

# Branch-Induced Heterogeneous Chain Motion in Precision Polyolefins

**(Supporting Information)**

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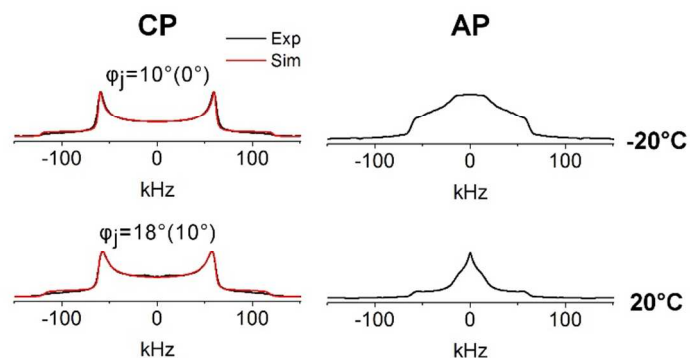
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## Instrumentation

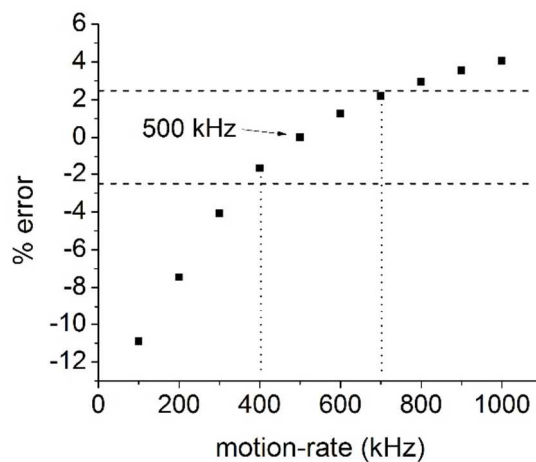
All NMR ( $^1\text{H}$ , 300MHz and  $^{13}\text{C}$ , 75 MHz) spectra were recorded in  $\text{CDCl}_3$  at room temperature and referenced to the corresponding residual signals ( $\text{CDCl}_3$ :  $^1\text{H}$  at 7.24 ppm,  $^{13}\text{C}$  at 77.23 ppm). High-resolution mass spectrometry was carried out in a Thermo Scientific Trace DSQ GC-MS spectrometer. Elemental analysis was performed by combustion using automatic analyzer. Gel permeation chromatography (GPC) was performed using an Agilent 1100 Series HPLC System (THF, 30°C) equipped with internal differential refractive index detector. Retention times were calibrated versus polystyrene standards. Differential Scanning Calorimetry (DSC) analyses were performed on a TA Instruments Q1000 calorimeter. All the analyses were obtained under He purge at a rate of  $10^\circ\text{C}\cdot\text{min}^{-1}$  with samples prepared in hermetically sealed pans. Samples were analyzed from  $-80^\circ\text{C}$  to  $300^\circ\text{C}$  with 5 minutes isothermal steps at the temperature extremes for each cycle. The data used in this work were obtained from the last of the three heating cycles performed. Calibration was performed with indium as the standard for both the heats of fusion and peak temperature transitions. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q5000 analyzer. All samples were analyzed with a temperature range from room temperature to  $650^\circ\text{C}$  in nitrogen at  $20^\circ\text{C}/\text{minutes}$  with a purge rate of 20 mL/min.



**Figure S1.** Experimental and simulated CP/AP lineshapes of PE21-D<sub>2</sub> at -20°C and 20°C.

Simulation assumed the fast-motion regime at 20°C and 500 kHz motion-rate at -20°C.

The 500 kHz motion-rate used in the simulation of PE21-D<sub>2</sub> at -20°C (Figure S1) allows certain variation. The figure below shows the % error obtained for different motion-rates.



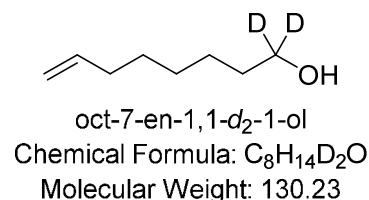
**Figure S2.** Signal intensity % error obtained when different motion-rates are considered. Values are relative to the signal intensity at the center of the pattern. Dashed lines define a  $\pm 2.5\%$  error limit.

## Materials

Chemical reagents used in this work were purchased from Sigma-Aldrich Co. and used as received, unless specified otherwise. Hexamethylphosphoramide, *tert*-butanol and propionitrile were distilled over CaH<sub>2</sub>. Dry solvents (tetrahydrofuran, dichloromethane, diethyl ether and toluene) were obtained from the Butler Laboratories' Solvent Purification System. Schrock's catalyst, 2,6-Diisopropylphenylimidoneophylidene molybdenum(VI) bis(hexafluoro-*t*-butoxide), was purchased from Strem Chemicals, Inc.

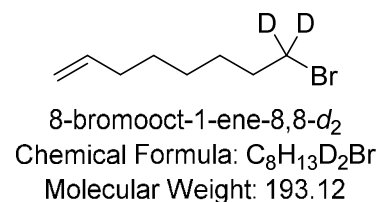
### 1 - Synthesis of deuterated spacer bromides

