MALLS and DLS Characterization of the Polymers.** All of the reported polymers were characterized by size-exclusion chromatography (SEC) in THF (1.0 ml/min) coupled with a multi-angle laser light scattering (MALLS) detector and a Refractometric Index (RI) detector. The RI detector was calibrated with polystyrene standards. Measurements were performed on highly diluted fractions eluting from a SEC consisting of a HP Agilent 1100 solvent delivery system/auto injector with an online solvent degasser, temperature-controlled column compartment. A Dawn DSP 18-angle laser light scattering detector (MALLS, laser wavelength  $\lambda = 632$  nm, Wyatt Technology, Santa Barbara, CA) was coupled to the SEC. A 30 cm column was used (Polymer Laboratories PLgel Mixed C, 5  $\mu$ m particle size) to separate polymer samples at 35 °C. A 60  $\mu$ L of a 2 mg/ml polymer solution was injected into the column. Software ASTRA 4.7 from Wyatt Technology was used to acquire data from the MALLS (dn/dc in THF 0.741). The  $M_w$  and  $M_n$  data were obtained by following classical light scattering treatments.<sup>1</sup> The particle sizes in THF solution by Dynamic Light Scattering (DLS) were measured on Zetasizer Nano Series (Malvern Instrument, Model: ZEN3600) at 25 °C.

**AFM Imaging Study.** Atomic force microscopy (AFM) was performed on a MFP-3D-SA AFM instrument (Asylum Research, Santa Barbara, CA) using silicon tips (type AC240TS) with a spring constant of 2 N·m<sup>-1</sup> at a resonance frequency of 70 kHz. All measurements were carried out in tapping (AC) mode. Samples were prepared by spin-casting polymer solutions (0.01 mg/ml) on freshly cleaved mica.

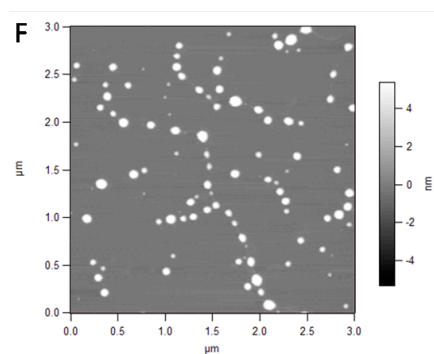
**Figure S1.** Top: AFM images of **DPE-1** spin-cast from heptane (0.01 mg/ml), Bottom: cross-section taken along the red line in the top-right AFM micrograph.



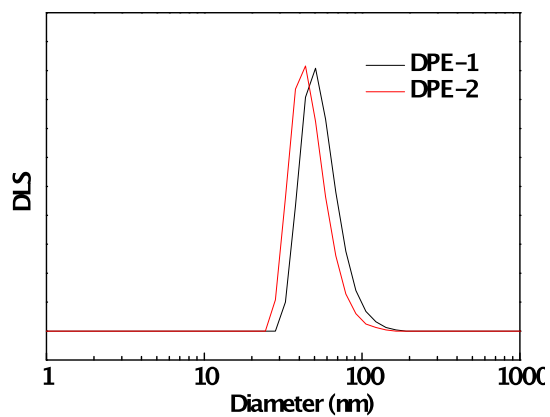
**Figure S2.** AFM images of **DPE-1** spin-cast from different solutions (0.01 mg/ml in heptane (A) and toluene (B)).



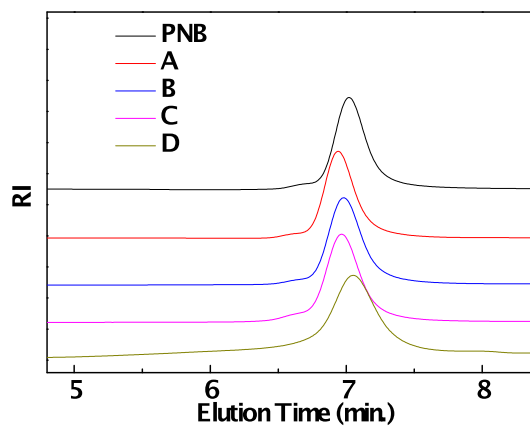
**Figure S3.** AFM image of **DPE 2** spin-cast from heptane solution (0.01 mg/ml).



