

Supporting Information for ja-2009-07521p

Precision Polyethylene: Changes in Morphology As a Function of Alkyl Branch Size

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Instrumentation and Analysis. All ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in CDCl_3 unless otherwise stated. Chemical shifts were referenced to residual signals from CDCl_3 (7.27 ppm for ^1H , 77.23 ppm for ^{13}C) with 0.03% v/v TMS as an internal reference. The NMR splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; and br, broad signal. Analysis of samples by gas chromatography (GC) was performed on a gas chromatograph, equipped with a flame ionization detector, using a capillary column coated with 5% diphenyl-95% dimethylpolysiloxane. High-resolution mass spectrometry (HRMS) was performed using a mass spectrometer in the electron ionization (EI) mode. The mass resolution was ~ 6000 for EI measured at Full-Width-Half-Maximum (FWHM) in the high resolution detection mode. Thin layer chromatography (TLC) was used to monitor all reactions and was performed on aluminum plates coated with silica gel (250 μm thickness). TLC plates were developed to produce a visible signature by any of the following: ultraviolet light, iodine, vanillin, KMnO_4 , or phosphomolybdic acid. Flash column chromatography was performed using ultra pure silica gel (40-63 μm , 60 Å pore size). All reactions were performed in flame-dried glassware under argon unless otherwise stated.

Gel permeation chromatography (GPC) was performed using an internal differential refractive index detector (DRI), internal differential viscosity detector (DP), and a Precision 2 angle light scattering detector (LS). The light scattering signal was collected at a 15 degree angle, and the three in-line detectors were operated in series in the order of LS-DRI-DP. The chromatography was performed at 45 °C using two columns (10 microns PD, 7.8 mm ID, 300 mm length) with HPLC grade tetrahydrofuran as the mobile phase at a flow rate of 1.0 mL/minute. 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 against narrow molecular weight polystyrene standards. All standards were selected to produce M_p or M_w values well beyond the expected polymer's range. The Precision LS was calibrated using narrow polystyrene standard having an $M_w = 65,500$ g/mol.

Fourier transform infrared (FT-IR) spectroscopy was carried out for monomers, unsaturated and saturated polymers. Monomers were prepared by droplet deposition and sandwiched between two KCl salt plates. Unsaturated and hydrogenated polymer samples were prepared by solution casting a thin film from tetrachloroethylene onto a KCl salt plate.

Differential scanning calorimetry (DSC) analysis was performed using a DSC equipped with a controlled cooling accessory at a heating rate of 10 °C/min. Calibrations were made using indium and freshly distilled *n*-octane as the standards for peak temperature transitions and indium for the enthalpy standard. All samples were prepared in hermetically sealed pans (5-10 mg/sample) and were run using an empty pan as a reference and empty cells as a subtracted baseline. The samples were scanned for multiple cycles to remove recrystallization differences between the samples and the results reported are of the third scan in the cycle.

Wide angle powder X-ray diffraction (WAXD) data were obtained on a Bruker D8 diffractometer equipped with liquid N₂ cooling system, using copper K_α radiation with $\lambda=1.54$ Å. The solid polymers ($T_m >$ room temperature), such as linear ADMET PE and methyl branched PE, were filled into a copper container of 10 by 10 mm² with a depth of 1mm. Prior to measurement, these solid samples were melted to remove any thermal history. As for liquid polyolefins ($T_m <$ room temperature), i.e., polymers with branches longer than the ethyl group, samples were put on top of a flat copper substrate to form a thin layer with ~1mm thickness. During the measurements, in order to reduce scattering from air and avoid chemical degradation by oxygen at

elevated temperatures, medium vacuum was applied to the sample chamber. XRD data were collected at the experimental scattering angle 2θ ranging from 5° to 45° , with a step of $0.1^\circ/\text{min}$. Temperature dependent measurements were addressed at temperatures varying from below glass transition temperature to above melting points, with cooling or heating rate of $10^\circ/\text{min}$.

Materials. Chemicals were purchased from the Aldrich Chemical Co. and used as received unless noted. Grubbs first generation catalyst, bis(tricyclohexylphosphine)-benzylidineruthenium (IV) dichloride, was obtained from Materia, Inc and stored in an argon-filled drybox prior to use. Wilkinson's rhodium hydrogenation catalyst $\text{RhCl}(\text{PPh}_3)_3$ was purchased from Strem Chemical and used as received. Tetrahydrofuran (THF) and xylenes was freshly distilled from Na/K alloy using benzophenone as the indicator. The starting hexanenitrile and alkenyl bromides along with hexamethylphosphoramide, triethylamine, and 1,9-decadiene were distilled over CaH_2 .