#### Oct-7-en-1,1-*d*<sub>2</sub>-1-ol (1a)



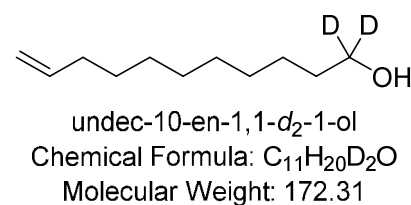
A solution of oct-7-enoic acid (5g, 35.2 mmol, 1 equivalent) in THF (30 mL) was slowly added into a flame-dried round-bottom flask containing lithium aluminum deuteride (LAD) dissolved in THF (1 mol.L<sup>-1</sup>, 49.2 mL, 1.4 equivalents). The temperature of the LAD solution was kept at 0°C during the addition of the acid. The reaction was allowed to proceed at room temperature under argon atmosphere and followed by TLC (thin layer chromatography). After one hour, the reaction mixture was quenched with 2 mL of deionized water (DIW), 2 mL of NaOH solution (15% w/v) and 6 mL of DIW, in that order. The mixture was filtered and concentrated to an oil which was subsequently dissolved in ether. The solution was dried over MgSO<sub>4</sub> for 45 minutes and filtered prior to evaporation. A white solid was obtained (4.35 g, 95%). No further purification was necessary. <sup>1</sup>H NMR (300 MHz, CHLOROFORM-*d*) δ ppm 1.17 - 1.45 (br, 6H) 1.54 (t, 2H, *J*=5.8 Hz) 2.04 (q, 2H, *J*=6.90 Hz) 4.84 - 5.08 (m, 2 H) 5.69 - 5.94 (ddt, 1H, *J*=16.90, 10.10, 6.60 Hz). <sup>13</sup>C NMR (75 MHz, CHLOROFORM-*d*) δ ppm 25.6, 28.92, 29.11, 29.41, 29.54, 32.58, 33.80, 114.06, 139.17. CG/CI-MS: [M+1]<sup>+</sup> calculated for C<sub>8</sub>H<sub>14</sub>D<sub>2</sub>O, m/z 131.1405; found m/z 131.1405. Elemental Analysis: calculated for C<sub>8</sub>H<sub>14</sub>D<sub>2</sub>O: C, 73.76; (H+D), 12.41. Found: C, 73.94; (H+D), 12.40.

### 8-bromooct-1-ene-8,8-*d*<sub>2</sub> (**1b**)



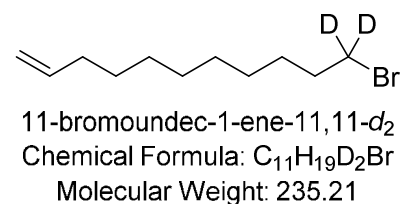
A solution of **1a** (4.36 g, 33.48 mmol) and CBr<sub>4</sub> (12.10 g, 36.49 mmol) in dichloromethane (15 mL) was prepared in a 50 mL round bottom flask equipped with a magnetic stirrer. This solution was cooled and maintained at 0°C in an ice bath. Triphenylphosphine (9.66 g, 36.83 mmol) was added to the cold solution in small portions through a powder funnel. After addition of the triphenylphosphine, the pale brown reaction mixture was stirred for an additional 2 hours at room temperature. The crude was then quickly poured into stirring hexanes. The precipitated solid was filtered and the liquid obtained was concentrated and purified by column chromatography and distilled under reduced pressure. Compound **1b** was obtained as a clear liquid (3.51 g, 54%). <sup>1</sup>H NMR (300 MHz, CHLOROFORM-*d*) δ ppm 1.22 - 1.53 (br, 6H) 1.85 (t, 2H, *J*=6.8 Hz) 1.96 - 2.18 (q, 2H, *J*=6.9 Hz) 4.83 - 5.15 (m, 2H) 5.65 - 6.01 (ddt, 1H, *J*<sub>1</sub>=16.9, *J*<sub>2</sub>=10.1, *J*<sub>3</sub>=6.7 Hz). <sup>13</sup>C NMR (75 MHz, CHLOROFORM-*d*) δ ppm 27.95, 28.22, 28.67, 32.52, 33.64, 114.35, 138.83. CG/CI-MS: [M]<sup>+</sup> calcd for C<sub>8</sub>H<sub>12</sub>D<sub>2</sub>Br, 192.0483; found 192.0483. Elemental Analysis: calcd for C<sub>8</sub>H<sub>13</sub>D<sub>2</sub>Br: C, 49.75; (H+D), 7.84. Found: C, 49.85; (H+D), 7.68.

### Undec-10-en-1,1-*d*<sub>2</sub>-1-ol (**1c**)



Zinc undecylenate (18.89 g, 43.8 mmol) was slowly added through a powder funnel into a LAD solution in THF (1M, 50 mL) at 0°C. The mixture was allowed to warm to room temperature and kept stirring under argon for one hour. The reaction was quenched with 2 mL of deionized water, 2 mL of NaOH 15% (w/v) and 6 mL deionized water in that order with 10 minutes intervals between each addition. The crude mixture was filtered and concentrated. The oil obtained was dissolved in ether and dried over MgSO<sub>4</sub> for 45 minutes. The product was purified by column chromatography. A white solid was obtained (12.38 g, 82.1%). <sup>1</sup>H NMR (300 MHz, CHLOROFORM-*d*) δ ppm 1.30 (br., 12H) 1.55 (t, 2H, *J*=6.1 Hz) 2.04 (q, 2H, *J*=6.7 Hz) 4.85 - 5.08 (m, 2H) 5.70 - 5.93 (ddt, 1H, *J*<sub>1</sub>=17.1, *J*<sub>2</sub>=10.4, *J*<sub>3</sub>=6.7 Hz). <sup>13</sup>C NMR (75 MHz, CHLOROFORM-*d*) δ ppm 25.67, 28.90, 29.09, 29.40, 29.53, 32.54, 33.78, 114.05 (vinyl CH<sub>2</sub>), 139.14 (vinyl CH). CG/CI-MS: [M+H]<sup>+</sup> calcd for C<sub>11</sub>H<sub>21</sub>D<sub>2</sub>O, 173.1874; found 173.1882. Elemental Analysis: calcd for C<sub>11</sub>H<sub>20</sub>D<sub>2</sub>O: C, 76.68; (H+D), 12.89. Found: C, 76.57; (H+D), 12.76