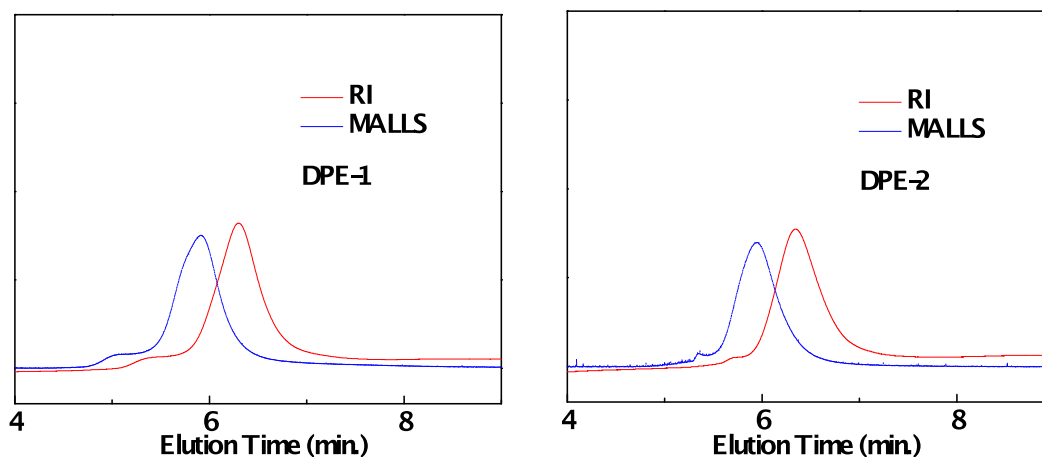
**Figure S4.** DLS (by number average) Graphs of the PE Denpols **DPE-1** and **2**.



**Figure S5.** SEC Graphs (RI detector) of all PNB-based Linear Polymers.

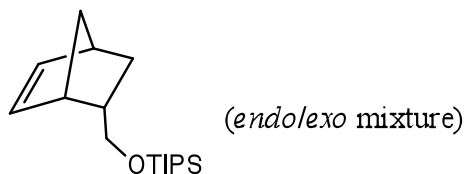


**Figure S6.** SEC Graphs (RI and MALLS detectors) of the PE Denpols **DPE-1** and **2**.



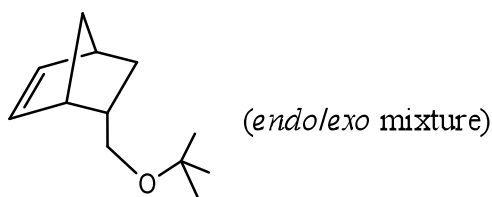
## Synthesis

### Synthesis of the Substituted Norbornenes **TIPS-NB** and **<sup>t</sup>Bu-NB**



To the mixture of Norbornene-2-methanol (mixture of *endo* and *exo*) (2.00 g, 16.1 mmol), TIPSCl (3.41 g, 17.7 mmol), Imidazole (3.29 g, 48.3 mmol) and small amount of DMAP was added 80 ml of DCM. The solution was stirred overnight at r.t. and then concentrated by rotavap. The residue was transferred to the top of a short layer of silica gel and flushed by hexane. The fractions were collected and the solvent was removed *in vacuo*. The resulting oil residue was further dried under high vacuum to afford 4.16 g of the product **TIPS-NB** (yield 92%). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>Cl)  $\delta$ : 6.14-6.08 (m, 1.0H), 6.08-6.00 (m, 0.45H), 5.96-5.90 (m, 0.56H), 3.77 (dd,  $J = 10.0$  Hz, 6.0 Hz, 0.47H), 3.55 (t,  $J = 9.0$  Hz, 0.45 H), 3.45 (dd,  $J = 9.5$  Hz, 6.0 Hz, 0.57H), 3.20 (t,  $J = 9.5$  Hz, 0.57 H), 2.96 (br, 0.57H), 2.83-2.73 (br, 1.44H), 2.35-2.25 (m, 0.55H), 1.8-1.7 (m, 0.57H),

