

## Supporting Information

### **Molecular Weight Dependence of Zero-Shear Viscosity in Atactic Polypropylene Bottlebrush Polymers**

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## Experimental Details

**Materials.** The following chemicals were purchased from Sigma-Aldrich and used as received: 9-Borabicyclo[3.3.1]nonane (9-BBN; 0.5M in THF), sodium hydroxide, hydrogen peroxide, triethylamine, hydrochloric acid, magnesium sulfate, oxalyl chloride, *exo*-5-norbornenecarboxylic acid ((1*R*,2*S*,4*R*)-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid), Cl<sub>2</sub>(3-BrPy)<sub>2</sub>(H<sub>2</sub>IMes)RuCHPh (**G3**), tetrahydrofuran (THF), toluene, and methanol. Vinyl-terminated atactic polypropylene (aPP) was obtained from ExxonMobil Chemical Company. The received aPP sample ( $M_n=859$  g/mol;  $D=1.88$ ) was precipitated into a large volume of methanol for purification. Precipitation also resulted in the removal of the low molecular weight aPP fractions, yielding a sample with  $M_n=1,750$  g/mol and  $D=1.65$  after precipitation. <sup>1</sup>H NMR spectroscopy after precipitation (500 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 5.81$ ppm (dq, 1H), 5.01ppm (m, 2H), 2.07ppm (m, 1H), 1.89ppm (m, 1H), 0.60 – 1.80ppm (m, 245H).

**Instrumentation.** <sup>1</sup>H NMR spectra were acquired on a Bruker Avance III 500 MHz spectrometer in a CDCl<sub>3</sub> solvent. Size exclusion chromatography (SEC) analysis was performed using an Agilent 1260 Infinity LC system equipped with 3 Waters Styragel columns in series, a Wyatt DAWN Heleos II 18-angle laser light scattering detector, and a Wyatt OPTILAB T-rEX refractive index (RI) detector. SEC samples were analyzed at 25 °C in a THF mobile phase at a flow rate of 1.0 mL min<sup>-1</sup>. Absolute molecular weights of the aPP-NB macromonomer and poly(aPP-NB) samples were determined using the in-line light scattering detector with a  $dn/dc = 0.079$  mL/g.<sup>1</sup> Thermal analysis by differential scanning calorimetry (DSC) was performed using a TA Instruments Discovery DSC apparatus. Samples were first heated to 50 °C (10 °C/min), then slowly cooled to -50 °C (5 °C/min), and finally heated a second time for analysis (5 °C/min). Rheological characterizations of all samples were conducted using a TA Instruments

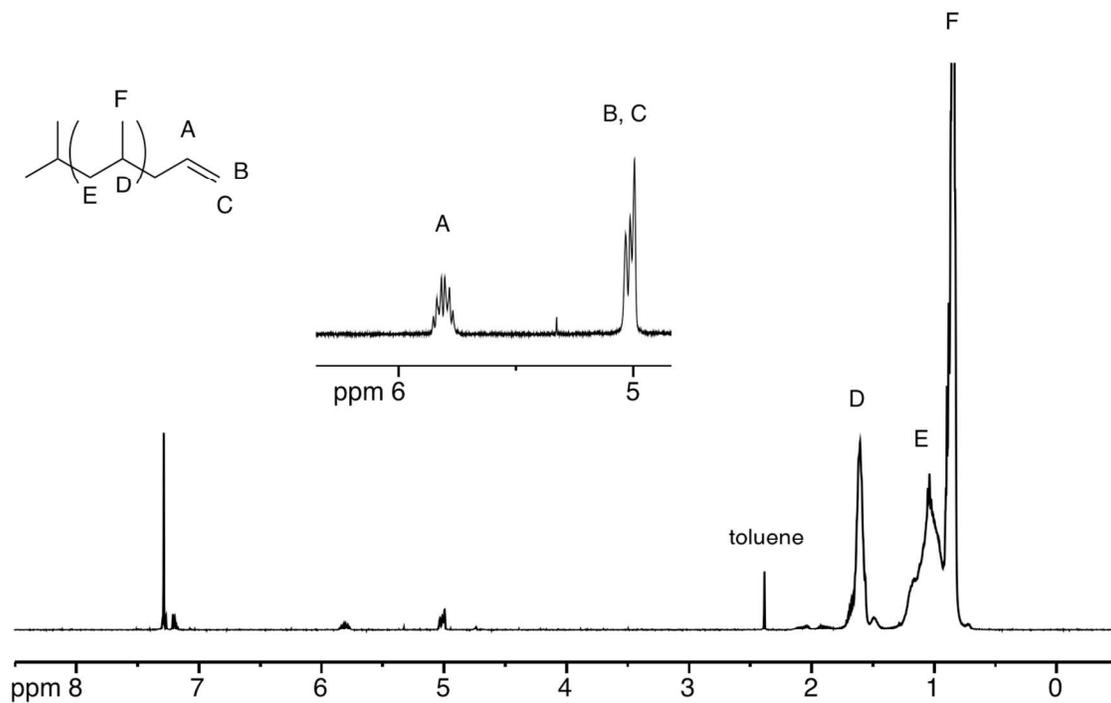
ARES rheometer. Samples were analyzed under nitrogen flow on 8 mm diameter parallel plates. All samples were first submitted to dynamic strain sweep analysis to determine the linear viscoelastic regime of the materials. Small-amplitude oscillatory shear (SAOS) measurements were then carried out at strains low enough to remain within the linear viscoelastic region and a frequency range of 100 – 0.01 rad/s.