### 11-bromoundec-1-ene-11,11-*d*<sub>2</sub> (**1d**)

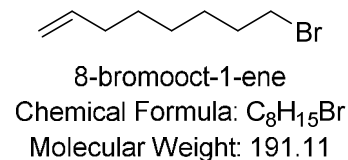


The synthesis followed the same procedure used for **1b**. Compound **1d** was prepared from a solution of **1c** (6.00 g, 34.82 mmol) and CBr<sub>4</sub> (12.59 g, 37.59 mmol) in dichloromethane (15

mL). Compound **1d** was obtained as a clear liquid (6.15 g, 75%).  $^1\text{H}$  NMR (300 MHz, CHLOROFORM-*d*)  $\delta$  ppm 1.19 - 1.51 (m, 12H) 1.77 - 1.91 (t, 2H,  $J=7.4$  Hz) 2.05 (q, 2H,  $J=6.7$  Hz) 4.86 - 5.08 (m, 2H) 5.73 - 5.93 (ddt, 1H,  $J_1=16.9$ ,  $J_2=10.4$ ,  $J_3=6.7$  Hz).  $^{13}\text{C}$  NMR (75 MHz, CHLOROFORM-*d*)  $\delta$  ppm 28.11, 28.75, 28.90, 29.08, 29.37, 32.59, 33.79, 114.11, 139.13. CG/CI-MS:  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{11}\text{H}_{19}\text{D}_2\text{Br}$ , 234.0952; found 234.0954. Elemental Analysis: calcd for  $\text{C}_{11}\text{H}_{19}\text{D}_2\text{Br}$ : C, 56.16; (H+D), 9.02; Br, 33.97. Found: C, 56.21; (H+D), 8.81; Br, 33.80.

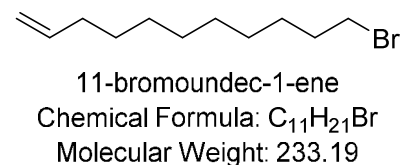
## 2 - Synthesis of non-deuterated spacer bromides

### 8-bromooct-1-ene (2a)



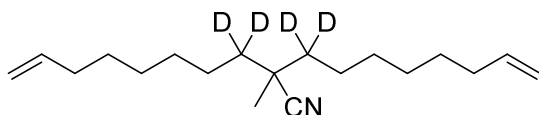
A 1M solution of 1,8-dibromooctane (100 g, 0.367 mol) using 1:1 THF:Toluene as the solvent was added to a round bottom flask and cooled to  $0^\circ\text{C}$ . Potassium *tert*-butoxide (61.88, 0.551 mol) was added in small portions over 30 minutes. After the addition, the reaction was quenched with 1M HCl. The mixture was extracted with ether and washed with saturated  $\text{Na}_2\text{CO}_3$ . The organic layer was then dried over  $\text{MgSO}_4$ , concentrated and distilled. Compound **2a** was obtained as a clear liquid (50 g, 71%).  $^1\text{H}$  NMR (300 MHz, CHLOROFORM-*d*)  $\delta$  ppm 1.21 - 1.53 (m, 6 H) 1.87 (quin, 2 H) 2.06 (q, 2 H) 3.42 (t, 2 H) 4.88 - 5.11 (m, 2 H) 5.81 (ddt, 1 H).  $^{13}\text{C}$  NMR (75 MHz, CHLOROFORM-*d*)  $\delta$  ppm 28.23, 28.44, 28.90, 32.98, 33.87, 34.20, 114.57, 139.05. CG/CI-MS:  $[\text{M}]^+$  calcd for  $\text{C}_8\text{H}_{15}\text{Br}$ , 190.0357; found 190.0351. Elemental Analysis: calcd for  $\text{C}_8\text{H}_{15}\text{Br}$ : C, 50.28; H, 7.91; Br, 41.81. Found: C, 50.38; H, 7.97; Br, 41.57.

### 11-bromoundec-1-ene (2b)



The synthesis followed the same procedure used for **1b**. Compound **2b** was prepared from a solution of 10-undecen-1-ol (100 g, 0.587 mol) and  $\text{CBr}_4$  (212.8 g, 0.639 mol) in dichloromethane (250 mL). Compound **2b** was obtained as a clear liquid (50 g, 36%).  $^1\text{H}$  NMR (300 MHz, CHLOROFORM-*d*)  $\delta$  ppm 1.18 - 1.52 (br, 12H) 1.86 (quint, 2H,  $J=7.1$  Hz) 2.05 (q, 2H,  $J=6.86$  Hz) 3.42 (t, 2H,  $J=6.86$  Hz) 4.86 - 5.09 (m, 2H) 5.74 - 5.92 (ddt, 1H,  $J_1=16.94$ ,  $J_2=10.2$ ,  $J_3=6.7$  Hz).  $^{13}\text{C}$  NMR (75 MHz, CHLOROFORM-*d*)  $\delta$  ppm 28.17, 28.75, 28.91, 29.08, 29.37, 32.83, 33.79, 34.06, 114.11, 139.14. CG/CI-MS:  $[\text{M}]^+$  calcd for  $\text{C}_{11}\text{H}_{21}\text{Br}$ , 232.0827; found 232.0819. Elemental Analysis: calcd for  $\text{C}_{11}\text{H}_{21}\text{Br}$ : C, 56.66; H, 9.08; Br, 34.27. Found: C, 56.92; H, 9.21; Br, 34.40.