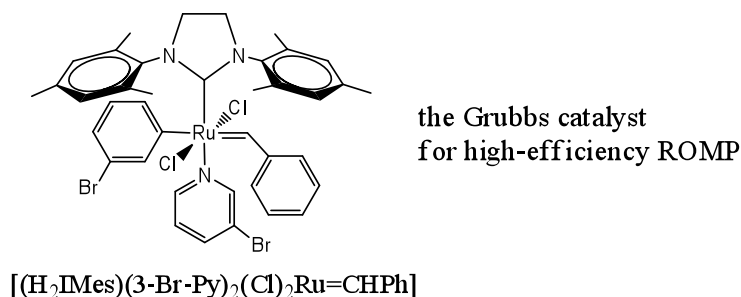
1.68-1.58 (m, 0.46H), 1.40 (m, 0.56H), 1.35-1.15 (m, 2H), 1.15-1.00 (m, 21H), 0.5-0.4 (m, 0.56H). Based on the  $^1\text{H}$  NMR, the ratio of *endo/exo* (or *exo/endo*) is  $\sim 0.80/1$ .  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$ : 136.99, 136.88, 136.71, 132.74, 67.7, 66.9, 49.4, 44.9, 43.77, 43.36, 42.26, 41.86, 41.83, 41.61, 29.23, 28.62, 18.1 (12C), 12.10 (3C), 12.08 (3C). HRMS (EI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{32}\text{OSi}$  ( $\text{M} + \text{H}$ ) $^+$  281.2301, found 281.2298.



To the mixture of Norbornene-2-methanol (mixture of *endo* and *exo*) (0.62 g, 5 mmol) and  $^t\text{Butyl}$ -2,2,2-trichloroacetimidate (1.31 g, 6 mmol) were added 12 ml of dry cyclohexane, followed by addition of  $\text{BF}_3\cdot\text{Et}_2\text{O}$  (0.07 ml). The above mixture was stirred at r.t. for 20 hrs. The reaction was quenched by addition of an excess amount of  $\text{NaHCO}_3$ . The solid residue in the mixture was filtered and the solution was concentrated. The oil residue was passed through a short silica gel column and washed by large amount of hexane. All the elution fractions were collected and the solvent was removed *in vacuo*. The resulting oil was further dried under high vacuum to afford the product  **$^t\text{Bu-NB}$**  (0.66g, yield 74%).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{Cl}$ )  $\delta$ : 6.14-6.08 (m, 1.0H), 6.18-6.00 (m, 2.75H), 5.96-5.86 (m, 1.00H), 3.42 (dd,  $J = 10.0$  Hz, 6.0 Hz, 0.89H), 3.20 (t,  $J = 9.0$  Hz, 0.89 H), 3.08 (dd,  $J = 9.5$  Hz, 6.0 Hz, 1.07H), 2.93-2.82 (m, 2.10H), 2.80-2.70 (m, 2.83H), 2.23 (m, 1.01H), 1.81 (m, 1.03H), 1.58 (m, 0.87H), 1.40 (m, 1.10H), 1.35-1.00 (m, 22.64H), 0.5-0.4 (m, 1.03H). Based on the  $^1\text{H}$  NMR, the ratio of *endo/exo* (or *exo/endo*) is  $\sim 0.84/1$ .  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$ : 137.16, 136.86, 136.60, 132.6, 72.46, 72.34, 66.3, 65.3, 49.4, 44.97, 43.91, 43.69, 42.3, 41.5, 39.55, 39.47, 30.01, 29.46,

27.67 (3C), 27.64 (3C). HRMS (EI)  $m/z$  calcd for  $C_{12}H_{20}O$  ( $M + H$ )<sup>+</sup> 181.1592, found 181.1590.

### General Procedure for the Synthesis of the PNB<sup>2</sup>:



**PNB:** To the mixture of the **TIPS-NB** (28.0 mg, 0.1 mmol) and **<sup>t</sup>Bu-NB** (342.6 mg, 1.9 mmol) were added 3 ml of THF, and then the solution was injected by an air-tight syringe into a pre-cooled solution (-20 °C) of the Grubbs catalyst (4.4. mg, 0.005 mmol in 7 ml of THF). The reaction was run for 30 min. at low temperature (-20 °C) before quenched by ethyl vinyl ether (EVE). The polymer was purified by precipitation in large excess amount of methanol. After being dried under high vacuum, the product was directly used in the next step. SEC (RI):  $M_n$   $2.86 \times 10^5$ ,  $M_w$   $3.20 \times 10^5$ , PDI 1.12.

