

Supporting Information

Decreasing the Alkyl Branch Frequency in Precision Polyethylene: The Effect of Alkyl Branch Size on Nanoscale Morphology

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A) Instrumentation

All ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra of starting materials, intermediates and monomers were recorded in CDCl_3 . For polymer characterization, ^1H NMR (500 MHz) and ^{13}C NMR (126 MHz) instrumentation were used and spectra were recorded in either CDCl_3 or C_6D_6 . Chemical shifts were referenced to signals from CDCl_3 (7.24 ppm for ^1H , 77.23 ppm for ^{13}C) with 0.03% v/v TMS and from C_6D_6 (7.16 ppm for ^1H , 128.39 ppm for ^{13}C) as an internal reference, and the temperature was maintained at either 25 or 65°C. High Resolution Mass Spectrometry (HRMS) was carried out using an Agilent 6210 TOF-MS mass spectrometer in the Direct Analysis in Real-Time (DART) mode with an IonSense DART Source. Thin layer chromatography (TLC) was used to monitor all reactions and was performed on glass plates coated with silica gel (250 μm thickness). Column chromatography was performed using ultrapure silica gel (40-63 μm , 60 Å pore size).

Gel Permeation Chromatography (GPC) was performed using an Alliance GPC 2000 with an internal differential refractive index detector (RID), internal differential viscosity detector (DP), and a precision angle light scattering detector (LS) at the Max Planck Institute for Polymer Research, Mainz, Germany. 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 a PLgel MIXED-B column (10 μm 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 μL 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). IR data were obtained using a Perkin-Elmer Spectrum One

FTIR equipped with a LiTaO₃ detector. The unsaturated polymer sample was prepared by solution-casting a thin film from toluene onto a KBr salt plate and the hydrogenated polymer sample was prepared by solution-casting a thin film from boiling toluene onto a KBr salt plate.

Differential scanning calorimetry (DSC) was performed using a TA Instruments DSC Q1000 equipped with a controlled cooling accessory at a heating and cooling 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.

Wide-angle X-ray diffraction (WAXD) data were collected on a Mar345 Image Plate Detector with plate diameter of 345 mm and outside dimensions (515 mm x 398 mm x 350 mm), using the Cu K α radiation ($\lambda = 0.15417$ nm) induced by a generator operating at 40 kV and 150 mA. Diffraction patterns were recorded for 2θ -values ranging from 10° to 40°. Each diffractogram for the in situ WAXD measurements was collected using an accumulation time of 300 seconds. The temperature control unit was attached to the sample holder, and all the cooling experiments were performed at either 1 °C/min or 50 °C/min.

Solid state NMR was carried out utilizing a Bruker spectrometer equipped with a Bruker Avance II+ console working at the ¹H Larmor frequency of 850 MHz. Polymer samples were tightly and evenly packed in 2.5 mm rotors, and CP-MAS spectra were acquired using 1 ms contact time and 10 kHz MAS conditions.

For TEM sample preparation, carbon black was evaporated under 10⁻³ atm onto mica slides to form uniform carbon layers of 5-10 nm thickness. The carbon layer was removed with DI water and regular mesh TEM copper grids were coated by dipping them in water. One drop of polymer stock solution (0.03 wt%) was deposited onto the carbon coated copper grid and solvent was evaporated at RT under the hood. TEM images were obtained on a Tecnai F20 (FEI)

transmission electron microscope operated at an acceleration voltage of 200 kV. In order to reduce beam damage to the polymer specimen, a low dose exposure protocol was applied for image acquisition.

Thickness images were obtained using a FEI Tecnai F20 electron microscope equipped with a Gatan imaging filter (GIF) and a slow scan CCD (charge-coupled device) camera. The GIF system allows both parallel-detection EELS and energy-filtered imaging/diffraction. A CCD camera can digitally collect electron images and diffraction patterns. By coupling the CCD camera to a computer, energy-filtered images could be acquired and processed in a quantitative manner. An energy window was used to select low energy range of electrons. Taking two consecutive images from the same sample, one with the slit positioned at the zero-loss peak and one without the slit, yielded two images, the elastical filtered image I_0 and the inelastic image I_t . After aligning both images for possible sample drift, the relative thickness, t , at each point of the images was given by: $t/\lambda = \ln(I_0/I_t)$, in which λ is the mean free path of the respective material for the respective electron energy (200 kV). Calculation of the mean free path scales the image to an absolute thickness mapping.

B) Materials

Chemicals were purchased from the Aldrich Chemical Co. and used as received unless otherwise noted. Grubb's first generation catalyst, bis(tricyclohexylphosphine)benzylidineruthenium(IV) dichloride, was kindly provided by Materia, Inc. Schrock's molybdenum metathesis catalyst, $[(CF_3)_2CH_2CO]_2(N-2,6-C_6H_3-i-Pr_2)Mo=CHC(CH_3)_2Ph$, and Wilkinson's rhodium hydrogenation catalyst, $RhCl(PPh_3)_3$, 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 obtained from the 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 CaH₂. All reactions were carried out in flame-dried glassware under argon unless otherwise stated.

C) Procedures

Synthesis of 11- Bromo-undec-1-ene (2). A solution of 11-undecen-1-ol, **1**, (34.11g, 0.20 mol) and CBr₄ (73.45 g, 0.22 mol) in CH₂Cl₂ (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 min. An exothermic reaction occurred, which was left stirring at 0 °C for 1h and 40 min, then at RT for 2 h. The crude product was filtered over a silica column, and the solution was concentrated by evaporation, until a white precipitate formed. The liquid was poured into 400 mL of hexane with stirring and more solid (triphenylphosphine oxide, O=PPh₃) precipitated. The solution was decanted leaving the solid in the flask, and the hexane solution was concentrated to obtain more precipitate. The solid was filtrated, and the hexane solution was evaporated to obtain 81.65 g of yellow liquid, which was fractionally distilled under reduced pressure (6 torr) to remove the bromoform, by-product. Compound **2** (41.9 g) was collected as a colorless liquid (yield= 90%). The ¹H NMR spectrum was consistent with the published spectrum.¹

Synthesis of 1,20- dibromo-eicos-10-ene (3). In a 50-mL round bottomed flask, 11-bromo-undec-1-ene, **2**, (50 g, 0.215mol) was mixed with 0.310 g, 3.76×10⁻⁴ mmol, of Grubbs 1st generation catalyst at RT (22 °C) and warmed to 45 °C for reaction under argon. It was left at 45 °C under Ar for 28 h and finally under vacuum (7 torr) for 24 h. The reaction was quenched with 5 mL ethyl vinyl ether, and the mixture was dissolved in 100 mL toluene. The toluene solution was concentrated and then poured into 1.0 L cold methanol. The methanol mixture was left in the refrigerator overnight, and white crystals were obtained. After vacuum filtration 15 g of a

crystalline material was obtained (yield = 80%). The ^1H NMR spectrum was consistent with the published spectrum.¹

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, 1.89×10^{-3} mmol, Wilkinson's 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 ^1H NMR spectrum was consistent with the published spectrum.¹

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 (3.92g, 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 Na_2CO_3 (15 mL), and 15 mL of water, followed by drying with magnesium sulfate. The solvents were evaporated and the crude product was further purified by column chromatography using hexane as the eluent. Compound **5** (4.85 g) was collected as a white solid (yield= 42%). The ^1H NMR spectrum was consistent with the published spectrum.¹