### 3 - Synthesis of pre-monomers



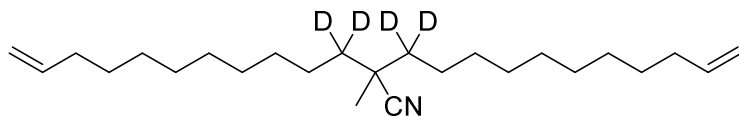
2-methyl-2-(oct-7-en-1-yl-1,1- $d_2$ )dec-9-enenitrile-3,3- $d_2$   
Chemical Formula:  $C_{19}H_{29}D_4N$   
Molecular Weight: 279.50

#### **2-methyl-2-(oct-7-en-1-yl-1,1- $d_2$ )dec-9-enenitrile-3,3- $d_2$ (**3a**)**

A solution of propionitrile (0.41 g, 7.44 mmol) in THF (10 mL) was prepared in a flame-dried three-necked round-bottomed flask equipped with a stir bar and argon inlet adaptor. The solution was cooled to  $-78^\circ\text{C}$  and 5 mL of lithium diisopropylamine

(LDA) solution in THF ( $2\text{ mol}\cdot\text{L}^{-1}$ ) was added. The temperature of the mixture was increased and maintained at  $0^\circ\text{C}$  for 45 minutes. After that, the reaction was cooled to  $-78^\circ\text{C}$  and **1b** (1.76 g, 9.08 mmol) was added. The temperature was increased to  $0^\circ\text{C}$  and maintained at this temperature for another 45 minutes. A second 5 mL portion of the LDA solution was added at  $-78^\circ\text{C}$ . The temperature was increased and maintained at  $0^\circ\text{C}$  for 45 minutes. The temperature was returned to  $-78^\circ\text{C}$  and **1b** (1.76 g, 9.08 mmol) was added. The reaction mixture was warmed to  $0^\circ\text{C}$  for 30 minutes and proceeded overnight at room temperature. The reaction was quenched with deionized water, extracted with ether and dried over  $\text{MgSO}_4$ . The crude was concentrated and purified by flash-column chromatography. Compound **3a** was obtained as pale yellow liquid (6.26 g, 81.3%).  $^1\text{H}$  NMR (300 MHz,  $\text{CHLOROFORM-}d$ )  $\delta$  ppm 1.05 - 1.55 (br, 19 H) 2.05 (q, 4H,  $J=6.1$  Hz) 4.78 - 5.11 (m, 4H) 5.63 - 6.08 (ddt, 2H,  $J_1=16.9$ ,  $J_2=10.1$ ,  $J_3=6.6$  Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CHLOROFORM-}d$ )  $\delta$  ppm 24.10, 24.80, 29.02, 29.12, 29.73, 33.94, 36.60, 114.49, 124.91, 139.16. CG/CI-MS:  $[\text{M}+\text{H}]^+$  calcd for  $C_{19}H_{30}D_4N$ , 280.2942; found 280.2949. Elemental Analysis: calcd for  $C_{19}H_{29}D_4N$ : C, 81.65; (H+D), 11.92; N, 5.01. Found: C, 81.62; (H+D), 12.00; N, 4.86.

#### **2-methyl-2-(undec-10-en-1-yl-1,1- $d_2$ )tridec-12-enenitrile-3,3- $d_2$ (**3b**)**



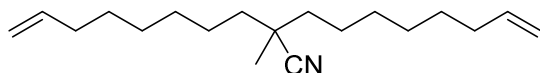
2-methyl-2-(undec-10-en-1-yl-1,1- $d_2$ )tridec-12-enenitrile-3,3- $d_2$   
Chemical Formula:  $C_{25}H_{41}D_4N$   
Molecular Weight: 363.67

The synthesis followed the same procedure used for **3a**. Compound **3b** was prepared from a solution of propionitrile (0.151 g, 2.75 mmol) in THF (2.75 mL),  $2\text{ mol}\cdot\text{L}^{-1}$  LDA solution in THF (3.36 mL, 6.71 mmol) and **1d** (1.58 g, 6.71 mmol).

Compound **3b** was obtained as a pale yellow liquid (800 mg 80%).  $^1\text{H}$  NMR (300 MHz,  $\text{CHLOROFORM-}d$ )  $\delta$  ppm 1.13 - 1.50 (br, 31H) 2.05 (q, 4H,  $J=6.9$  Hz) 4.87 - 5.07 (m, 4H) 5.72 - 5.92 (ddt, 2H,  $J_1=16.9$ ,  $J_2=10.2$ ,  $J_3=6.7$  Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CHLOROFORM-}d$ )  $\delta$  ppm

24.10, 24.83, 29.15, 29.33, 29.64, 29.66, 29.70, 29.88, 34.03, 36.61, 114.31, 124.97, 139.38. CG/CI-MS:  $[M+H]^+$  calcd for  $C_{25}H_{42}D_4N$ , 364.3881; found 364.3893. Elemental Analysis: calcd for  $C_{25}H_{41}D_4N$ : C, 82.57; (H+D), 12.49; N, 3.85. Found: C, 82.77; (H+D), 12.63; N, 3.87.