Synthesis and Characterization of 3,3-dimethylbutanenitrile (2i). 1-bromo-2,2-dimethylpropane (**1i**) (5.0 g, 33.10 mmol), NaCN (4.87 g, 99.31 mmol), and acetone (30 mL) were transferred to a three-neck round bottom flask equipped with a stir bar, condenser, and argon inlet adaptor. The solution was stirred and refluxed for 3 hours at 63°C . After cooling the solution at room temperature 30 mL of water was added, extracted three times with ether (100 mL), and washed with brine (150 mL). After drying over MgSO_4 , the solution was filtered, concentrated by rotary evaporation, and purified by flash column chromatography (hexane). After purification 2.0 g (62 % yield) of material was collected. The following spectral properties were observed: ^1H NMR (CDCl_3): $\delta(\text{ppm})$ 1.08 (s, 9H), 2.21 (s, 2H); ^{13}C NMR (CDCl_3): $\delta(\text{ppm})$ 29.07, 30.78, 32.27, 118.67; EI/HRMS: $[\text{M}]^+$ calculated for

C₆H₁₁N: 97.0891, found: 97.0888. Elemental analysis calculated for C₆H₁₁N: 74.17 C, 11.41 H, 14.42 N; found 74.19 C, 11.39 H, 14.40 N.

Synthesis and Characterization of 2-cyclohexylacetonitrile (2j). After purification 2.03 g (66 % yield) of material was collected. The following spectral properties were observed: ¹H NMR (CDCl₃): δ(ppm) 1.14 (m, 5H), 1.70 (m, 6H), 2.20 (d, 2H) ; ¹³C NMR (CDCl₃): δ(ppm) 24.76, 25.74, 32.42, 34.80, 118.99; EI/HRMS: [M]⁺ calculated for C₈H₁₃N: 123.1048, found: 123.1043. Elemental analysis calculated for C₈H₁₃N: 77.99 C, 10.64 H, 11.37 N; found 77.95 C, 10.66 H, 11.38 N.

General Monomer Synthesis. Nitriles **3a-k** and monomers **4a-k** were synthesized according to previously published procedures.

2-propyl-2-(undec-10-enyl)tridec-12-enenitrile (3c). After purification, 6.46 g (96% yield) of a pale yellow liquid was collected. The following spectral properties were observed: ¹H NMR (CDCl₃): δ(ppm) 0.99 (t, 3H, -CH₃), 1.29-1.56 (m, 35H), 2.04 (q, 4H), 4.97 (m, 4H, vinyl CH₂), 5.82 (m, 2H, vinyl CH); ¹³C NMR (CDCl₃): δ(ppm) 8.89 (CH₃), 14.33, 22.87, 24.46, 29.13, 29.32, 29.63, 29.65, 29.71, 29.98, 31.81, 34.01, 35.83, 41.31, 114.33 (vinyl CH₂), 124.52 (-CN), 139.39 (vinyl CH); EI/HRMS: [M]⁺ calculated for C₂₇H₄₉N: 387.6847, found: 387.6720. Elemental analysis calculated for C₂₇H₄₉N: 83.65 C, 12.74 H, 3.61 N; found 83.59 C, 12.67 H, 3.74 N.

2-pentyl-2-(undec-10-enyl)tridec-12-enenitrile (3e). After purification, 7.66 g (99% yield) of a pale yellow liquid was collected. The following spectral properties were observed: ¹H NMR (CDCl₃): δ(ppm) 0.90 (t, 3H, -CH₃), 1.29-1.56 (m, 42H), 2.04 (q, 4H), 4.97 (m, 4H, vinyl CH₂), 5.82 (m, 2H, vinyl CH); ¹³C NMR (CDCl₃): δ(ppm) 14.24 (CH₃), 22.80, 24.48, 24.51, 29.15, 29.33, 29.62, 29.66, 29.71, 29.99, 31.83, 34.01, 36.38, 40.88, 114.34 (vinyl CH₂), 124.69 (-CN), 139.41 (vinyl CH); EI/HRMS: [M]⁺ calculated for C₂₉H₅₃N: 415.7378, found: 415.4346. Elemental

analysis calculated for $C_{29}H_{53}N$: 83.78 C, 12.85 H, 3.37 N; found 83.41 C, 13.37 H, 3.49 N.

2-isopropyl-2-(undec-10-enyl)tridec-12-enenitrile (3g). After purification, 4.60 g (99% yield) of a pale yellow liquid was collected. The following spectral properties were observed: 1H NMR ($CDCl_3$): δ (ppm), 1.32 (d, 6H), 1.59 (br, 32H), 2.32 (m, 4H), 5.26 (m, 4H, vinyl CH_2), 6.09 (m, 2H, vinyl CH); ^{13}C NMR ($CDCl_3$): δ (ppm) 17.88, 24.53, 29.13, 29.31, 29.64, 29.72, 30.09, 32.07, 33.12, 34.01, 45.22, 114.30, 123.83, 139.25; EI/HRMS: $[M]^+$ calculated for $C_{27}H_{49}N$: 387.3865, found: 387.3861. Elemental analysis calculated for $C_{27}H_{49}N$: 83.65 C, 12.74 H, 3.61 N; found 83.62 C, 12.75 H, 3.62 N.