Synthesis of 2-methyl-2-(eicos-19-en-1-yl)docos-21-enenitrile (7a). Into a 100 mL 3-neck round bottomed flask equipped with a stir bar, THF (5 ml) was added and cooled to -78 °C under nitrogen. Diisopropyl amine (0.6 mL) and 2.0 mL of 2.0 M *n*-BuLi (freshly titrated) were added and warmed to 0 °C to prepare lithium diisopropyl amine (LDA) solution in situ. The LDA solution was cooled to -78 °C and propionitrile **6a** (0.090 mL, 1.29 mmol) was added. The mixture was allowed to return to RT and was stirred for 30 min at RT. Separately, 20-bromo-

eicos-1-ene, **5**, (1.171 g, 3.26 mmol) was added to a 50 mL flame-dried Schlenk flask and kept under high vacuum prior to use at 50°C, the LDA solution was transferred to the Schlenk flask at -78 °C, and the resulting mixture was slowly warmed to 0°C and stirred for 12 h at that temperature. The reaction was quenched with addition of diethyl ether (40 mL) and water (10 mL). The organic phase was extracted three times with ether (3x 30 mL), washed with brine, and dried over MgSO₄(s). The solvents were evaporated and the crude product was further purified by column chromatography using toluene/hexane as the eluent. Because of the very similar retardation factors between mono and di-alkylated nitriles, the toluene/hexane concentration was varied during the separation (toluene concentration was increased from 5% to 30% in 5% increments for each 250 mL portion of eluent.) After purification, 0.861 g of compound **7a** was collected as white crystals (yield = 86%). The following spectral properties were observed; ¹H NMR (CDCl₃) δ ppm 0.92 (s, 3H), 1.14 - 1.52 (br, 68 H), 2.05 (td, J₁=7.64 Hz, J₂=6.51 Hz, 4 H), 4.85 - 5.09 (m, 4 H), 5.66 - 5.95 (m, 2 H); ¹³C NMR (CDCl₃): δ (ppm) 18.10, 24.22, 24.98, 29.18, 29.44, 29.69, 29.82, 29.93, 30.07, 34.02, 36.82, 36.95, 39.62, 114.25 (vinyl CH₂), 126.34 (-CN), 139.46 (vinyl CH); EI/HRMS: [M]⁺ calculated for C₄₃H₈₁N: 611.6364, found: 611.6314. Elemental analysis calculated for C₄₃H₈₁N: 84.37 C, 13.37 H, 2.29 N; found: 84.24 C, 13.65 H, 2.38 N.

Synthesis of 2-ethyl-2-(icos-19-en-1-yl)docos-21-enenitrile (7b). The same procedure described above for the synthesis of compound **7a** was followed. After purification, 0.439 g of compound **7b** was collected as white crystals (yield = 86%). The following spectral properties were observed; ¹H NMR (CDCl₃) δ ppm 1.00 (t, J=7.36 Hz, 3H), 1.18 - 1.44 (br, 70 H), 2.04 (td, J₁=7.65 Hz, J₂=6.51 Hz, 4 H), 4.87 - 5.08 (m, 4 H), 5.69 - 6.11 (m, 2 H); ¹³C NMR (CDCl₃): δ (ppm) 24.53, 24.93, 29.14, 29.40, 29.69, 29.82, 29.95, 33.96, 34.09, 35.77, 41.33, 114.29 (vinyl

CH₂), 124.51 (-CN), 139.52 (vinyl CH); EI/HRMS: [M]⁺ calculated for C₄₄H₈₃N: 626.6598, found: 626.6611. Elemental analysis calculated for C₄₄H₈₃N: 84.40 C, 13.36 H, 2.22 N; found: 83.53 C, 13.23 H, 2.22 N.

Synthesis of 2-propyl-2-(icos-19-en-1-yl)docos-21-enenitrile (7c). The same procedure described above for the synthesis of compound **7a** was followed. After purification, 0.543 g of compound **7c** was collected as white crystals (yield = 73%). The following spectral properties were observed; ¹H NMR (CDCl₃) δ ppm 0.96 (t, *J*=6.79 Hz, 3 H), 1.19-1.45 (br, 72 H), 2.05 (td, *J*₁=7.63 Hz, *J*₂=6.50 Hz, 4 H), 4.88 - 5.07 (m, 4 H), 5.72 - 5.94 (m, 2 H); ¹³C NMR (CDCl₃): δ (ppm) 14.42, 15.80, 16.63, 24.50, 29.19, 29.33, 29.88, 30.02, 34.02, 34.16, 36.37, 40.79, 114.24 (vinyl CH₂), 124.74 (-CN), 139.51 (vinyl CH); EI/HRMS: [M]⁺ calculated for C₄₅H₈₅N: 640.9755, found: 640.6762. Elemental analysis calculated for C₄₅H₈₅N: 84.43 C, 13.38 H, 2.19 N; found: 84.58 C, 13.19 H, 2.20 N.

Synthesis of 2-iso-propyl-2-(icos-19-en-1-yl)docos-21-enenitrile (7d). The same procedure described above for the synthesis of compound **7a** was followed. After purification, 0.569 g of compound **7d** was collected as white crystals (yield = 83%). The following spectral properties were observed; ¹H NMR (CDCl₃) δ ppm 1.02 (d, *J*=6.80 Hz, 6 H), 1.16-1.44 (br, 72 H), 2.06 (td, *J*₁=7.64 Hz, *J*₂=6.52 Hz, 4 H), 4.88 - 5.07 (m, 4 H), 5.73 - 5.92 (m, 2 H); ¹³C NMR (CDCl₃): δ (ppm) 14.45, 15.66, 16.64, 24.50, 29.21, 29.35, 29.90, 30.02, 34.04, 34.13, 35.63, 41.10, 114.29 (vinyl CH₂), 124.48 (-CN), 139.52 (vinyl CH); EI/HRMS: [M]⁺ calculated for C₄₅H₈₅N: 640.6755, found: 640.6777. Elemental analysis calculated for C₄₅H₈₅N: 84.43 C, 13.38 H, 2.19 N; found: 84.21 C, 13.24 H, 2.16 N.

Synthesis of 2-iso-butyl-2-(icos-19-en-1-yl)docos-21-enenitrile (7f). The same procedure described above for the synthesis of compound **7a** was followed. After purification, 0.435 g of

compound **7f** was collected as white crystals (yield = 56%). The following spectral properties were observed; ^1H NMR (CDCl_3) δ ppm 1.07 (d, $J=6.79$ Hz, 6 H), 1.13-1.48 (s, 74 H), 2.04 (td, $J_1=7.65$ Hz, $J_2=6.50$ Hz, 4 H), 4.88 - 5.09 (m, 4 H), 5.73 - 5.92 (m, 2 H); ^{13}C NMR (CDCl_3): δ (ppm) 23.27, 23.31, 25.51, 25.62, 26.71, 29.13, 29.35, 29.68, 29.79, 30.01, 30.34, 30.45, 34.07, 35.06, 35.17, 44.07, 44.18, 114.24 (vinyl CH_2), 124.73 (-CN), 139.50 (vinyl CH); EI/HRMS: $[\text{M}]^+$ calculated for $\text{C}_{46}\text{H}_{87}\text{N}$: 654.6911, found: 654.6911. Elemental analysis calculated for $\text{C}_{46}\text{H}_{87}\text{N}$: 84.45 C, 13.40 H, 2.14 N; found: 84.47 C, 13.32 H, 2.17 N.