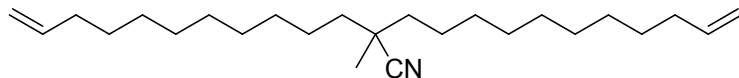
### 2-methyl-2-(oct-7-en-1-yl)dec-9-enitrile (3c)



2-methyl-2-(oct-7-en-1-yl)dec-9-enitrile  
Chemical Formula:  $C_{19}H_{33}N$   
Molecular Weight: 275.48

The synthesis followed the same procedure used for **3a**. Compound **3c** was prepared from a solution of propionitrile (1.18 g, 21.42 mmol) in THF (20 mL), 2 mol.L<sup>-1</sup> LDA solution in THF (26.16 mL, 52.32 mmol) and **2a** (10 g, 52.32 mmol). Compound **3c** was obtained as a pale yellow liquid (5.48 g, 93%). <sup>1</sup>H NMR (300 MHz, CHLOROFORM-*d*)  $\delta$  ppm 1.19 - 1.54 (br, 23H) 1.97 - 2.13 (q, 4H,  $J=6.6$  Hz) 4.87 - 5.07 (m, 4H) 5.82 (ddt, 2H,  $J_1=17$ ,  $J_2=10.2$ ,  $J_3=6.7$  Hz). <sup>13</sup>C NMR (75 MHz, CHLOROFORM-*d*)  $\delta$  ppm 23.98, 24.78, 28.79, 28.89, 29.54, 33.72, 36.70, 39.42, 114.27, 124.66, 138.93. CG/CI-MS:  $[M+H]^+$  calcd for  $C_{19}H_{34}N$ , 276.2691; found 276.2705. Elemental Analysis: calcd for  $C_{19}H_{33}N$ : C, 82.84; H, 12.07. Found: C, 82.99; H, 12.13.

### 2-methyl-2-(undec-10-en-1-yl)tridec-12-enitrile (3d)

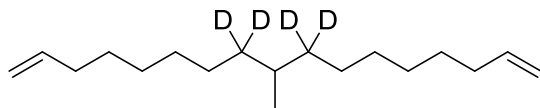


2-methyl-2-(undec-10-en-1-yl)tridec-12-enitrile  
Chemical Formula:  $C_{25}H_{45}N$   
Molecular Weight: 359.64

The synthesis followed the same procedure used for **3a**. Compound **3d** was prepared from a solution of propionitrile (0.968 g, 17.57 mmol) in THF (18 mL), 2 mol.L<sup>-1</sup> LDA solution in THF (35.50 mL, 42.88 mmol) and **2b** (10 g, 42.88 mmol). Compound **3d** was obtained as a pale yellow liquid (99%). <sup>1</sup>H NMR (300 MHz, CHLOROFORM-*d*)  $\delta$  ppm 1.10 - 1.52 (br, 35H) 2.05 (q, 4H,  $J=6.8$  Hz) 4.87 - 5.07 (m, 4H) 5.72 - 5.92 (ddt, 2H,  $J_1=17.1$ ,  $J_2=10.4$ ,  $J_3=6.7$  Hz). <sup>13</sup>C NMR (75 MHz, CHLOROFORM-*d*)  $\delta$  ppm 23.98, 24.80, 28.91, 29.09, 29.40, 29.43, 29.47, 29.69, 33.79, 36.69, 39.43, 114.08, 124.69, 139.13. CG/CI-MS:  $[M+H]^+$  calcd for  $C_{25}H_{46}N$ , 360.3630; found 360.3624. Elemental Analysis: calcd for  $C_{25}H_{45}N$ : C, 83.49; H, 12.61; N, 3.89. Found: C, 83.36; H, 12.65; N, 3.96.

## 4 - Synthesis of monomers

### 9-methylheptadeca-1,16-diene-8,8,10,10-*d*<sub>4</sub> (4a)



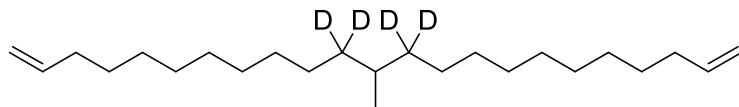
9-methylheptadeca-1,16-diene-8,8,10,10-*d*<sub>4</sub>

Chemical Formula: C<sub>18</sub>H<sub>30</sub>D<sub>4</sub>

Molecular Weight: 254.49

Hexamethylphosphoramide (HMPA) (5.53 g, 30.84 mmol), potassium metal chunks (1.68 g, 42.93 mmol) and ether (40 mL) were added to a flame-dried three-necked round-bottomed flask equipped with stir bar, argon inlet adaptor and addition funnel. A solution of **3a** (1.69 g, 6.05 mmol) and *tert*-butanol (1.17 g, 15.72 mmol) in ether (30 mL) was transferred to the addition funnel and added dropwise at 0°C under argon atmosphere. After the addition, the reaction was allowed to proceed for 4 hours at 0°C and overnight at room temperature. The remaining pieces of potassium were removed and the reaction was quenched with deionized water. The organic layer was extracted with ether, dried over MgSO<sub>4</sub>, concentrated and purified by flash-column chromatography (hexanes). Compound **4a** was obtained as a clear liquid (1.46 g, 95%). <sup>1</sup>H NMR (300 MHz, CHLOROFORM-*d*) δ ppm 0.84 (d, 3H, *J*=6.6 Hz) 1.14 - 1.48 (br, 17H) 2.05 (q, 4H, *J*=7.0 Hz) 4.86 - 5.11 (m, 4H) 5.83 (ddt, 2H, *J*<sub>1</sub>=17, *J*<sub>2</sub>=10.2, *J*<sub>3</sub>=6.7 Hz). <sup>13</sup>C NMR (75 MHz, CHLOROFORM-*d*) δ ppm 19.63, 26.84, 28.99, 29.23, 29.83, 32.38, 33.85, 114.05, 139.23. CG/CI-MS: [M]<sup>+</sup> calcd for C<sub>18</sub>H<sub>30</sub>D<sub>4</sub>, 254.2912; found 254.2913. Elemental Analysis: calcd for C<sub>18</sub>H<sub>30</sub>D<sub>4</sub>: C, 84.92; (H+D), 13.49. Found: C, 85.13; (H+D), 13.73

