

# Decreasing the Alkyl Branch Frequency in Precision Polyethylene: Pushing the Limits towards Longer Run Lengths

**(Supporting Information)**

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**Instrumentation and Analysis.** All  $^1\text{H}$  NMR (300 MHz) and  $^{13}\text{C}$  NMR (75 MHz) spectra were recorded in  $\text{CDCl}_3$  unless otherwise stated. Chemical shifts were referenced to signals from  $\text{CDCl}_3$  (7.24 ppm for  $^1\text{H}$ , 77.23 ppm for  $^{13}\text{C}$ ) with 0.03% v/v TMS and from  $\text{C}_6\text{D}_6$  (7.16 ppm for  $^1\text{H}$ , 128.62 ppm for  $^{13}\text{C}$ ) as an internal reference. For all the NMR work the solvents were chloroform-*d* or benzene-*d* and the temperature was 25 or 75 °C. High-resolution mass spectrometry (HRMS) was carried out using a Agilent 6210 TOF-MS mass spectrometer in the direct analysis in real-time (DART) mode with the IonSense DART Source. Thin layer chromatography (TLC) was used to monitor all reactions and was performed on glass plates coated with silica gel (250  $\mu\text{m}$  thickness). Column chromatography was performed using ultrapure silica gel (40-63  $\mu\text{m}$ , 60 Å pore size). For the purification of 38-bromooctatriacont-1-ene (**8**), ultrapure silica gel (5-20  $\mu\text{m}$ , 60 Å pore size) was purchased from SiliCycle<sup>®</sup>. Gel permeation chromatography (GPC) was performed using Alliance GPC 2000 with an internal differential refractive index detector (DRI), internal differential viscosity detector (DP), and a precision angle light scattering detector (LS). The light scattering signal was collected at a 15° angle, and the three in-line detectors were operated in series in the order LS-DRI-DP. The chromatography was performed at 135 °C using PLgel MIXED-B column (10  $\mu\text{m}$  PD, 8.0 mm ID, 300 mm total length) with HPLC grade 1,2,4-trichlorobenzene as the mobile phase at a flow rate of 1.0 mL/min. Injections were made at 0.05-0.07% w/v sample concentration using a 322.5  $\mu\text{L}$  injection volume. In the case of universal calibration, retention times were calibrated versus narrow-range molecular weight polystyrene standards (purchased from Polymer Standard Service PSS in Mainz, Germany).

Differential scanning calorimetry (DSC) was performed using a TA Instruments DSC Q1000 equipped with a controlled cooling accessory at a heating rate of 10 °C/min unless otherwise specified. Calibrations were made using indium and freshly distilled *n*-octane as the standards for peak temperature transitions and indium for the enthalpy standard. IR data was obtained using a Perkin-Elmer Spectrum One FTIR outfitted with a  $\text{LiTaO}_3$  detector. The unsaturated polymer sample was prepared by solution-casting a thin film from toluene onto a KBr salt plate and hydrogenated polymer sample was prepared by solution-casting a thin film from boiling toluene onto a KBr salt plate. Wide-angle X-ray (WAXS) powder diffraction data were collected on a Mar345 Image Plate Detector with plate diameter of 345 mm and outside dimensions (515 mm \* 398 mm \* 350 mm), using the  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15417$  nm) induced by a generator operating at 40 kV and 150 mA. Diffraction patterns were recorded for  $2\theta$ -values ranging from 10° to 40°.

**Materials.** Chemicals were purchased from the Aldrich Chemical Co. and used as received unless otherwise noted. Grubbs' first generation catalyst,

bis(tricyclohexylphosphine)benzylidineruthenium(IV) dichloride, was kindly provided by Materia, Inc. Schrock's molybdenum metathesis catalyst,  $[(\text{CF}_3)_2\text{CH}_3\text{CO}]_2(\text{N}-2,6-\text{C}_6\text{H}_3-i\text{-Pr}_2)\text{Mo}=\text{CHC}(\text{CH}_3)_2\text{Ph}$ , and Wilkinson's rhodium hydrogenation catalyst,  $\text{RhCl}(\text{PPh}_3)_3$  were purchased from Strem Chemical. Ruthenium and Molybdenum catalysts were stored in an argon-filled glovebox prior to use. Tetrahydrofuran (THF) and toluene were freshly used from Butler Polymer Research Laboratories anhydrous solvent preparation unit. HPLC grade 1,2,4-trichlorobenzene was purchased from the Applichem GmbH. All the nitriles and alkenyl bromide starting materials, as well as hexamethylphosphoramide and diisopropyl amine were distilled over  $\text{CaH}_2$ . All reactions were carried out in flame-dried glassware under argon unless otherwise stated.