### General Procedure for the Synthesis of the HPNB (A)<sup>3</sup>:

**A:** The polymer PNB was added into a 50 ml RBF, following the addition of p-Toluenesulfonylhydrazide (1.48 g, 7.9 mmol), tripropylamine (1.51 ml, 7.9 mmol), trace amount of 2, 6-Di-*tert*-butyl-methylphenol (BHT) and 11 ml of xylene. The mixture was refluxed overnight. The reduced polymer was purified by precipitation in large excess amount of methanol and dried under vacuum. Yield 0.20 g. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)



$\delta$ : 3.71-3.45 (m, 0.2 H), 3.45-3.00 (m, 4.7H), 2.12-1.55 (m, 8.6H), 1.53-0.58 (m, 38.6H).

SEC (RI):  $M_n$   $3.31 \times 10^5$ ,  $M_w$   $3.77 \times 10^5$ , PDI 1.14.

**General Procedure for the Synthesis of the HPNB-OH (B):**

**B:** The polymer **A** (0.16 g) was dissolved in 10 ml of THF, to which 1.5 ml of TBAF solution (1M in THF) was added. The mixture was stirred for 2 days at room temperature. The deprotected polymer was purified by precipitation in large excess amount of methanol and dried under vacuum. Yield 0.18 g.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$ : 3.72-3.46 (m, 0.2 H), 3.46-3.00 (m, 7.2H), 2.14-1.62 (m, 13.8H), 1.53-0.59 (m, 47.2H). SEC (RI):  $M_n$   $3.15 \times 10^5$ ,  $M_w$   $3.49 \times 10^5$ , PDI 1.11.

**General Procedure for the Synthesis of the HPNB-BU (C):**

**C:** The polymer **B** (0.18 g) was added into a 50 ml RBF and dissolved in 20 ml of anhydrous THF, followed by the addition of 1, 3, 5-collidine (0.20 ml, 1.5 mmol) and trace amount of phenothiazine. After cooling the solution to 0 °C, 3-butenoyl chloride (0.15 g, 1.5 mmol) dissolved in 5 ml of anhydrous THF was slowly added into the above polymer solution. The mixture was stirred at 0 °C for 0.5 hr, and then warmed up to r.t. for further 4 hrs. The above mixture was filtered and the filtrate was concentrated to one tenth of its volume *in vacuo* and precipitated in large excess of methanol. Yield 0.16 g.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$ : 6.00-5.85 (m, 1 H), 5.22-5.10 (m, 2H), 3.85-4.20 (m, 2H), 3.45-3.00 (m, 24.8H), 2.17-1.62 (m, 47.6H), 1.53-0.58 (m, 163.4H). Based on the  $^1\text{H}$  NMR data, the mole ratio of 3-butenate is 1 per 33.5 unit, which is close to the feeding ratio. SEC (RI):  $M_n$   $3.33 \times 10^5$ ,  $M_w$   $3.73 \times 10^5$ , PDI 1.12.

### General Procedure for the Synthesis of the LMVCWC (**D**):

**D**: The polymer **C** (0.128 g) was added into a 25 ml of RBF, followed by addition of the catalyst precursor **Pd-2** (32.8 mg), NaBAF (51.8 mg) and 12 ml of DCM. The mixture was stirred for 1 day and then filtrated through Celite. It was dried under vacuum to yield 0.20 g of **D**. Since the LMVCWC is polymer and air-sensitive, purification was unsuccessful through the traditional precipitation and no further purification was tried. Because of the peak overlap in the  $^1\text{H}$  NMR, the Pd(II) tethering couldn't be calculated. However, after the complexation,  $^1\text{H}$  NMR shows all the olefin on polymer **C** disappeared, which confirms that all the 3-butenate functionalities reacted with the Pd(II) catalyst for tethering. The catalyst **D** was directly used for polymerization without further purification. SEC (RI):  $M_n$   $2.69 \times 10^5$ ,  $M_w$   $3.68 \times 10^5$ , PDI 1.37.