Synthesis of 2-butyl-2-(icos-19-en-1-yl)docos-21-enitrile (7e). The same procedure described above for the synthesis of compound **7a** was followed. After purification, 0.435 g of compound **7e** was collected as white crystals (yield = 85%). The following spectral properties were observed; ^1H NMR (CDCl_3) δ (ppm) 0.94 (t, $J=6.79$, 3H), 1.20-1.35 (m, 74H), 2.05 (td, $J_1=7.63$ Hz, $J_2=6.51$ Hz, 4 H), 4.91-5.04 (m, 4H), 5.78-5.87 (m, 2H) ; ^{13}C NMR (CDCl_3) : δ (ppm) 14.14, 23.11, 24.49, 26.66, 29.18, 29.39, 29.58, 29.66, 29.74, 29.85, 29.92, 34.05, 36.33, 40.83, 114.29 (vinyl CH_2), 129.92 (-CN), 139.50 (vinyl CH); EI/HRMS: $[\text{M}]^+$ calculated for $\text{C}_{46}\text{H}_{87}\text{N}$: 653.6839, found: 653.6917. Elemental analysis calculated for $\text{C}_{46}\text{H}_{87}\text{N}$: 84.45 C, 13.40 H, 2.14 N; found: 84.47 C, 13.38 H, 2.17 N.

Synthesis of 2-pentyl-2-(icos-19-en-1-yl)docos-21-enitrile (7g). The same procedure described above for the synthesis of compound **7a** was followed. After purification, 0.435 g of compound **7g** was collected as white crystals (yield = 42%). The following spectral properties were observed; ^1H NMR (CDCl_3) δ ppm 0.91 (t, $J=6.80$ Hz, 3 H), 1.14 - 1.47 (m, 76 H), 2.05 (td, $J_1=7.64$ Hz, $J_2=6.51$ Hz, 4 H), 4.86 - 5.08 (m, 4 H), 5.72 - 5.92 (m, 2 H); ^{13}C NMR (CDCl_3): δ (ppm) 14.23, 22.64, 24.11, 24.25, 24.51, 26.52, 29.05, 29.19, 29.32, 29.59, 29.72, 29.99, 32.12, 33.99, 36.26, 40.80, 114.25 (vinyl CH_2), 124.80 (-CN), 139.49 (vinyl CH); EI/HRMS: $[\text{M}]^+$

calculated for C₄₇H₈₉N: 668.7068, found: 668.7098. Elemental analysis calculated for C₄₇H₈₉N: 84.48 C, 13.42 H, 2.10 N; found: 84.66 C, 13.32 H, 2.23 N.

Synthesis of 2-hexyl-2-(icos-19-en-1-yl)docos-21-enenitrile (7h). The same procedure described above for the synthesis of compound **7a** was followed. After purification, 0.581 g of compound **7h** was collected as white crystals (yield = 70%). The following spectral properties were observed; ¹H NMR (CDCl₃) δ ppm 0.88 (t, J=6.79, 3 H), 1.10 - 1.45 (br, 78 H), 2.04 (td, J₁=7.63 Hz, J₂=6.51 Hz, 4 H), 4.85 - 5.08 (m, 4 H), 5.68 - 5.95 (m, 2 H); ¹³C NMR (CDCl₃): δ (ppm) 14.40, 22.87, 22.99, 26.57, 26.69, 26.93, 29.08, 29.20, 29.44, 29.68, 29.79, 29.91, 30.39, 32.66, 33.85, 33.97, 34.09, 37.55, 37.67, 114.30 (vinyl CH₂), 124.80 (-CN), 139.48 (vinyl CH); EI/HRMS: [M]⁺ calculated for C₄₈H₉₁N: 682.7224, found: 682.7241. Elemental analysis calculated for C₄₈H₉₁N: 84.50 C, 13.44 H, 2.05 N; found: 84.53 C, 13.45 H, 2.19 N.

Synthesis of 2-heptyl-2-(icos-19-en-1-yl)docos-21-enenitrile (7i). The same procedure described above for the synthesis of compound **7a** was followed. After purification, 0.581 g of compound **7i** was collected as white crystals (yield = 38%). The following spectral properties were observed; ¹H NMR δ ppm 0.87 (t, J=6.80 Hz, 3 H), 1.06 - 1.43 (m, 80 H), 2.05 (td, J₁=7.60 Hz, J₂=6.54 Hz, 4 H), 4.86 - 5.08 (m, 4 H), 5.72 - 5.93 (m, 2 H); ¹³C NMR (CDCl₃): δ (ppm) 14.83, 20.06, 20.46, 20.60, 26.89, 29.17, 29.31, 29.44, 29.71, 29.84, 29.98, 30.38, 32.79, 33.86, 34.00, 37.35, 37.48, 49.41, 114.26 (vinyl CH₂), 124.31 (-CN), 139.45 (vinyl CH); EI/HRMS: [M]⁺ calculated for C₄₉H₉₃N: 696.7381, found: 696.7402. Elemental analysis calculated for C₄₉H₉₃N: 84.53 C, 13.46 H, 2.01 N; found: 83.65 C, 13.40 H, 1.98 N.

Synthesis of 2-octyl-2-(icos-19-en-1-yl)docos-21-enenitrile (7j). The same procedure described above for the synthesis of compound **7a** was followed. After purification, 0.581 g of compound **7j** was collected as white crystals (yield = 95%). The following spectral properties

were observed; ^1H NMR δ ppm 0.88 (t, $J=6.79$ Hz, 3 H), 1.11 - 1.41 (m, 82 H), 2.06 (td, $J_1=7.64$ Hz, $J_2=6.49$ Hz, 4 H), 4.88 - 5.11 (m, 4 H), 5.74 - 5.98 (m, 2 H); ^{13}C NMR (CDCl_3): δ (ppm) 14.97, 20.09, 20.38, 20.55, 26.89, 29.15, 29.44, 29.48, 29.71, 29.94, 29.92, 30.33, 32.88, 33.97, 37.40, 48.44, 114.30 (vinyl CH_2), 124.34 (-CN), 139.50 (vinyl CH); EI/HRMS: $[\text{M}]^+$ calculated for $\text{C}_{50}\text{H}_{95}\text{N}$: 710.7537, found: 710.7554. Elemental analysis calculated for $\text{C}_{50}\text{H}_{95}\text{N}$: 84.55 C, 13.48 H, 1.97 N; found: 84.54 C, 13.42 H, 2.06 N.

Synthesis of dodecanenitrile (6k). In a flame-dried 250 ml three neck round bottomed flask equipped with reflux condenser and stir bar, 1-bromodecane (10.89 g, 49.25 mmol) was added and dissolved in 35 mL of anhydrous DMF. Sodium cyanide (3.088 g, 63.00 mmol) was dissolved in 50 mL anhydrous DMF and added to the 1-bromodecane solution in one portion under Ar flow. The reaction mixture was stirred for 24 h at 65 °C and then quenched with 100 mL DI water. The organic phase was extracted with Et_2O (3x50 mL) and dried over MgSO_4 . The crude product was filtered, concentrated, and further purified via column chromatography with hexane/EtOAc 9/1 as eluent to give dodecanenitrile (5.29 g, 31.64 mmol) as a colorless oil (yield = 64%). The following spectral properties were observed; ^1H NMR (CDCl_3) δ ppm 0.87 (t, $J=6.80$ Hz, 3 H), 1.26 (br. s., 12 H), 1.37 - 1.51 (m, 2 H), 1.56 - 1.72 (m, 2 H), 2.32 (t, $J=7.08$ Hz, 2 H); ^{13}C NMR (CDCl_3) δ ppm 14.04, 17.05, 22.64, 25.37, 28.63, 28.75, 29.25, 29.30, 29.45, 31.84, 119.76 (-CN); EI/HRMS: $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{12}\text{H}_{23}\text{N}$: 185.2012, found: 185.2018. Elemental analysis calculated for $\text{C}_{12}\text{H}_{23}\text{N}$: 78.97 C, 12.65 H, 8.37 N; found: 79.03 C, 12.74 H, 8.30 N.