### Synthesis of 11- Bromo-undec-1-ene (2)

A solution of 11-undecen-1-ol, **1**, (34.11g, 0.20 mol) and  $\text{CBr}_4$  (73.45 g, 0.22 mol) in  $\text{CH}_2\text{Cl}_2$  (120 mL) was prepared in a 500-mL round bottomed flask and cooled to 0 °C. Triphenyl phosphine (58g, 0.22 mol) was added in small portions over a period of 20 minutes. An exothermic reaction occurred, which was left stirring at 0 °C for 1hr and 40 min, then at RT for 2 hours. The crude product was filtered over a silica column, and the solution was concentrated by evaporation. A white precipitate was formed. The liquid was poured into 400 mL of hexane with stirring and more solid (triphenylphosphine oxide,  $\text{O}=\text{PPh}_3$ ) precipitated. The solution was decanted leaving the solid in the flask, and the hexane solution was concentrated, to obtain more precipitation. The solid was filtrated, and the hexane solution was evaporated to obtain 81.65 g of yellow liquid. This liquid was fractionally distilled under reduced pressure (6 torr) to remove reaction by-product, bromoform. 41.9 g of compound **2** was collected as a colorless liquid. (Yield= 90 %) The  $^1\text{H}$  NMR spectrum was consistent with the published spectrum.<sup>10</sup>

### Synthesis of 1,20- dibromo-eicos-10-ene (3)

In a 50-mL round bottomed flask 11-bromo-undec-1-ene, **2**, (50g, 0.215mol) was mixed with 0.310g,  $3.76 \times 10^{-4}$  mmol, of Grubbs 1<sup>st</sup> generation catalyst at RT (22 °C) and warmed at 45 °C for 4hr, under argon. It was left at 45 °C under Ar for 24 hr and finally under vacuum (7 torr) for 24 hr. The reaction was quenched with 5 mL ethyl vinyl ether and dissolved in 100 mL toluene. The toluene solution was concentrated and precipitated by pouring into 1.0 L cold methanol. The methanol was left in the refrigerator overnight, and white crystals were obtained, filtered under vacuum, and dried in a vacuum oven yielding 15 g of a crystalline material. (Yield = 80%) The  $^1\text{H}$  NMR spectrum was consistent with the published spectrum.<sup>10</sup>

### Synthesis of 1,20-Dibromoeicosane (4)

Compound **3**, 1,20-dibromo-eicos-10-ene (10.691 g, 24.44 mmol) was dissolved in 90 mL degassed toluene, placed in a Parr bomb with 1.1 mg,  $1.89 \times 10^{-3}$  mmol of Wilkinson catalyst and left to react at 55 °C under 900 psi of hydrogen for 4 days. Purification of the product by column chromatography with toluene afforded 10.30 g of a white solid. (Yield = 96 %) The  $^1\text{H}$  NMR spectrum was consistent with the published spectrum.<sup>10</sup>

### Synthesis of 20-Bromo-eicos-1-ene (5)

In a 250 mL round bottomed flask, compound **4** (10.30 g, 23.4 mmol) was dissolved in 2:1 THF/toluene mixture producing a 1 M solution. The mixture was cooled using an ice water bath, and potassium tert-butoxide (3.92 g, 35.1 mmol) was added in small portions over 30 min. After addition, the reaction turned cloudy and was allowed to stir at 0 °C for 1 h. The reaction was quenched using water (25 mL), followed by 1 M HCl (25 mL). The organic layer was extracted and washed with 1M HCl (15 mL), saturated  $\text{Na}_2\text{CO}_3$  (15 mL), and 15 mL of water, followed by drying with magnesium sulfate. Solvents were evaporated and the crude product was further purified by column chromatography using hexane as the eluent. 4.85 g of compound **5** was collected as a white solid. (Yield = 42%) The  $^1\text{H}$  NMR spectrum was consistent with the published spectrum.<sup>10</sup>

### Synthesis of 1,38-dibromooctatriacont-18-ene (6)

Compound **5**, 20-bromo-eicos-1-ene, **5**, (4.252 g, 1.18 mmol) in a flame dried reaction tube was placed under vacuum ( $10^{-3}$  atm) for 2 hours at 75 °C. Grubbs 1<sup>st</sup> generation catalyst (0.004 g,  $4.85 \times 10^{-3}$ ) was added, and the mixture was left at 75 °C under vacuum ( $10^{-3}$  atm) for 24 hours. The reaction was quenched with 5 mL ethyl vinyl ether and dissolved in 15 mL toluene. The toluene solution was concentrated and precipitated by pouring into 1.0 L of methanol. Crystals were filtered and dried under vacuum overnight. 3.818 g of compound **6** was recovered as white crystals. (Yield = 94%)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm), 1.20-1.38 (br, 64H,  $\text{CH}_2$ ), 2.01-2.08 (q, 4H, allyl  $\text{CH}_2$ ), 3.42 (t, 4H,  $\text{CH}_2\text{Br}$ ), 5.39 (m, 2H, vinyl CH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 28.3, 29.4, 29.6, 29.8, 32.8, 33.1, 34.7, 130.125 (vinyl CH, *cis*), 130.58 (vinyl CH, *trans*).; DART/HRMS:  $[\text{M}]^+$  calculated for  $\text{C}_{38}\text{H}_{74}^{79}\text{Br}_2$ : 688.8422, found: 688.4157. Calculated for  $\text{C}_{38}\text{H}_{74}^{81}\text{Br}_2$ : 6692.9042, found: 6692.4304. Elemental analysis calculated for  $\text{C}_{38}\text{H}_{74}\text{Br}_2$ : 66.07 C, 10.80 H; found: 65.35 C, 10.75 H.