### General Procedure for the Synthesis of the PE Denpols:

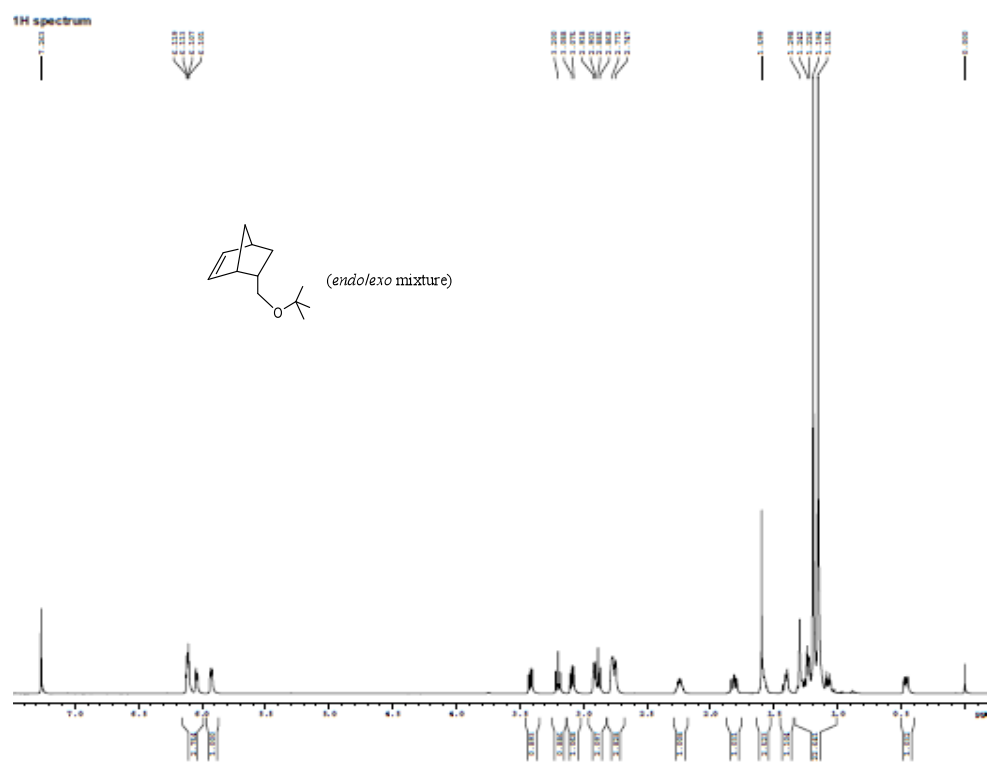
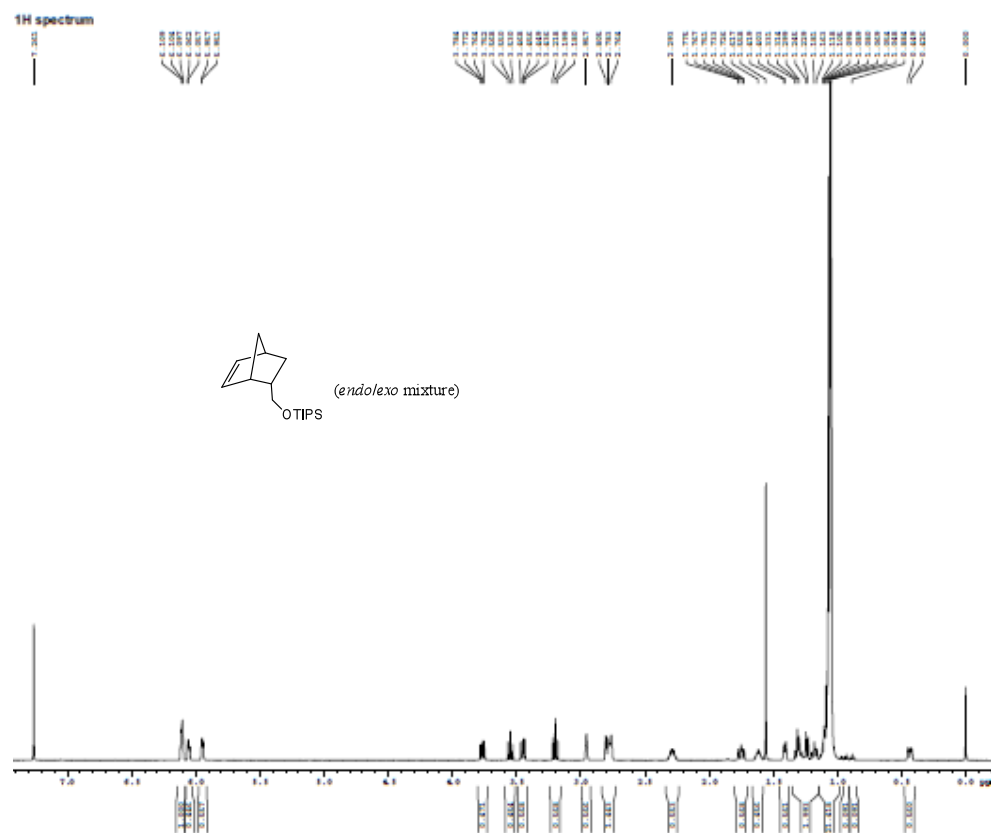
Synthesis of **DPE-1**: The LMVCWC **D** (40 mg) was dissolved in a mixture of 6 ml of chlorobenzene and 12 ml of toluene. The solution was bubbled with 0.1 atm of ethylene under vigorous stirring for 20 hrs. Then the polymerization was quenched by addition of excess amount of  $\text{Et}_3\text{SiH}$ , followed by addition of 50 ml of toluene. The solution was passed through Celite to remove solid residue. After concentrated *in vacuo* to remove the solvent, it was re-dissolved in THF and the crude polymer was purified by gel filtration column using Sepharose CL-2B (Sigma-Aldrich) to yield **DPE-1** (107 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.40-3.00 (m, 2H), 2.15-1.65 (m, 5.05H), 1.40-0.70 (br, 377.1H). SEC-MALLS:  $M_n$   $4.39 \times 10^6$ ,  $M_w$   $4.83 \times 10^6$ , PDI 1.10. Based on the PNB backbone