Synthesis of 2-nonyl-2-(icos-19-en-1-yl)docos-21-enenitrile (7k). The same procedure described above for the synthesis of compound **7a** was followed using the dodecanenitrile synthesized from 1-bromodecane. After purification, 0.659 g of compound **7k** was collected as

white crystals (yield = 78%). The following spectral properties were observed; ^1H NMR δ ppm 0.89 (t, $J=6.80$ Hz, 3 H), 1.14 - 1.47 (m, 84 H), 2.04 (td, $J_1=7.62$ Hz, $J_2=6.56$ Hz, 4 H), 4.86 - 5.08 (m, 4 H), 5.71 - 5.94 (m, 2 H); ^{13}C NMR (CDCl_3): δ (ppm) 14.23, 22.65, 24.18, 24.24, 24.56, 26.50, 29.02, 29.24, 29.33, 29.61, 29.80, 29.97, 32.16, 33.92, 36.28, 40.84, 114.24 (vinyl CH_2), 124.81 (-CN), 139.50 (vinyl CH); EI/HRMS: $[\text{M}]^+$ calculated for $\text{C}_{51}\text{H}_{97}\text{N}$: 724.7694, found: 724.7710. Elemental analysis calculated for $\text{C}_{51}\text{H}_{97}\text{N}$: 84.57 C, 13.50 H, 1.93 N; found: 84.75 C, 13.61 H, 1.98 N.

Synthesis of 2-decyl-2-(icos-19-en-1-yl)docos-21-enenitrile (7l). The same procedure described above for the synthesis of compound **7a** was followed. After purification, 0.553 g of compound **7l** was collected as white crystals (yield = 56%). The following spectral properties were observed; ^1H NMR (CDCl_3) δ ppm 0.91 (t, $J=6.79$ Hz, 3 H), 1.12 - 1.45 (m, 86 H), 2.06 (td, $J_1=7.63$ Hz, $J_2=6.58$ Hz, 4 H), 4.84 - 5.06 (m, 4 H), 5.72 - 5.95 (m, 2 H); ^{13}C NMR (CDCl_3): δ (ppm) 14.21, 22.67, 24.19, 24.22, 24.58, 26.52, 29.04, 29.20, 29.35, 29.63, 29.84, 29.94, 32.18, 33.94, 36.28, 40.85, 114.25 (vinyl CH_2), 124.80 (-CN), 139.49 (vinyl CH); EI/HRMS: $[\text{M}]^+$ calculated for $\text{C}_{52}\text{H}_{99}\text{N}$: 738.7850, found: 738.7881. Elemental analysis calculated for $\text{C}_{52}\text{H}_{99}\text{N}$: 84.59 C, 13.51 H, 1.90 N; found: 84.82 C, 13.60 H, 2.00 N.

Synthesis of 2-pentadecyl-2-(icos-19-en-1-yl)docos-21-enenitrile (7m). The same procedure described above for the synthesis of compound **7a** was followed. After purification, 0.737 g of compound **7m** was collected as white crystals (yield = 65%). The following spectral properties were observed; ^1H NMR (CDCl_3) δ ppm 0.90 (d, $J=6.79$ Hz, 3 H), 1.10 - 1.46 (m, 96 H), 2.05 (td, $J_1=7.61$ Hz, $J_2=6.51$ Hz, 4 H), 4.85 - 5.09 (m, 4 H), 5.75 - 5.90 (m, 2 H); ^{13}C NMR (CDCl_3): δ ppm 14.34, 22.92, 26.93, 29.18, 29.39, 29.59, 29.74, 29.85, 29.90, 29.94, 30.38, 32.16, 33.92, 34.05, 37.61, 114.28 (vinyl CH_2), 124.79 (-CN), 139.49 (vinyl CH); EI/HRMS: $[\text{M}]^+$ calculated

for C₅₇H₁₀₉N: 808.8639, found: 808.8655. Elemental analysis calculated for C₅₇H₁₀₉N: 84.68 C, 13.59 H, 1.73 N; found: 84.81 C, 13.33 H, 1.82 N.

Synthesis of 21-methylhentetraconta-1,40-diene (8a). Potassium metal (0.45 g, 11.5 mmol), HMPA (0.9 mL, 6.76 mmol), and diethyl ether (20 mL) were transferred to a 100 mL 3 necked round bottomed flask equipped with a stir bar, addition funnel, and argon inlet adaptor. A solution of the alkylcyano α,ω -diolefin **8a** (0.861 g, 1.34 mmol) and t-BuOH (0.6 mL, 10.38 mmol) in diethyl ether (20 mL) was added dropwise to the reactor at 0 °C. The reaction mixture was warmed to RT and stirred for 25 h. The reaction was quenched with isopropanol (20 mL), extracted three times with diethyl ether (3x50 mL), washed with brine (50 mL) and dried over MgSO₄. The solution was filtered, concentrated by rotary evaporation and purified by column chromatography using hexane as the eluent. Compound **8a** was collected as white crystals (0.659 g, 1.12 mmol) (yield= 84%). The following spectral properties were observed; ¹H NMR (CDCl₃) δ ppm 0.84 (d, *J*=6.20 Hz, 3 H), 1.27 (br, 68 H), 2.05 (td, *J*₁=7.64 Hz, *J*₂=6.51 Hz, 4 H), 4.83 - 5.10 (m, 4 H), 5.71 - 5.94 (m, 2 H) ¹³C NMR (CDCl₃): δ ppm 19.95, 27.31, 29.18, 29.39, 29.74, 29.85, 29.93, 30.26, 34.05, 37.32, 114.28 (vinyl CH₂), 139.51 (vinyl CH). Elemental analysis calculated for C₄₂H₈₂: 85.92 C, 14.08 H; found: 85.78 C, 14.24 H.

Synthesis of 21-ethylhentetraconta-1,40-diene (8b). The same procedure described above for the synthesis of compound **8a** was followed. After purification, 0.519 g of compound **8b** was collected as white crystals (yield = 95%). The following spectral properties were observed; ¹H NMR (CDCl₃); δ ppm 0.90 (t, *J*=6.80 Hz, 3 H), 1.05 - 1.45 (m, 70 H), 2.04 (td, *J*₁=7.65 Hz, *J*₂=6.51 Hz, 4 H), 4.84 - 5.09 (m, 4 H), 5.74 - 5.90 (m, 2 H) ¹³C NMR (CDCl₃): δ ppm 14.36, 22.96, 26.61, 26.93, 29.19, 29.39, 29.75, 29.86, 29.90, 29.94, 30.39, 32.63, 33.89, 33.92, 34.05,

37.63, 114.28 (vinyl CH₂), 139.49 (vinyl CH). Elemental analysis calculated for C₄₃H₈₄: 85.92 C, 14.08 H; found: 86.08 C, 14.09 H.