### Synthesis of 1,38-dibromooctatriacontane (7)

Compound **6**, 1,38-dibromooctatriacont-18-ene, (3.818g, 0.553 mmol) was dissolved in 50 mL degassed toluene, placed in a Parr bomb with 0.55 mg,  $0.85 \times 10^{-3}$  mmol of Wilkinson catalyst and left to react at 90 °C under 900 psi of hydrogen for 36 hours. The toluene solution was concentrated and precipitated by pouring into 0.5 L of methanol. Crystals were filtered and dried under vacuum overnight. 3.605 g of compound **7** was recovered as white crystals. (Yield = 94%)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm), 1.30-1.45 (br, 72H,  $\text{CH}_2$ ), 3.42 (t, 4H,  $\text{CH}_2\text{Br}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) :  $\delta$  (ppm) 28.5, 29.0, 29.7, 29.9, 33.2, 34.0 DART/HRMS:  $[\text{M}]^+$  calculated for  $\text{C}_{38}\text{H}_{76}\text{Br}_2$ : 690.4314, found: 690.4261. Elemental analysis calculated for  $\text{C}_{38}\text{H}_{76}\text{Br}_2$ : 66.07 C, 10.79 H; found: 64.84 C, 10.75 H.

### Synthesis of 38-bromooctatriacont-1-ene (8)

In a 250 mL round bottomed flask, compound **7** (3.324g, 0.481 mmol) was dissolved in a 2:1 toluene/THF (150 mL/75 mL) mixture. The mixture was warmed to 40 °C and potassium tert-butoxide (0.086g, 0.771 mmol) was added under Argon flow. The reaction mixture was stirred at 40 °C for 24 hours. Solvents were evaporated and crude product was purified by column chromatography using hexane as the eluent and SiliCycle<sup>®</sup> silica gel with 5-20  $\mu\text{m}$  particle size. 0.923 g of compound **8** was recovered after purification. (Yield= 31%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm), 1.30-1.45 (br, 68H,  $\text{CH}_2$ ), 2.01-2.08 (q, 4H, allyl  $\text{CH}_2$ ), 3.42 (t, 4H,  $\text{CH}_2\text{Br}$ ), 4.91-5.04 (m, 4H, vinyl  $\text{CH}_2$ ), 5.78-5.87 (m, 2H, vinyl CH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) :  $\delta$  (ppm) 27.1, 29.2, 29.3, 29.9, 30.4, 33.8, 36.3, 114.3, 139.4; DART/HRMS:  $[\text{M}]^+$  calculated for  $\text{C}_{38}\text{H}_{75}\text{Br}$ : 609.4974, found: 609.4981. Elemental analysis calculated for  $\text{C}_{38}\text{H}_{75}\text{Br}$ : 74.59 C, 12.35 H; found: 74.22 C, 11.94 H.

### Synthesis of 2-butyl-2-(octatriacont-37-en-1-yl)tetracont-39-enenitrile (10)

Compound **8**, (1.290g, 0.210 mmol) was placed in a flame dried 25 mL reaction tube and stirred under vacuum for 2 hour at 85 °C. In a separate flame dried 50 mL 2-neck round bottomed flask, diisopropyl amine (0.22g, 2.10 mmol) was dissolved in 5 mL of anhydrous THF. A 1.4 mL sample of 1.5 M (freshly distilled) n-BuLi (2.10 mmol) was added slowly at -78 °C for 5 minutes under Argon flow. The LDA solution was warmed to 0 °C and stirred for 30 minutes, then cooled to -78 °C prior to adding 0.11g hexanenitrile **9** (1.13 mmol) over 5 minutes. The reaction mixture was warmed to 0 °C and stirred for 30 minutes. This solution was slowly transferred via cannula to the reaction flask for the alkylation reaction in one portion at RT (alkylating agent **8** was not soluble at RT in THF). The reaction temperature was increased to 50 °C to dissolve compound **8** and stirred for 12 hours under Argon flow.