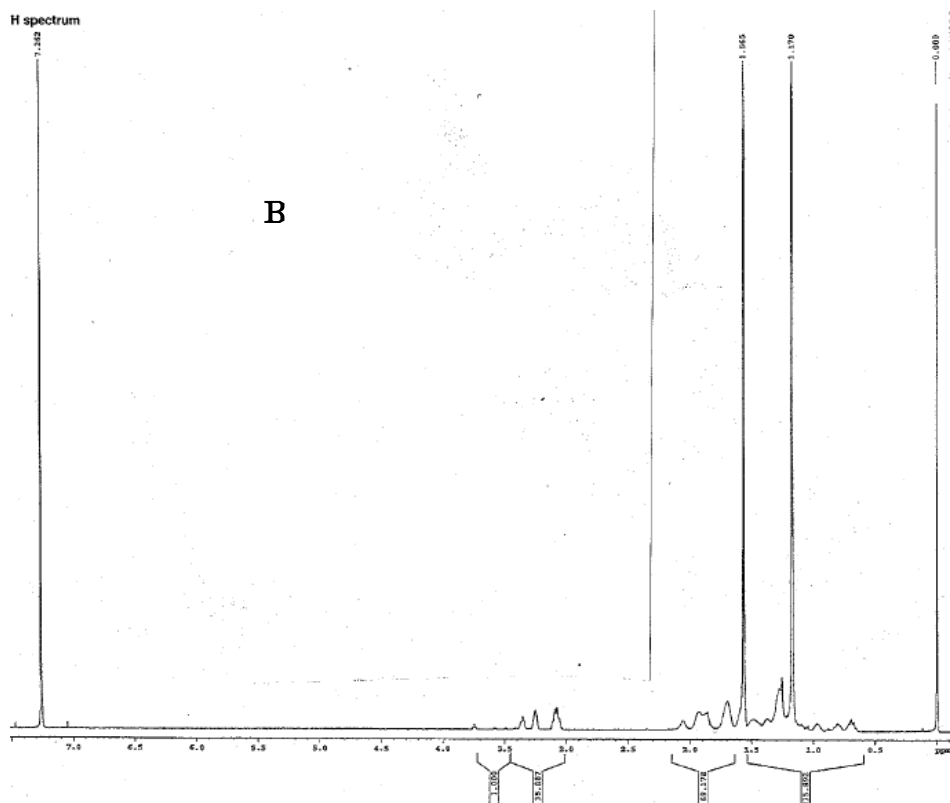
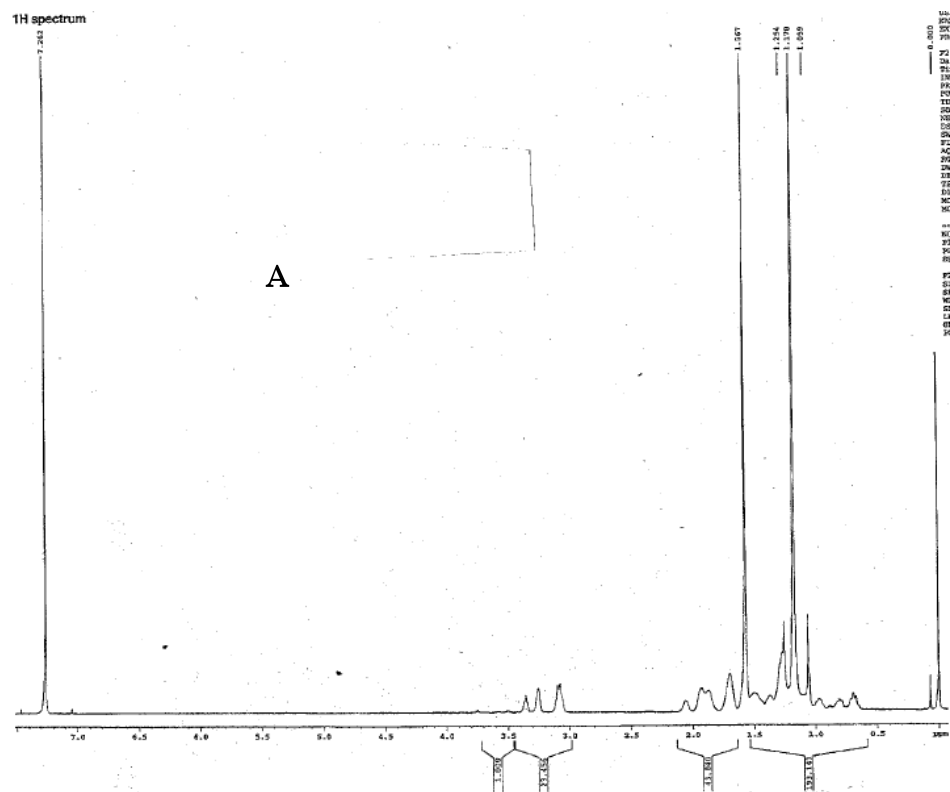
(assume its  $M_n$  is 300K) and the  $^1\text{H}$  NMR, the calculated molecular weight of the **DPE-1** is 4.22 million Dalton. This is very close to the value measured by SEC-MALLS. DLS:  $D_h$  (number average): 56.4 nm.