**Synthesis of hydroxyl-terminated atactic polypropylene (aPP-OH).** Vinyl-terminated aPP was converted to aPP-OH via consecutive hydroboration/oxidation of the terminal olefin. First, vinyl-terminated aPP (10 g, 5.7 mmol) was dissolved in THF (50 mL) under an argon atmosphere. The solution was cooled to -20 °C before slowly adding a solution of 9-BBN in THF (25 ml, 12.5 mmol). After stirring for 18 hours at room temperature, the solution was again cooled to -20 °C and methanol (5 ml) was added slowly. Aqueous sodium hydroxide (10 ml, 6N) and hydrogen peroxide (14.2 ml, 125 mmol) were then added, and the solution was gradually heated to 40 °C and stirred for 4 hours. The resulting solution was cooled to room temperature, and the solvent was removed by rotary evaporation. The residual polymer was dissolved in chloroform (50 mL), and the solution was washed once with dilute HCl (pH of 5) and three times with deionized water. The chloroform solution was then dried over magnesium sulfate. The product was precipitated into methanol (500 ml) at 0 °C and dried in vacuo. Yield: 8.71 g (87.1%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ = 3.66ppm (t, 2H), 0.60 – 1.80ppm (m, 260H). <sup>1</sup>H NMR spectrum is presented in Figure S2.

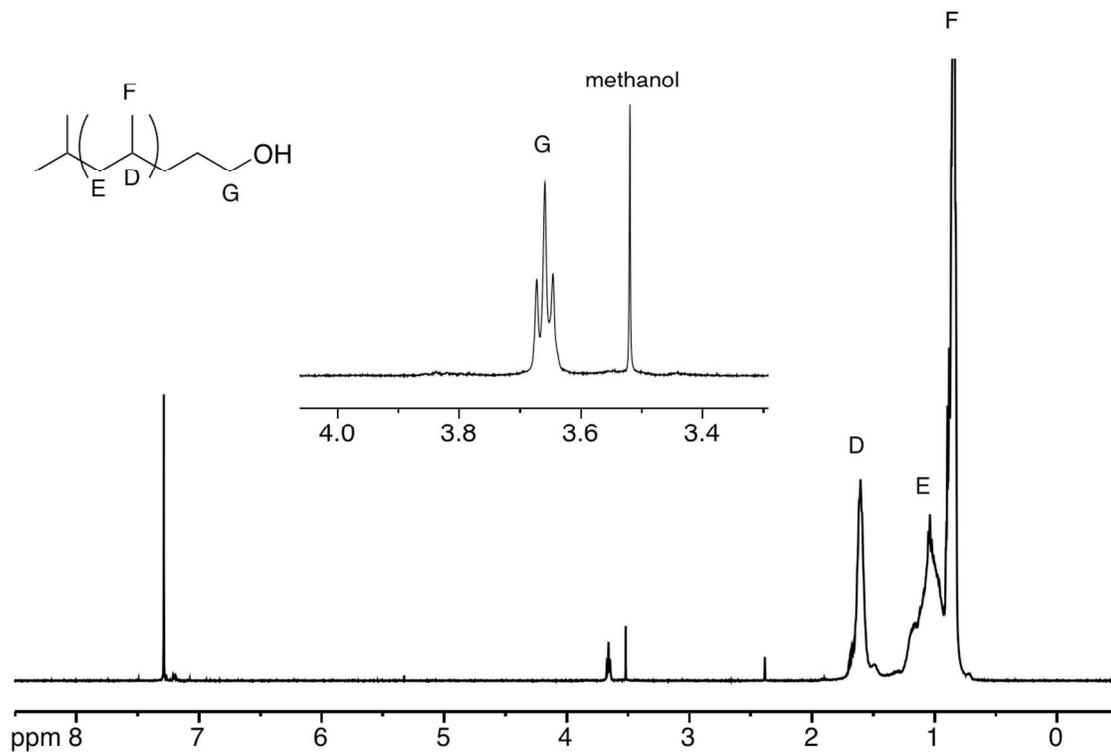
**Synthesis of norbornenyl-functionalized atactic polypropylene (aPP-NB).** *Exo*-5-norbornenecarboxylic acid (10 g, 72 mmol) was dissolved in deoxygenated toluene (50 mL) in a 250-mL round-bottom flask under an argon atmosphere. Oxalyl chloride (6.2 mL, 72 mmol) was slowly added to the solution with constant stirring. Excess pressure in the reaction flask was