Solvents were evaporated and crude product was purified by column chromatography (hexane/toluene 9:1) as eluent. 0.292g, 0.025 mmol, of compound **10** was recovered as white solid. (Yield= 24%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm), 0.94 (t, 3H, CH<sub>3</sub>), 1.22-1.34 (br, 146H, CH<sub>2</sub>), 2.01-2.08 (q, 4H, allyl CH<sub>2</sub>), 4.90-5.03 (m, 4H, vinyl CH<sub>2</sub>), 5.76-5.88 (m, 2H, vinyl CH); <sup>13</sup>C NMR (CDCl<sub>3</sub>) : δ (ppm) 14.1, 23.1, 24.5, 26.7, 29.1, 29.4, 29.7, 29.9, 34.1, 36.1, 36.4, 40.9, 114.3, 124.8, 139.5; DART/HRMS: [M]<sup>+</sup> calculated for C<sub>82</sub>H<sub>159</sub>N: 1159.2545, found: 1159.2538. Elemental analysis calculated for C<sub>82</sub>H<sub>159</sub>N: 84.97 C, 13.83 H, 1.21 N; found: 85.06 C, 13.66 H, 1.23 N.

### Synthesis of 39-butylheptaheptaconta-1,76-diene (**11**)

Potassium metal (0.340g, 8.69 mmol), HMPA (0.9mL, 4.87 mmol), and anhydrous THF (45 mL) were transferred to a 100 mL flame dried 3-necked round bottomed flask equipped with a stir barr. Compound **10** (0.292g, 0.025 mmol) was added to the slurry in one portion at RT under Argon flow. The temperature was raised to 40 °C to dissolve compound **10** and 0.45 mL of *t*-BuOH (7.78 mmol) was added. The reaction mixture was stirred for 24 hours and quenched with isopropanol (10 mL). Solvents were evaporated and crude product was purified by column chromatography using hexane as the eluent. 0.253g, 0.022 mmol, of compound **11** was recovered as white solid. (Yield= 88%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm), 0.90 (t, 3H, CH<sub>3</sub>), 1.24-1.32 (br, 146H, CH<sub>2</sub>), 1.35-1.41 (m, 1H, CH), 2.01-2.08 (q, 4H, allyl CH<sub>2</sub>), 4.90-5.03 (m, 4H, vinyl CH<sub>2</sub>), 5.76-5.88 (m, 2H, vinyl CH); <sup>13</sup>C NMR (CDCl<sub>3</sub>) : δ (ppm) 14.3, 23.4, 27.1, 29.2, 29.4, 29.8, 29.9, 30.4, 32.1, 33.9, 34.0, 34.2, 37.8, 114.3, 139.5; Elemental analysis calculated for C<sub>81</sub>H<sub>160</sub>: 85.78 C, 14.22 H; found: 85.52 C, 14.36 H.

### Polymerization of 39-butylheptaheptaconta-1,76-diene (**11**)

Compound **11** (0.155g, 0.137 mmol) was put in a 25 mL reaction tube and left under vacuum for 2 hours at 90 °C. The reaction tube was cooled to RT and placed into the glove box. Schrock Catalyst (0.09g) was added, and the reaction tube was put under vacuum again. Polymerization was started by raising the temperature to 100 °C and left under vacuum for 24 hours. Polymerization was quenched by opening the tube to the air and dissolved in 10 mL of toluene. After precipitation over 0.5 L of methanol and filtration, 0.130 g of polymer **12** was recovered as white solid. (Yield=84%) <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 0.91 (t, CH<sub>3</sub>), 1.21-1.36 (m, CH<sub>2</sub>), 1.98 (q, allyl CH<sub>2</sub>), 5.40 (m, vinyl CH); <sup>13</sup>C NMR (CDCl<sub>3</sub>) : δ (ppm) 14.26, 23.36, 27.05, 29.46, 29.87, 30.43, 32.77, 33.81, 34.22, 37.83, 130.53

### Synthesis of polymer (**13**)

In a 125 mL Parr bomb glass sleeve, unsaturated polymer **12** (0.110 g) was dissolved in 50 mL of degassed toluene. Wilkinson's hydrogenation catalyst (0.7 mg, 7.6×10<sup>-4</sup> mmol) was added, and the

bomb was charged with 900 psi of hydrogen. The reaction was allowed to proceed for three days at 90 °C. The polymer solution was concentrated and precipitated in 0.5 L of methanol. The precipitate was filtered and dried under vacuum overnight. 0.95 g of polymer **13** was recovered as a white solid. (Yield=86%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ (ppm) 0.91 (d, CH<sub>3</sub>), 1.21-1.47 (m, CH<sub>2</sub>), 1.56 (m, CH); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) : δ (ppm) 14.27, 29.92.