Synthesis of **DPE-2**: The TBDPS protected 2,2-dimethyl-pent-4-en-1-ol (**T-OH**, 1.27 g, 1.89 mmol) was dissolved in a mixture of 5 ml of chlorobenzene and 10 ml of toluene, followed by addition of 50 mg of the catalyst **D**. The solution was bubbled by 0.1 atm of ethylene under vigorous stirring for 20 hrs. Then the polymerization was quenched by addition of excess amount of  $\text{Et}_3\text{SiH}$ , followed by addition of 50 ml of toluene. The solution was passed through Celite to remove solid residue. After concentrated *in vacuo* to remove toluene, it was re-dissolved in THF and the crude polymer was further purified by gel filtration column using Sepharose CL-2B (Sigma-Aldrich), and totally 147 mg of the polymer **DPE-2** was achieved.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.65 (s, 4H), 7.35 (s, 6H), 3.40-3.19 (m, 2.35H), 3.16-3.01 (m, 0.36), 2.20-1.65 (m, 5.94 H), 1.41-0.71 (br, 87.6H). SEC-MALLS:  $M_n$   $4.55 \times 10^6$ ,  $M_w$   $4.99 \times 10^6$ , PDI 1.10. Based on the  $M_n$  and  $^1\text{H}$  NMR data, calculation shows each denpol contains 4900 TBDPS-protected alcohol groups. Based on the PNB backbone (assume its  $M_n$  is 300K) and the  $^1\text{H}$  NMR, the calculated molecular weight of the **DPE-2** is 4.17 million Dalton. This is very close to the value measured by SEC-MALLS. DLS:  $D_h$  (number average): 47.9 nm.