relieved from the headspace using a bubbler. The reaction mixture was first stirred at room temperature for 30 minutes, then at 60 °C for one hour and 70 °C for one additional hour before cooling back down to room temperature. Any remaining oxalyl chloride was removed under gentle vacuum along with ~10% of the toluene solvent. In a separate flask triethylamine (10.3 mL, 73.8 mmol), aPP-OH (25.5 g, 13.8 mmol), and toluene (125 mL) were mixed and degassed by consecutive freeze-pump-thaw cycles. This mixture was added to the reaction flask via cannulation. The resulting solution was heated to 100 °C and stirred for 12 hours. The solution was then cooled down to room temperature, and the product was isolated by twice precipitating in copious amounts of methanol. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ = 6.15ppm (m, 2H), 4.09ppm (m, 2H), 3.07ppm (s, 1H), 2.95ppm (s, 1H), 2.25ppm (dd, 1H), 1.95ppm (dt, 1H), 0.60 – 1.80ppm (m, 276H). <sup>1</sup>H NMR spectrum is presented in Figure S3.

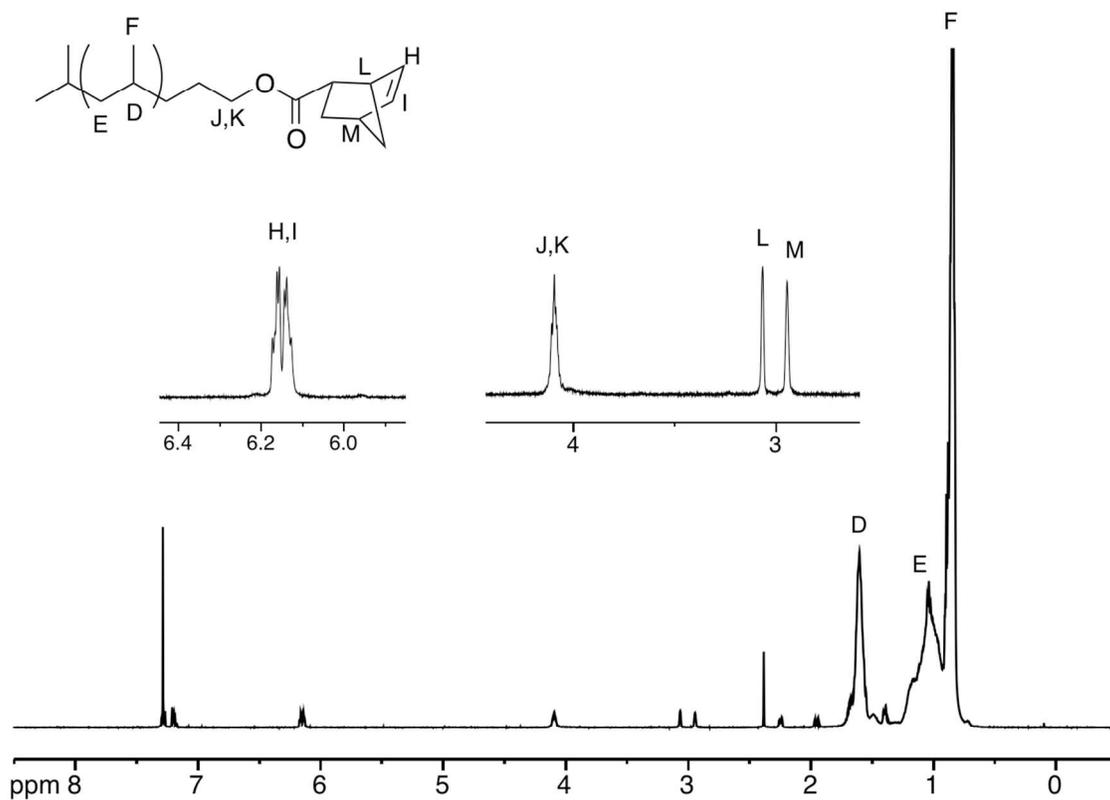
**Ring-opening metathesis polymerization (ROMP) of aPP-NB macromonomers.** In a typical reaction, aPP-NB (200 mg, 0.1 mmol) was added to a 20 mL scintillation vial and dissolved in THF (3 mL). The vial was sealed with a rubber septum and purged with argon gas. In a separate scintillation vial, a stock solution of Grubbs' catalyst in THF was prepared and a portion (1 mL, 0.002 mmol) was added quickly to the aPP-NB solution. The stock solution was used within 2 minutes of its preparation to minimize the amount of catalyst deactivation upon dissolution in solvent. The reaction mixture was quenched with excess ethyl vinyl ether (0.5 mL). The product was purified by precipitation in methanol (250 mL) and dried under vacuum overnight. All steps were carried out at room temperature.