Synthesis of 21-propylhentetraconta-1,40-diene (8c). The same procedure described above for the synthesis of compound **8a** was followed. After purification, 0.349 g of compound **8c** was collected as white crystals (yield = 76%). The following spectral properties were observed; ¹H NMR (CDCl₃) δ ppm 0.96 (t, *J*=6.80 Hz, 3 H), 1.27 (s, 34 H), 2.05 (td, *J*₁=7.63 Hz, *J*₂=6.50 Hz, 4 H), 4.83 - 5.10 (m, 4 H), 5.70 - 5.94 (m, 2 H) ¹³C NMR (CDCl₃) δ ppm 14.47, 17.90, 24.50, 29.18, 29.38, 29.66, 29.74, 29.85, 29.92, 34.05, 36.36, 40.86, 114.28 (vinyl CH₂), 139.49 (vinyl CH). Elemental analysis calculated for C₄₄H₈₆: 85.91 C, 14.09 H; found: 86.04 C, 14.10 H.

Synthesis of 21-iso-propylhentetraconta-1,40-diene (8d). The same procedure described above for the synthesis of compound **8a** was followed. After purification, 0.473 g of compound **8d** was collected as white crystals (yield = 82%). The following spectral properties were observed; ¹H NMR (CDCl₃) δ ppm 0.82 (d, *J*=6.50 Hz, 6 H), 1.27 (s, 72 H), 2.06 (td, *J*₁=7.64 Hz, *J*₂=6.52 Hz, 4 H), 4.80 - 5.13 (m, 4 H), 5.71 - 5.95 (m, 2 H) ¹³C NMR (CDCl₃) δ ppm 19.43, 27.99, 29.18, 29.39, 29.74, 29.94, 30.41, 30.75, 34.05, 43.91, 114.28 (vinyl CH₂), 139.51 (vinyl CH). Elemental analysis calculated for C₄₄H₈₆: 85.91 C, 14.09 H; found: 86.11 C, 14.18 H.

Synthesis of 21-butylhentetraconta-1,40-diene (8e). The same procedure described above for the synthesis of compound **8a** was followed. After purification, 0.229 g of compound **8e** was collected as white crystals (yield = 98%). The following spectral properties were observed; ¹H NMR (CDCl₃): δ (ppm) 0.91 (t, *J*=6.79, 3H), 1.24-1.41 (br, 74H), 2.05 (td, *J*₁=7.63 Hz, *J*₂=6.51 Hz, 4 H), 4.91-5.04 (m, 4H), 5.78-5.87 (m, 2H) ; ¹³C NMR (CDCl₃) : δ (ppm) 14.42, 23.43, 26.97, 29.22, 29.43, 29.42, 29.79, 29.90, 29.98, 30.43, 33.65, 33.96, 37.64, 114.31 (vinyl CH₂),

139.45 (vinyl CH); Elemental analysis calculated for C₄₅H₈₈: 85.90 C, 14.10 H; found: 85.93 C, 14.06 H.

Synthesis of 21-*iso*-butylhentetraconta-1,40-diene (8f). The same procedure described above for the synthesis of compound **8a** was followed. After purification, 0.329 g of compound **8f** was collected as white crystals (yield = 71%). The following spectral properties were observed; ¹H NMR (CDCl₃) δ ppm 0.86 (d, *J*=6.51 Hz, 6 H), 1.27 (s, 74 H), 2.04 (td, *J*₁=7.65 Hz, *J*₂=6.50 Hz, 4 H), 4.85 - 5.11 (m, 4 H), 5.70 - 5.94 (m, 2 H); ¹³C NMR (CDCl₃) δ ppm 23.23, 25.53, 26.70, 29.18, 29.40, 29.75, 29.86, 29.94, 30.41, 34.05, 34.10, 35.13, 44.11, 114.29 (vinyl CH₂), 139.49 (vinyl CH). Elemental analysis calculated for C₄₅H₈₈: 85.90 C, 14.10 H; found: 86.17 C, 14.02 H.

Synthesis of 21-pentylhentetraconta-1,40-diene (8g). The same procedure described above for the synthesis of compound **8a** was followed. After purification, 0.265 g of compound **8g** was collected as white crystals (yield = 85%). The following spectral properties were observed; ¹H NMR (CDCl₃) δ ppm 0.91 (t, *J*=6.79 Hz, 3 H), 1.14 - 1.47 (m, 76 H), 2.05 (td, *J*₁=7.64 Hz, *J*₂=6.51 Hz, 4 H), 4.86 - 5.08 (m, 4 H), 5.72 - 5.92 (m, 2 H); ¹³C NMR (CDCl₃) δ ppm 14.36, 22.95, 26.60, 26.92, 29.18, 29.39, 29.74, 29.85, 29.94, 30.38, 32.62, 33.91, 34.05, 37.62, 114.28 (vinyl CH₂), 139.49 (vinyl CH). Elemental analysis calculated for C₄₅H₈₈: 85.90 C, 14.10 H; found: 86.00 C, 14.04 H.

Synthesis of 21-hexylhentetraconta-1,40-diene (8h). The same procedure described above for the synthesis of compound **8a** was followed. After purification, 0.416 g of compound **8h** was collected as white crystals (yield = 88%). The following spectral properties were observed; ¹H NMR (CDCl₃) δ ppm 0.89 (t, *J*=6.80 Hz, 3 H), 1.27 (br, 78 H), 2.04 (td, *J*₁=7.63 Hz, *J*₂=6.51 Hz, 4 H), 4.87 - 5.07 (m, 4 H), 5.74 - 5.91 (m, 2 H); ¹³C NMR (CDCl₃) δ ppm 14.35, 22.94, 26.92,

29.18, 29.39, 29.74, 29.85, 29.90, 29.93, 30.06, 30.38, 32.19, 33.92, 33.94, 34.05, 37.62, 114.28 (vinyl CH₂), 139.49 (vinyl CH). Elemental analysis calculated for C₄₆H₉₀: 85.89 C, 14.11 H; found: 86.00 C, 14.17 H.

Synthesis of 21-heptylhentetraconta-1,40-diene (8i). The same procedure described above for the synthesis of compound **8a** was followed. After purification, 0.262 g of compound **8i** was collected as white crystals (yield = 93%). The following spectral properties were observed; ¹H NMR (CDCl₃) δ ppm 0.88 (t, *J*=6.80 Hz, 3 H), 1.26 (br, 80 H), 2.05 (td, *J*₁=7.60 Hz, *J*₂=6.54 Hz, 4 H), 4.85 - 5.09 (m, 4 H), 5.70 - 5.91 (m, 2 H); ¹³C NMR (CDCl₃) δ ppm 14.35, 22.93, 26.93, 29.18, 29.39, 29.62, 29.74, 29.85, 29.94, 30.38, 32.17, 33.92, 34.05, 37.62, 114.28 (vinyl CH₂), 139.50 (vinyl CH). Elemental analysis calculated for C₄₈H₉₄: 85.89 C, 14.11 H; found: 85.63 C, 14.25 H.