### 12-methyltricoso-1,22-diene-11,11,13,13-*d*<sub>4</sub> (**4b**)

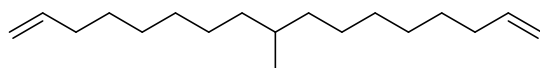


12-methyltricoso-1,22-diene-11,11,13,13-*d*<sub>4</sub>

Chemical Formula: C<sub>24</sub>H<sub>42</sub>D<sub>4</sub>

Molecular Weight: 338.66

The synthesis followed the same procedure used for **4a**. Compound **4b** was prepared by addition of a solution of **3b** (2.60 g, 7.15 mmol), *tert*-butanol (1.38 g, 18.61 mmol) in ether (30 mL) into a mixture of HMPA (6.53 g, 36.44 mmol) and K (2.0 g, 51.16 mmol) in ether (45 mL). Compound **4b** was obtained as a clear liquid (2.18 g, 90%). <sup>1</sup>H NMR (300 MHz, CHLOROFORM-*d*) δ ppm 0.84 (d, 3H, *J*=6.6 Hz) 1.14 - 1.48 (m, 29H) 2.05 (q, 4H, *J*=6.8 Hz) 4.86 - 5.09 (m, 4H) 5.70 - 5.93 (ddt, 2H, *J*<sub>1</sub>=17.1, *J*<sub>2</sub>=10.2, *J*<sub>3</sub>=6.7 Hz). <sup>13</sup>C NMR (75 MHz, CHLOROFORM-*d*) δ ppm 19.86, 27.11, 29.19, 29.40, 29.76, 29.87, 29.96, 30.21, 32.61, 34.06, 114.26, 139.45. CG/CI-MS: [M]<sup>+</sup> calcd for C<sub>24</sub>H<sub>42</sub>D<sub>4</sub>, 338.3850; found 338.3850. Elemental Analysis: calcd for C<sub>24</sub>H<sub>42</sub>D<sub>4</sub>: C, 85.09; (H+D), 13.72. Found: C, 85.24; (H+D), 14.01.



9-methylheptadeca-1,16-diene

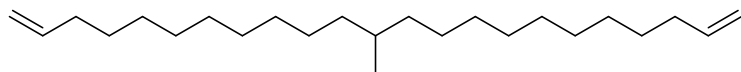
Chemical Formula: C<sub>18</sub>H<sub>34</sub>

Molecular Weight: 250.47

The synthesis followed the same procedure used for **4a**. Compound **4c** was prepared by addition of a solution of **3c** (5.48 g, 19.89 mmol), *tert*-butanol (3.83 g, 51.67 mmol) in ether (85 mL) into a mixture of HMPA (18.18 g, 101.5 mmol) and K (5.5 g, 140.7 mmol) in ether (120 mL). Compound **4c** was obtained as a clear liquid (3.87 g, 78%). <sup>1</sup>H NMR

(300 MHz, CHLOROFORM-*d*)  $\delta$  ppm 0.85 (d, 3H,  $J=6.3$  Hz) 0.98 - 1.47 (br, 21H) 2.05 (q, 4H,  $J=6.8$  Hz) 4.87 - 5.08 (m, 4H) 5.83 (ddt, 2H,  $J_1=17.0$ ,  $J_2=10.2$ ,  $J_3=6.6$  Hz).  $^{13}\text{C}$  NMR (75 MHz, CHLOROFORM-*d*)  $\delta$  ppm 19.93, 27.25, 29.19, 29.43, 30.08, 32.96, 34.06, 37.28, 114.26, 138.44. CG/EI-MS:  $[\text{M}]^+$  calcd for  $\text{C}_{18}\text{H}_{34}$ , 250.2660; found 250.2648. Elemental Analysis: calcd for  $\text{C}_{18}\text{H}_{34}$ : C, 86.32; H, 13.68. Found: C, 86.29; H, 13.49.

### 12-methyltricoso-1,22-diene (4d)



12-methyltricoso-1,22-diene  
Chemical Formula:  $\text{C}_{24}\text{H}_{46}$   
Molecular Weight: 334.63

The synthesis followed the same procedure used for **4a**. Compound **4d** was prepared by addition of a solution of **3d** (4.38 g, 12.18 mmol), *tert*-butanol (2.35 g, 31.71 mmol) in ether (55 mL) into a mixture of

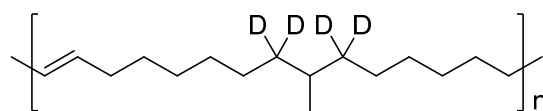
HMPA (11.13 g, 62.11 mmol) and K (3.38 g, 86.47 mmol) in ether (75 mL). Compound **4d** was obtained as a clear (3.0 g, 74%).  $^1\text{H}$  NMR (300 MHz, CHLOROFORM-*d*)  $\delta$  ppm 0.85 (d, 3H,  $J=6.4$  Hz) 1.00 - 1.47 (br, 33H) 2.05 (q, 4H,  $J=6.8$  Hz) 4.89 - 5.08 (m, 4H) 5.73 - 5.93 (ddt, 2H,  $J_1=17.1$ ,  $J_2=10.1$ ,  $J_3=6.7$  Hz).  $^{13}\text{C}$  NMR (75 MHz, CHLOROFORM-*d*)  $\delta$  ppm 19.74, 27.11, 28.97, 29.19, 29.55, 29.66, 29.73, 30.05, 32.76, 33.85, 37.11, 114.05, 139.23. CG/EI-MS:  $[\text{M}]^+$  calcd for  $\text{C}_{24}\text{H}_{46}$ , 334.3599; found 334.3587. Elemental Analysis: calcd for  $\text{C}_{24}\text{H}_{46}$ : C, 86.14; H, 13.86. Found: C, 86.31; H, 13.85.