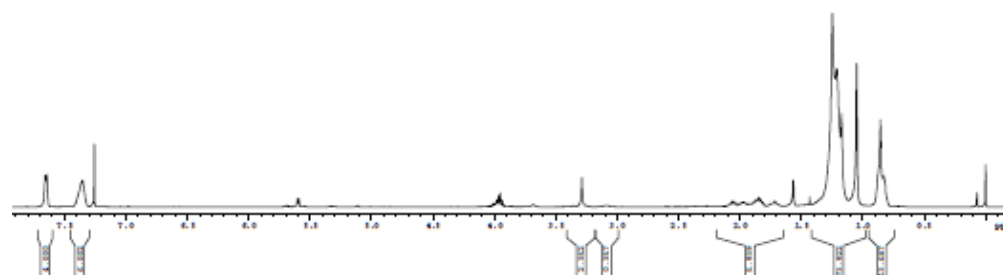
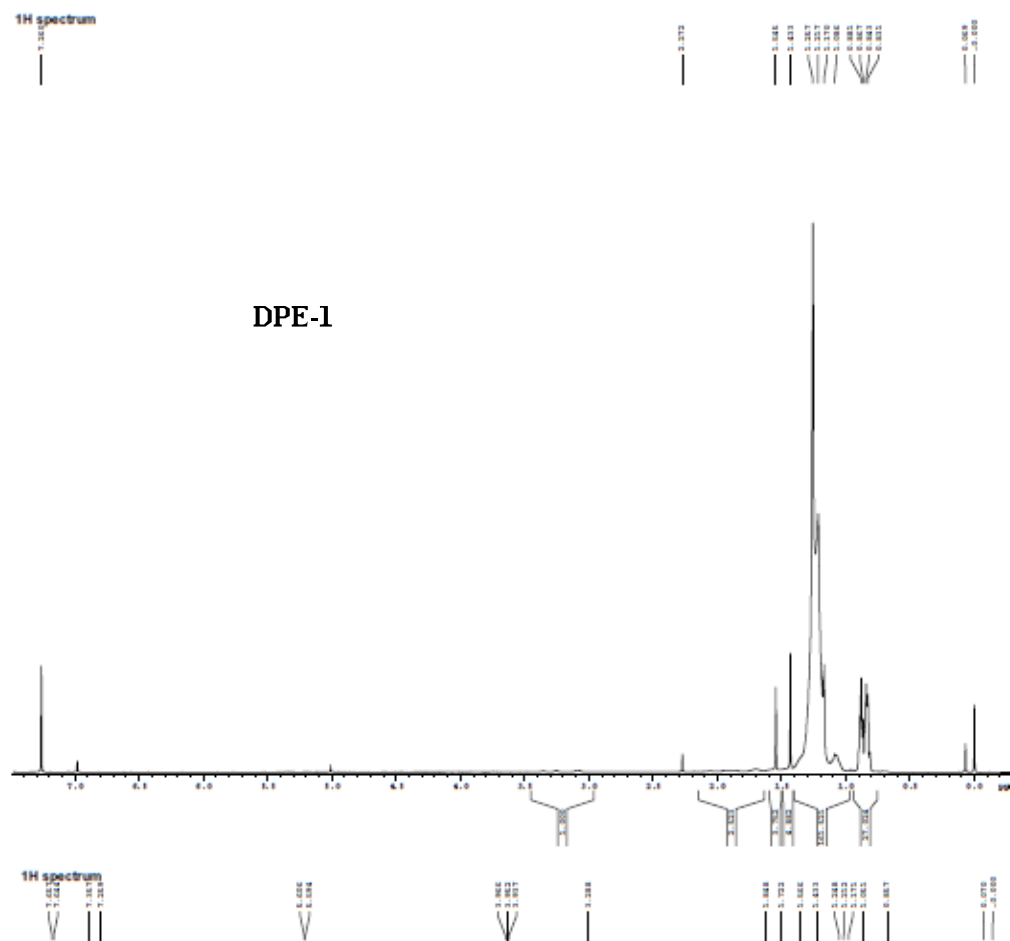
The small peak before the main peak of the purified **DPE-1** and **DPE-2** might come from the inter-chain by-product as described in the paper, however its amount is little compared with the main peak.

# Spectrum









## References:

1. (a) Chen, G.; Ma, X. S.; Guan, Z. *J. Am. Chem. Soc.* **2003**, *125*, 6697–6704. (b) Chen, G., Guan, Z. *J. Am. Chem. Soc.* **2004**, *126*, 2662–2663. (c) Chen, G.; Huynh, D.; Felgner, P. L.; Guan, Z. *J. Am. Chem. Soc.* **2006**, *128*, 4298–4302. (d) Sun, G.; Guan, Z. *Macromolecules* **2010**, *43*, 4829-4832.
2. Choi, T. L.; Grubbs, R. H. *Angew. Chem. Int. Edit.* **2003**, *42* (15), 1743-1746.
3. Katsumata, T.; Shiotsuki, M.; Sanda, F.; Masuda, T. *Polymer* **2009**, *50*, 1389-1394.