Synthesis of 21-octylhentetraconta-1,40-diene (8j). The same procedure described above for the synthesis of compound **8a** was followed. After purification, 0.452 g of compound **8j** was collected as white crystals (yield = 85%). The following spectral properties were observed; ¹H NMR (CDCl₃) δ ppm 0.89 (t, *J*=6.80 Hz, 3 H), 1.27 (br, 82 H), 2.06 (td, *J*₁=7.64 Hz, *J*₂=6.49 Hz, 4 H), 4.82 - 5.12 (m, 4 H), 5.69 - 6.00 (m, 2 H); ¹³C NMR (CDCl₃) δ ppm 14.35, 22.92, 26.92, 29.18, 29.38, 29.60, 29.74, 29.85, 29.94, 30.38, 32.16, 33.92, 34.05, 37.61, 114.29 (vinyl CH₂), 139.51 (vinyl CH). Elemental analysis calculated for C₄₉H₉₆: 85.88 C, 14.12 H; found: 85.84 C, 13.98 H.

Synthesis of 21-nonylhentetraconta-1,40-diene (8k). The same procedure described above for the synthesis of compound **8a** was followed. After purification, 0.452 g of compound **8k** was collected as white crystals (yield = 85%). The following spectral properties were observed; ¹H NMR (CDCl₃) δ ppm 0.89 (t, *J*=6.80 Hz, 3 H), 1.04 - 1.45 (br, 84 H), 2.04 (td, *J*₁=7.62 Hz,

$J_2=6.56$ Hz, 4 H), 4.86 - 5.07 (m, 3 H), 5.73 - 5.91 (m, 1 H); ^{13}C NMR (CDCl_3) δ ppm 14.35, 22.92, 26.93, 29.19, 29.39, 29.60, 29.74, 29.85, 29.90, 29.94, 30.38, 32.16, 33.92, 34.05, 37.62, 114.28 (vinyl CH_2), 139.50 (vinyl CH). Elemental analysis calculated for $\text{C}_{50}\text{H}_{98}$: 85.87 C, 14.13 H; found: 85.79 C, 14.20 H.

Synthesis of 21-decylhentetraconta-1,40-diene (8l). The same procedure described above for the synthesis of compound **8a** was followed. After purification, 0.425 g of compound **8l** was collected as white crystals (yield = 84%). The following spectral properties were observed; ^1H NMR (CDCl_3) δ ppm 0.88 (t, $J=6.80$ Hz, 3 H), 1.27 (br, 86 H), 2.06 (td, $J_1=7.63$ Hz, $J_2=6.58$ Hz, 4 H), 4.83 - 5.10 (m, 4 H), 5.70 - 5.95 (m, 2 H); ^{13}C NMR (CDCl_3) δ ppm 14.36, 22.93, 26.93, 29.19, 29.40, 29.60, 29.75, 29.86, 29.94, 30.39, 32.16, 33.92, 34.06, 37.61, 114.29 (vinyl CH_2), 139.50 (vinyl CH). Elemental analysis calculated for $\text{C}_{51}\text{H}_{100}$: 85.87 C, 14.13 H; found: 85.64 C, 14.27 H.

Synthesis of 21-pentadecylhentetraconta-1,40-diene (8m). The same procedure described above for the synthesis of compound **8a** was followed. After purification, 0.437 g of compound **8m** was collected as white crystals (yield = 90%). The following spectral properties were observed; ^1H NMR (CDCl_3) δ ppm 0.87 (t, $J=6.80$ Hz, 3 H), 1.27 (br, 96 H), 2.05 (td, $J_1=7.61$ Hz, $J_2=6.51$ Hz, 4 H), 4.86 - 5.07 (m, 4 H), 5.73 - 5.91 (m, 2 H); ^{13}C NMR (CDCl_3) δ ppm 14.34, 22.92, 26.93, 29.18, 29.39, 29.59, 29.74, 29.85, 29.90, 29.94, 30.38, 32.16, 33.92, 34.05, 37.61, 114.28 (vinyl CH_2), 139.49 (vinyl CH). Elemental analysis calculated for $\text{C}_{56}\text{H}_{110}$: 85.85 C, 14.15 H; found: 85.72 C, 14.22 H.

Polymerization of 21-methylhentetraconta-1,40-diene (9a). Monomer **8a** (0.335 g, 0.57 mmol) was placed in a 25 mL flame dried Schlenk tube under Ar and heated to 75 °C using an oil bath and high vacuum (10^{-5} torr). After 2 h of stirring at these conditions, the monomer was

cooled to room temperature and the Schlenk tube was placed into the glove box. Schrock's catalyst (0.9 mg, 1.17×10^{-3} mmol; catalyst to monomer ratio = 1:500) was added, and the Schlenk tube was removed from the glove box and connected to high vacuum. Polymerization was initiated by melting the monomer at 50 °C and the temperature was set to 85 °C to enable stirring of the viscous polymer melt. After 24 h, the polymer was cooled to RT and another 0.9 mg portion of Schrock catalyst was added in the glove box. After 24 h of polymerization at 85 °C, the Schlenk tube was opened to air and the polymer was dissolved in 5 mL of toluene. The polymer solution was poured into acidic methanol to precipitate the polymer. The polymer was filtered, re-dissolved and re-precipitated two more times to remove the traces of catalyst. Polymer **9a** (0.295 g) was recovered as a white solid (yield=92%). The following spectral properties were observed; ^1H NMR (300 MHz, C_6D_6) δ ppm 0.97 (d, $J=6.20$ Hz, 3 H), 1.38 (br, 68 H), 1.96 - 2.24 (m, 4 H), 5.38 - 5.64 (m, 2 H); ^{13}C NMR (75 MHz, C_6D_6) δ ppm 26.06, 27.97, 29.99, 30.54, 30.90, 33.43, 33.67, 37.18, 38.00, 131.16.

Polymerization of 21-ethylhentacont-1,40-diene (9b). The same procedure described above for the synthesis of polymer **9a** was followed. After purification, 0.320 g of compound **9b** was collected (yield = 87%). The following spectral properties were observed; ^1H NMR (500 MHz, CDCl_3) δ ppm 0.89 (t, $J=6.80$ Hz, 3 H), 1.06 - 1.44 (br, 70 H), 1.88 - 2.09 (m, 4 H), 5.28 - 5.46 (m, 2 H); ^{13}C NMR (126 MHz, CDCl_3) δ ppm 14.36, 22.96, 26.61, 26.94, 27.44, 29.42, 29.56, 29.77, 29.8, 29.90, 29.95, 30.01, 30.40, 32.63, 32.84, 33.88, 33.93, 37.63, 130.11, 130.57.

Polymerization of 21-propylhentacont-1,40-diene (9c). The same procedure described above for the synthesis of polymer **9a** was followed. After purification, 0.320 g of compound **9c** was collected (yield = 92%). The following spectral properties were observed; ^1H NMR (299 MHz, CDCl_3) δ ppm 0.89 (t, $J=6.20$ Hz, 3 H), 1.27 (br, 72 H), 1.85 - 2.14 (m, 4 H), 5.28 - 5.51

(m, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ ppm 14.79, 20.05, 26.93, 29.42, 29.78, 29.95, 30.41, 32.84, 33.93, 36.35, 37.41, 130.57.

Polymerization of 21-iso-propylhentetraconta-1,40-diene (9d). The same procedure described above for the synthesis of polymer **9a** was followed. After purification, 0.320 g of compound **9d** was collected (yield = 90%). The following spectral properties were observed; ^1H NMR (299 MHz, CDCl_3) δ ppm 0.81 (d, $J=6.50$ Hz, 6 H), 1.26 (br, 70 H), 1.85 - 2.11 (m, 4 H), 5.28 - 5.48 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ ppm 19.43, 28.00, 29.42, 29.78, 29.95, 30.42, 30.75, 32.84, 43.92, 130.58.