## 5 - Polymerization

### ADMET polymerization: General procedure

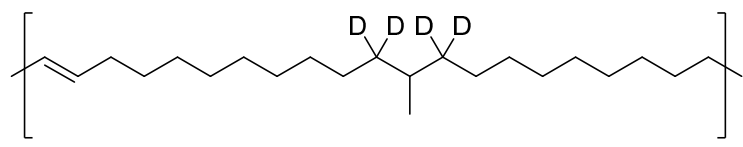
The monomer ( $\alpha,\omega$ -diene) was added into a flame-dried Schlenk tube equipped with a stir bar. The liquid monomer was degassed by bubbling argon under stirring for 30 minutes. Vacuum was applied another 30 minutes to guarantee removal of dissolved oxygen and volatile contaminants. After that, the reaction flask was sealed and taken to a glove box where Schrock's catalyst was added (500:1 mol monomer to catalyst ratio). The reaction flask was then sealed under argon atmosphere and taken to a vacuum line. The polymerization proceeded at 70°C (oil bath) for 72 hours. After that, the highly viscous reaction mixture was dissolved in toluene and quenched by exposure to air under stirring at room temperature. The dissolved unsaturated polymer was precipitated into cold methanol and collected by vacuum filtration. Removal of residual toluene and methanol was carried out by drying the melted polymer under vacuum.

### u-PE15-D<sub>4</sub> (5a)



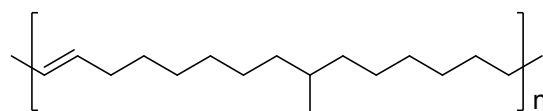
Unsaturated polymer **5a** was prepared from 1 g of **4a**. Obtained 842 mg of soft material.  $^1\text{H}$  NMR (300 MHz, CHLOROFORM-*d*)  $\delta$  ppm 0.84 (d, 3H,  $J=6.6$  Hz) 1.26 (br, 17H) 1.81 - 2.21 (br, 4H) 5.21 - 5.54 (m, 2H).  $^{13}\text{C}$  NMR (75 MHz, CHLOROFORM-*d*)  $\delta$  ppm 19.63, 26.77, 26.89, 27.25, 29.24, 29.28, 29.41, 29.51, 29.63, 29.72, 29.88, 29.99, 32.41, 32.66, 129.86, 130.33. GPC data:  $M_n=28\,049$ ; PDI ( $M_w/M_n$ ) = 3.28.

#### u-PE21-D<sub>4</sub> (5b)



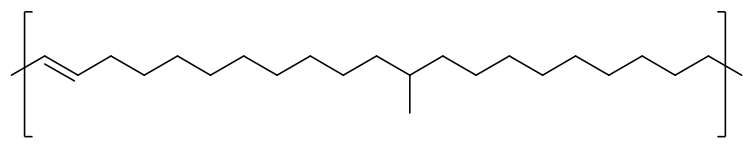
Unsaturated polymer **5b** was prepared from 1.12 g of **4b**. Obtained 953 mg of solid material.  $^1\text{H}$  NMR (300 MHz, CHLOROFORM-*d*)  $\delta$  ppm 0.84 (d, 3H,  $J=6.4$  Hz) 1.27 (br, 29H) 1.98 (br, 4H) 5.24 - 5.49 (m, 2H).  $^{13}\text{C}$  NMR (75 MHz, CHLOROFORM-*d*)  $\delta$  ppm 19.85, 27.14, 27.44, 29.42, 29.56, 29.79, 29.91, 29.98, 30.23, 32.63, 32.85, 130.06, 130.53. GPC data:  $M_n=46\,831$ ; PDI ( $M_w/M_n$ ) = 2.24.

#### u-PE15 (5c)



Unsaturated polymer **5c** was prepared from 1 g of **4c**. Obtained 840 mg of soft material.  $^1\text{H}$  NMR (300 MHz, CHLOROFORM-*d*)  $\delta$  ppm 0.84 (d, 3H,  $J=6.3$  Hz) 0.98 - 1.42 (br, 21H) 1.87 - 2.09 (br, 4H) 5.27 - 5.49 (m, 2H).  $^{13}\text{C}$  NMR (75 MHz, CHLOROFORM-*d*)  $\delta$  ppm 19.73, 27.10, 29.27, 29.72, 29.92, 32.65, 32.78, 37.13, 130.33. GPC data:  $M_n=68\,371$ ; PDI ( $M_w/M_n$ ) = 1.65.

#### u-PE21 (5d)



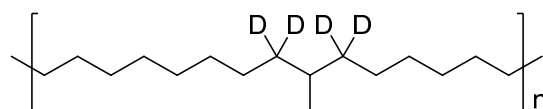
Unsaturated polymer **5d** was prepared from 878 mg of **4d**. Obtained: 725 mg of solid material.  $^1\text{H}$  NMR (300 MHz, CHLOROFORM-*d*)  $\delta$  ppm 0.84 (d, 3H,  $J=6.3$  Hz) 1.01 - 1.44 (br, 33H) 1.97 (br, 4H) 5.28 - 5.48 (m, 2H).  $^{13}\text{C}$  NMR (75 MHz, CHLOROFORM-*d*)  $\delta$  ppm 19.74, 27.13, 29.22, 29.58, 29.70, 29.77, 30.07, 32.65, 32.79, 37.14, 130.33. GPC data:  $M_n=29\,918$ ; PDI ( $M_w/M_n$ ) = 2.32.