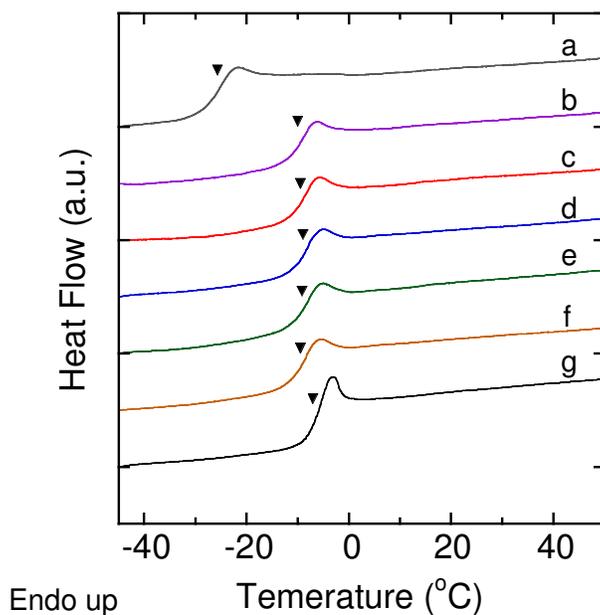
**Figure S1.**  $^1\text{H}$  NMR of vinyl-terminated atactic polypropylene ( $\text{CDCl}_3$ , 500 MHz).



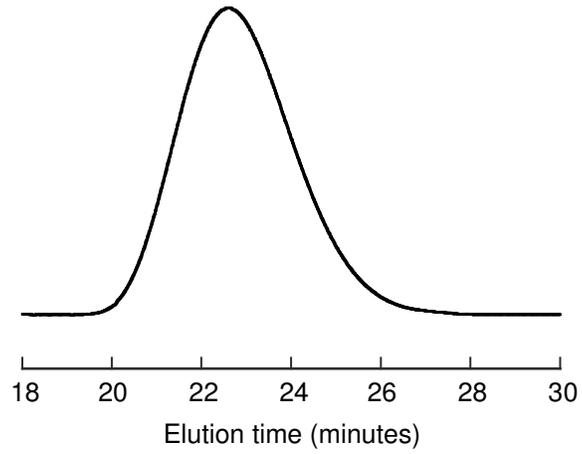
**Figure S2.**  $^1\text{H}$  NMR of hydroxyl-terminated atactic polypropylene (aPP-OH) ( $\text{CDCl}_3$ , 500 MHz).