Polymerization of 21-butylhentetraconta-1,40-diene (9e). The same procedure described above for the synthesis of polymer **9a** was followed. After purification, 0.270 g of compound **9e** was collected (yield = 90%). The following spectral properties were observed; ^1H NMR (299 MHz, CDCl_3) δ ppm 0.90 (t, $J=6.80$ Hz, 3 H), 1.01 - 1.49 (br, 74 H), 1.86 - 2.13 (m, 4 H), 5.25 - 5.47 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ ppm 14.40, 23.40, 26.94, 29.41, 29.77, 29.95, 30.40, 32.84, 33.93, 37.60, 130.57.

Polymerization of 21-iso-butylhentetraconta-1,40-diene (9f). The same procedure described above for the synthesis of polymer **9a** was followed. After purification, 0.270 g of compound **9f** was collected (yield = 83%). The following spectral properties were observed; ^1H NMR (299 MHz, CDCl_3) δ ppm 0.86 (d, $J=6.50$ Hz, 6 H), 1.27 (br, 74 H), 1.85 - 2.13 (m, 4 H), 5.25 - 5.50 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ ppm 23.23, 25.53, 26.71, 29.41, 29.56, 29.78, 29.95, 30.41, 32.84, 34.11, 35.13, 44.10, 130.11, 130.57.

Polymerization of 21-pentylhentetraconta-1,40-diene (9g). The same procedure described above for the synthesis of polymer **9a** was followed. After purification, 0.298 g of compound **9g** was collected (yield = 89%). The following spectral properties were observed; ^1H NMR (500

MHz, CDCl₃) δ ppm 0.83 (t, $J=6.80$ Hz, 3 H), 1.27 (br, 76 H), 1.86 - 2.10 (m, 4 H), 5.27 - 5.48 (m, 2 H); ¹³C NMR (126 MHz, CDCl₃) δ ppm 11.11, 26.13, 26.98, 27.44, 29.42, 29.56, 29.77, 29.81, 29.90, 29.95, 30.40, 32.84, 33.45, 39.09, 130.12, 130.58.

Polymerization of 21-hexylhentetraconta-1,40-diene (9h). The same procedure described above for the synthesis of polymer **9a** was followed. After purification, 0.233 g of compound **9h** was collected (yield = 84%). The following spectral properties were observed; ¹H NMR (500 MHz, CDCl₃) δ ppm 0.89 (t, $J=6.80$ Hz, 3 H), 1.03 - 1.46 (br, 78 H), 1.85 - 2.10 (m, 4 H), 5.29 - 5.48 (m, 2 H); ¹³C NMR (126 MHz, CDCl₃) δ ppm 14.38, 22.97, 26.94, 26.97, 27.47, 29.44, 29.59, 29.81, 29.84, 29.93, 29.98, 30.10, 30.43, 32.19, 32.22, 32.87, 33.96, 37.66, 130.14, 130.60.

Polymerization of 21-heptylhentetraconta-1,40-diene (9i). The same procedure described above for the synthesis of polymer **9a** was followed. After purification, 0.165 g of compound **9i** was collected (yield = 88%). The following spectral properties were observed; ¹H NMR (500 MHz, CDCl₃) δ ppm 0.88 (t, $J=6.80$ Hz, 3 H), 1.26 (br, 80 H), 1.87 - 2.10 (m, 4 H), 5.26 - 5.47 (m, 2 H); ¹³C NMR (126 MHz, CDCl₃) δ ppm 14.35, 22.93, 26.94, 27.45, 29.42, 29.56, 29.63, 29.78, 29.90, 29.96, 30.36, 30.40, 32.18, 32.84, 33.94, 37.63, 130.11, 130.57.

Polymerization of 21-octylhentetraconta-1,40-diene (9j). The same procedure described above for the synthesis of polymer **9a** was followed. After purification, 0.232 g of compound **9j** was collected (yield = 90%). The following spectral properties were observed; ¹H NMR (500 MHz, CDCl₃) δ ppm 0.91 (t, $J=6.80$ Hz, 3 H), 1.29 (br, 82 H), 1.88 - 2.13 (m, 4 H), 5.28 - 5.50 (m, 2 H); ¹³C NMR (126 MHz, CDCl₃) δ ppm 14.24, 22.92, 27.10, 27.53, 29.46, 29.60, 29.80, 29.92, 29.98, 30.43, 32.20, 32.84, 34.21, 37.87, 130.16, 130.64.

Polymerization of 21-nonylhentetraconta-1,40-diene (9k). The same procedure described above for the synthesis of polymer **9a** was followed. After purification, 0.330 g of compound **9k** was collected (yield = 90%). The following spectral properties were observed; ¹H NMR (500 MHz, CDCl₃) δ ppm 0.89 (t, *J*=6.80 Hz, 3 H), 1.27 (br, 84 H), 1.88 - 2.15 (m, 4 H), 5.29 - 5.52 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ ppm 14.37, 22.96, 26.61, 26.94, 29.42, 29.78, 29.95, 30.40, 32.63, 32.84, 33.93, 37.63, 130.11, 130.58.

Polymerization of 21-decylhentetraconta-1,40-diene (9l). The same procedure described above for the synthesis of polymer **9a** was followed. After purification, 0.272 g of compound **9l** was collected (yield = 71%). The following spectral properties were observed; ¹H NMR (500 MHz, CDCl₃) δ ppm 0.90 (t, *J*=6.80 Hz, 3 H), 1.02 - 1.46 (br, 86 H), 1.87 - 2.11 (m, 4 H), 5.25 - 5.49 (m, 2 H); ¹³C NMR (126 MHz, CDCl₃) δ ppm 14.35, 22.93, 26.94, 27.44, 29.42, 29.56, 29.60, 29.78, 29.90, 29.96, 30.39, 32.16, 32.84, 33.94, 37.62, 130.11, 130.57.

Polymerization of 21-pentadecylhentetraconta-1,40-diene (9m). The same procedure described above for the synthesis of polymer **9a** was followed. After purification, 0.296 g of compound **4-28m** was collected (yield = 86%). The following spectral properties were observed; ¹H NMR (500 MHz, CDCl₃) δ ppm 0.88 (t, *J*=6.80 Hz, 3 H), 1.27 (br, 96 H), 1.87 - 2.10 (m, 4 H), 5.29 - 5.49 (m, 2 H); ¹³C NMR (126 MHz, CDCl₃) δ ppm 14.35, 22.92, 26.94, 29.42, 29.60, 29.78, 29.90, 29.96, 30.40, 32.16, 32.85, 33.94, 37.62, 130.10, 130.57.

Hydrogenation of methyl branched polymer (10a). In a 125 mL Parr bomb glass sleeve, unsaturated polymer **9a** (0.252 g) was dissolved in 40 mL degassed toluene. Wilkinson's hydrogenation catalyst (0.7 mg, 7.6×10⁻⁴ mmol; catalyst to monomer ratio 1:250) 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 poured into acidic methanol and the

resulting precipitate was then filtered and dissolved in 5 mL toluene. The polymer was re-dissolved and re-precipitated two more times to remove the traces of catalyst. Polymer **10a** (0.177 g) was collected as a white solid (yield = 70%). The following spectral properties were observed; ^1H NMR (500 MHz, C_6D_6) δ ppm 0.96 (d, $J=6.20$ Hz, 3 H), 1.17 - 1.56 (br, 74 H); ^{13}C NMR (126 MHz, C_6D_6) δ ppm 19.84, 27.42, 29.99, 30.34, 33.12, 37.34.