### 6 - Saturated Polymers

#### General procedure for hydrogenation/deuteration

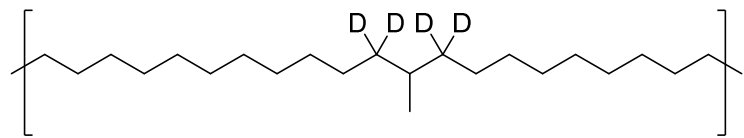
Unsaturated polymer dissolved in toluene (40 mL) was added to a Parr bomb glass sleeve and degassed by bubbling argon for 30 minutes. Palladium on carbon (10 wt. %) was added (15 mg / 100 mg of unsaturated polymer) to the solution. The bomb was purged and charged with 800 psi of H<sub>2</sub> (**5a-b**, **6a-b**) or D<sub>2</sub> gas (**5c-d**, **6c-d**). The reaction was allowed to proceed for 72 hours at 80°C (oil bath) under stirring. The catalyst was removed by vacuum filtration through a Celite bed. The polymer solution was precipitated in cold methanol (1 L). The precipitate was filtered and dried under vacuum.

#### PE15-D<sub>4</sub> (**6a**)



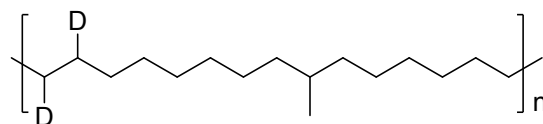
Polymer **6a** was obtained from 0.396 g of **5a**. The saturated polymer **6a** was obtained as an off-white solid (662 mg). <sup>1</sup>H NMR (300 MHz, CHLOROFORM-*d*) δ ppm 0.84 (d, 3H, *J*=6.6 Hz) 1.16 - 1.36 (br, 25H). <sup>13</sup>C NMR (75 MHz, CHLOROFORM-*d*) δ ppm 19.81, 27.08, 29.90, 29.95, 30.19, 32.57. GPC data: *M<sub>n</sub>* = 28 049; PDI (*M<sub>w</sub>*/*M<sub>n</sub>*) = 3.28. DSC data: *T<sub>m</sub>* = 38.46°C, Δ*H<sub>f</sub>* = 76.58 J/g ; *T<sub>c</sub>* = 27.53°C, Δ*H<sub>c</sub>* = 78.77 J.g<sup>-1</sup>. TGA data: *T<sub>95%</sub>* = 396.29°C, *T<sub>50%</sub>* = 427.92°C (*T<sub>x%</sub>*, temperature where (100-x)% weight loss is observed).

#### PE21-D<sub>4</sub> (**6b**)



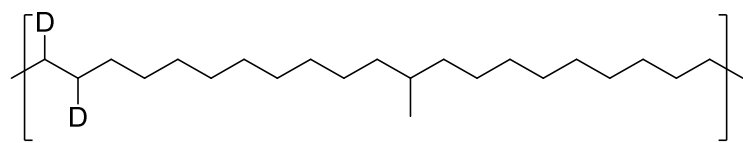
Polymer **6b** was obtained from 0.900 g of **5b**. The saturated polymer **6b** was obtained as an off-white solid. <sup>1</sup>H NMR (300 MHz, CHLOROFORM-*d*) δ ppm 0.84 (d, 3H, *J*=6.4 Hz) 1.13 - 1.40 (br, 37H). <sup>13</sup>C NMR (75 MHz, CHLOROFORM-*d*) δ ppm 19.65, 26.92, 29.74, 30.03, 32.40. GPC data: *M<sub>n</sub>* = 60 091; PDI (*M<sub>w</sub>*/*M<sub>n</sub>*) = 2.24. DSC data: *T<sub>m</sub>* = 62.73°C, Δ*H<sub>f</sub>* = 103.3 J/g ; *T<sub>c</sub>* = 54.52°C , Δ*H<sub>c</sub>* = 99.57 J.g<sup>-1</sup>. TGA data: *T<sub>95%</sub>* = 402.26°C, *T<sub>50%</sub>* = 432.50°C.

#### PE15-D<sub>2</sub> (**6c**)



Polymer **6c** was obtained from 0.426 g of **5c**. The saturated polymer **6c** was obtained as an off-white solid (275 mg). <sup>1</sup>H NMR (300 MHz, CHLOROFORM-*d*) δ ppm 0.84 (d, 3H, *J*=6.3 Hz) 0.98 - 1.46 (br, 25 H). <sup>13</sup>C NMR (75 MHz, CHLOROFORM-*d*) δ ppm 19.74, 27.12, 29.62, 29.72, 29.77, 30.07, 32.77, 32.12, 37.12. GPC data: *M<sub>n</sub>* = 55 703; PDI (*M<sub>w</sub>*/*M<sub>n</sub>*) = 2.33. DSC data: *T<sub>m</sub>* = 38.8°C, Δ*H<sub>f</sub>* = 76.8 J/g ; *T<sub>c</sub>* = 28.61°C , Δ*H<sub>c</sub>* = 57.70 J.g<sup>-1</sup>. TGA data: *T<sub>95%</sub>* = 401.48°C, *T<sub>50%</sub>* = 429.27°C.

### PE21-D<sub>2</sub> (6d)



Polymer **6d** was obtained from 0.370 g of **5d**. The saturated polymer **6a** was obtained as an off-white solid (0.285 g). <sup>1</sup>H NMR (300 MHz, CHLOROFORM-*d*) δ ppm 0.84 (d, 3H, *J*=6.3 Hz) 0.99 - 1.44 (m, 37H). <sup>13</sup>C NMR (75 MHz, CHLOROFORM-*d*) δ ppm 19.76, 27.13, 29.62, 29.75, 30.07, 32.78, 37.13. GPC data: *M<sub>n</sub>* = 27 628; PDI (*M<sub>w</sub>*/*M<sub>n</sub>*) = 2.16. DSC data: *T<sub>m</sub>* = 61.7°C, Δ*H<sub>f</sub>* = 100.8 J·g<sup>-1</sup>; *T<sub>c</sub>* = 55.01°C, Δ*H<sub>c</sub>* = 103.4 J/g. TGA data: *T*<sub>95%</sub> = 391.16°C, *T*<sub>50%</sub> = 430.20°C.