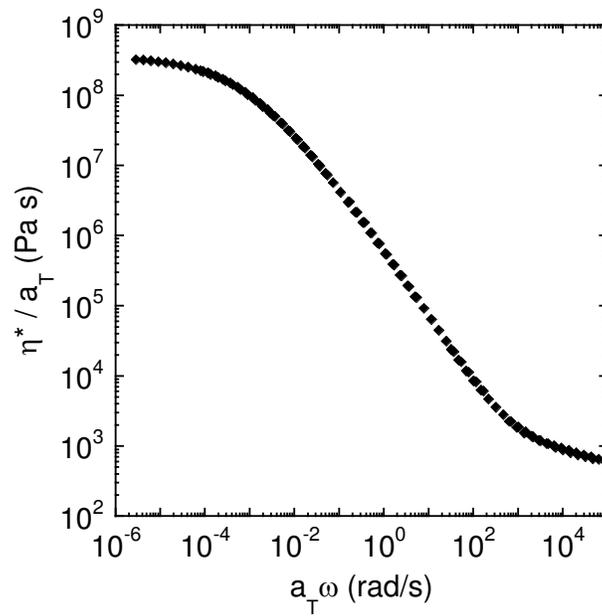
**Figure S3.**  $^1\text{H}$  NMR of norbornenyl-terminated atactic polypropylene (aPP-NB) ( $\text{CDCl}_3$ , 500 MHz).



**Figure S4.** DSC heating curves of (a) aPP-NB, (b) poly(aPP-NB)<sub>11</sub>, (c) poly(aPP-NB)<sub>26</sub>, (d) poly(aPP-NB)<sub>74</sub>, (e) poly(aPP-NB)<sub>215</sub>, (f) poly(aPP-NB)<sub>732</sub> (g) aPP\_Linear. Markers indicate  $T_g$  midpoint values. Curves are second heating scans at  $5\text{ }^\circ\text{C}/\text{min}$ .

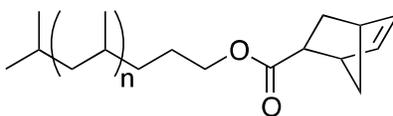


**Figure S5.** SEC trace (RI signal) of aPP\_Linear.



**Figure S6.** Reduced complex viscosity versus reduced frequency master curve of aPP\_Linear at  $T_{\text{ref}} = T_g + 34$  °C.

## Calculation of backbone DP required for bottlebrush L/D = 1



**Figure S7.** Structure of aPP-NB macromonomer.

$M_n = 2050$  g/mol for the aPP-NB macromonomer (Figure S5). Thus,  $n = 43.5$  based on the following calculation:

$$M_n = 2050 = 14(12) + 22(1) + 2(16) + n(42) \Rightarrow n = 43.5$$

If the radius of a bottlebrush is the distance from the end of a side chain to the norbornene ring, and the average two-carbon distance of a fully extended side chain is 0.25 nm, then the bottlebrush radius is:

$$R = 0.25\text{nm} \times (3.5 + n) = 0.25\text{nm} \times (47) = 11.75\text{nm}$$

The brush diameter is:

$$D = 2R = 23.5\text{nm}$$

The backbone of a bottlebrush polymer is poly(norbornene), which contains five carbons per repeat unit in the main chain (or 2.5 two-carbon lengths per repeat unit). The presence of a ring in the main chain is assumed to be negligible in calculating the all-trans, fully extended length. Thus, the average length per backbone repeat unit is estimated:

$$L_{r.u.} = 2.5 \times 0.25\text{nm} = 0.625\text{nm}$$

This is corroborated by Xia *et al.*<sup>2</sup> who calculated a length of 0.62 nm per repeat unit of bottlebrush polymers with poly(norbornene) backbones based on atomic force microscopy results. To achieve a backbone length (L) equal to the brush diameter (L/D=1), the backbone DP would be:

$$DP = \frac{L}{L_{r.u.}} = \frac{L}{0.625\text{nm}} = \frac{D}{0.625\text{nm}} = \frac{23.5\text{nm}}{0.625\text{nm}} = 37.6$$

## Calculation of critical molecular weight for linear aPP

The critical molecular weight for entanglements ( $M_c$ ) was estimated using the empirical relationship:

$$M_c = 3.42M_e p^{-0.534}$$

where  $M_e$  is the entanglement molar mass and  $p$  is the packing length. Literature values of  $M_e=4390$  g/mol and  $p = 2.88$  Å for atactic polypropylene yield  $M_c = 8534$  g/mol.<sup>3</sup>

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<sup>1</sup> Xu, Z.; Mays, J.; Chen, X.; Hadjichristidis, N.; Schilling, F.; Bair, H.; Pearson, D. S.; Fetters, L. J. *Macromolecules* **1985**, *18*, 2560–2566.

<sup>2</sup> Xia, Y.; Kornfield, J.A.; Grubbs, R.H. *Macromolecules* **2009**, *42*, 3761–3766.

<sup>3</sup> Fetters, L. J.; Lohse, D. J.; Colby, R. H. In *Physical Properties of Polymers Handbook*; Mark, J., Ed.; Springer: New York, 2007; 447–454.