Hydrogenation of ethyl branched polymer (10b). The same procedure described above for the synthesis of saturated polymer **10a** was followed. After purification, 0.273 g of polymer **10b** was collected (yield = 96%). The following spectral properties were observed; ^1H NMR (500 MHz, C_6D_6) δ ppm 0.90 (t, $J=6.80$ Hz, 3 H), 1.28 (br, 76 H); ^{13}C NMR (126 MHz, C_6D_6) δ ppm 11.19, 26.44, 27.16, 29.99, 30.46, 33.76, 39.41.

Hydrogenation of propyl branched polymer (10c). The same procedure described above for the synthesis of saturated polymer **10a** was followed. After purification, 0.200 g of polymer **10c** was collected (yield = 96%). The following spectral properties were observed; ^1H NMR (500 MHz, C_6D_6) δ ppm 0.95 (t, $J=6.80$ Hz, 3 H), 1.38 (s, 78 H); ^{13}C NMR (126 MHz, C_6D_6) δ ppm 14.55, 20.20, 27.16, 29.99, 30.49, 34.25, 36.66, 37.70.

Hydrogenation of *iso*-propyl branched polymer (10d). The same procedure described above for the synthesis of saturated polymer **10a** was followed. After purification, 0.302 g of polymer **4-29d** was collected (yield = 93%). The following spectral properties were observed; ^1H NMR (500 MHz, C_6D_6) δ ppm 0.93 (d, $J=6.50$ Hz, 6 H), 1.38 (br, 78 H); ^{13}C NMR (126 MHz, C_6D_6) δ ppm 19.37, 28.20, 29.84, 29.99, 30.48, 31.14, 44.23.

Hydrogenation of butyl branched polymer (10e). The same procedure from the synthesis of saturated polymer **10a** was followed. After the purification, 0.302 g of polymer **10e** were collected (yield = 93%). The following spectral properties were observed; ^1H NMR (500 MHz,

C₆D₆) δ ppm 0.92 (t, $J=6.80$ Hz, 3 H), 1.29 (br, 80 H); ¹³C NMR (126 MHz, C₆D₆) δ ppm 14.28, 22.68, 26.80, 29.99, 30.45, 32.75, 34.27, 37.88.

Hydrogenation of *iso*-butyl branched polymer (10f). The same procedure described above for the synthesis of saturated polymer **10a** was followed. After purification, 0.037 g of polymer **10f** was collected (yield = 28%). The following spectral properties were observed; ¹H NMR (500 MHz, C₆D₆) δ ppm 1.07 (d, $J=6.59$ Hz, 6 H), 1.37 - 1.61 (br, 80 H); ¹³C NMR (126 MHz, C₆D₆) δ ppm 23.09, 25.75, 26.95, 29.99, 30.49, 34.49, 35.56, 44.43.

Hydrogenation of pentyl branched polymer (10g). The same procedure described above for the synthesis of saturated polymer **10a** was followed. After purification, 0.141 g of polymer **10g** was collected (yield = 85%). The following spectral properties were observed; ¹H NMR (500 MHz, C₆D₆) δ ppm 0.91 (t, $J=6.80$ Hz, 3 H), 1.29 (s, 82 H); ¹³C NMR (126 MHz, C₆D₆) δ ppm 14.29, 22.96, 26.77, 27.12, 29.99, 30.46, 32.47, 32.71, 34.24, 37.91.

Hydrogenation of hexyl branched polymer (10h). The same procedure described above for the synthesis of saturated polymer **10a** was followed. After purification, 0.205 g of polymer **10h** was collected (yield = 85%). The following spectral properties were observed; ¹H NMR (500 MHz, C₆D₆) δ ppm 0.91 (t, $J=6.80$ Hz, 3 H), 1.29 (br, 84 H); ¹³C NMR (126 MHz, C₆D₆) δ ppm 14.27, 22.92, 27.09, 27.12, 29.99, 30.09, 30.56, 32.24, 34.23, 37.90.

Hydrogenation of heptyl branched polymer (10i). The same procedure described above for the synthesis of saturated polymer **10a** was followed. After purification, 0.205 g of polymer **10i** was collected (yield = 85%). The following spectral properties were observed; ¹H NMR (500 MHz, C₆D₆) δ ppm 1.05 (t, $J=6.80$ Hz, 3 H), 1.49 (br. s., 86 H); ¹³C NMR (126 MHz, C₆D₆) δ ppm 14.27, 22.88, 27.12, 27.18, 29.63, 29.99, 30.04, 30.45, 30.48, 32.17, 34.28, 37.97.

Hydrogenation of octyl branched polymer (10j). The same procedure described above for the synthesis of saturated polymer **10a** was followed. After purification, 0.186 g of polymer **10i** was collected (yield = 89%). The following spectral properties were observed; ^1H NMR (500 MHz, C_6D_6) δ ppm 0.91 (t, $J=6.80$ Hz, 3 H), 1.36 (br. s., 75 H); ^{13}C NMR (126 MHz, C_6D_6) δ ppm 14.04, 22.86, 27.14, 27.17, 29.60, 29.94, 29.99, 30.04, 30.33, 30.47, 32.14, 34.18, 37.96.

Hydrogenation of nonyl branched polymer (10k). The same procedure described above for the synthesis of saturated polymer **10a** was followed. After purification, 0.263 g of polymer **10k** was collected (yield = 88%). The following spectral properties were observed; ^1H NMR (500 MHz, C_6D_6) δ ppm 0.90 (t, $J=6.80$ Hz, 3 H), 1.28 (br, 89 H); ^{13}C NMR (126 MHz, C_6D_6) δ ppm 14.26, 22.94, 27.03, 27.07, 29.99, 30.09, 30.48, 30.51, 32.23, 34.11, 37.97.

Hydrogenation of decyl branched polymer (10l). The same procedure described above for the synthesis of saturated polymer **10a** was followed. After purification, 0.263 g of polymer **10l** was collected (yield = 88%). The following spectral properties were observed; ^1H NMR (500 MHz, C_6D_6) δ ppm 0.91 (t, $J=6.80$ Hz, 3 H), 1.28 (br, 92 H); ^{13}C NMR (126 MHz, C_6D_6) δ ppm 14.24, 22.85, 27.08, 27.15, 29.59, 29.99, 30.07, 30.48, 30.51, 32.12, 34.31, 37.89.

Hydrogenation of pentadecyl branched polymer (10m). The same procedure described above for the synthesis of saturated polymer **10a** was followed. After the purification, 0.215 g of polymer **10k** was collected (yield = 86%). The following spectral properties were observed; ^1H NMR (500 MHz, C_6D_6) δ ppm 0.88 (t, $J=6.80$ Hz, 3 H), 1.28 (s, 83 H); ^{13}C NMR (126 MHz, C_6D_6) δ ppm 14.35, 22.84, 27.15, 27.21, 29.59, 29.99, 30.01, 30.42, 30.45, 32.23, 34.31, 37.93.

References

1. Baughman, T.; Sworen, J.; Wagener, K. *Tetrahedron* **2004**, 60, (48), 10943-10948.