2-isobutyl-2-(undec-10-enyl)tridec-12-enenitrile (3h). After purification, 2.344 g (62%) of yellow liquid was collected. The following spectral properties were observed: 1H NMR ($CDCl_3$): δ (ppm) 0.99 (d, 6H, CH_3), 1.27-1.54 (m, 34H, CH_2), 1.80 (m, 1H, CH), 2.02 (q, 4H, allyl CH_2), 4.95 (m, 4H, vinyl CH_2), 5.79 (m, 2H, vinyl CH) ; ^{13}C NMR ($CDCl_3$): δ (ppm) 24.26, 24.40, 25.07, 29.13, 29.31, 29.64, 29.70, 29.97, 34.01, 37.03, 39.70, 45.18, 114.34 (vinyl CH_2), 125.03 (-CN), 139.40 (vinyl CH); EI/HRMS: $[M]^+$ calculated for $C_{28}H_{51}N$: 401.4022, found: 401.4117. Elemental analysis calculated for $C_{28}H_{51}N$: 83.72 C, 12.80 H, 3.49 N; found: 83.70 C, 12.93 H, 3.56 N.

2-tert-butyl-2-(undec-10-enyl)tridec-12-enenitrile (3i). After purification, 4.0 g (97% yield) of a pale yellow liquid was collected. The following spectral properties were observed: 1H NMR ($CDCl_3$): δ (ppm), 1.05 (s, 9H), 1.29 (br, 32H), 2.03 (q, 4H), 4.96 (m, 4H, vinyl CH_2), 5.80 (m, 2H, vinyl CH); ^{13}C NMR ($CDCl_3$): δ (ppm) 26.38, 27.46, 29.12, 29.31, 29.59, 29.64, 29.73, 30.39, 33.71, 34.00, 37.29, 48.84, 114.27, 122.95, 139.26; EI/HRMS: $[M]^+$ calculated for $C_{28}H_{51}N$: 401.4022, found: 401.4019.

Elemental analysis calculated for $C_{28}H_{51}N$: 83.72 C, 12.80 H, 3.49 N; found 83.73 C, 12.79 H, 3.48 N.

2-cyclohexyl-2-(undec-10-enyl)tridec-12-enenitrile (3j). After purification, 3.40 g (98% yield) of a pale yellow liquid was collected. The following spectral properties were observed: 1H NMR ($CDCl_3$): δ (ppm), 1.16-1.82 (br, 43H), 2.06 (q, 4H), 4.96 (m, 4H, vinyl CH_2), 5.83 (m, 2H, vinyl CH); ^{13}C NMR ($CDCl_3$): δ (ppm) 24.62, 26.42, 26.76, 27.83, 29.14, 29.32, 29.65, 29.73, 30.11, 33.25, 34.01, 41.94, 44.91, 114.3, 124.12, 139.34; EI/HRMS: $[M]^+$ calculated for $C_{30}H_{53}N$: 427.4178, found: 427.4175. Elemental analysis calculated for $C_{30}H_{53}N$: 84.24 C, 12.49 H, 3.27 N; found 84.21 C, 12.50 H, 3.29 N.

1-adamantyl-2-(undec-10-enyl)tridec-12-enenitrile (3k). After purification, 0.950 g (83%) of yellow liquid was collected. The following spectral properties were observed: 1H NMR ($CDCl_3$): δ (ppm), 1.27 (m, 28H, CH_2), 1.61-1.68 (m, 11H, CH_2 and CH), 2.02 (q, 4H, allyl CH_2), 4.95 (m, 4H, vinyl CH_2), 5.79 (m, 2H, vinyl CH) ; ^{13}C NMR ($CDCl_3$): δ (ppm) 27.46, 28.75, 29.15, 29.34, 29.64, 30.42, 32.12, 34.02, 37.00, 37.45, 38.71, 49.52, 114.33 (vinyl CH_2), 122.67 (-CN), 139.44 (vinyl CH); EI/HRMS: $[M]^+$ calculated for $C_{34}H_{57}N$: 479.4505, found: 479.4517. Elemental analysis calculated for $C_{34}H_{57}N$: 85.11 C, 11.97 H, 2.92 N; found: 84.96 C, 12.23 H, 2.93 N.

2-Propyltricos-1,22-diene (4c). After purification, 10.76 g (99% yield) of a colorless liquid was collected. The following spectral properties were observed: 1H NMR ($CDCl_3$): δ (ppm) 0.90 (t, 3H), 1.23-1.41 (m, 37H), 2.04 (q, 4H), 4.97 (m, 4H), 5.82 (m, 2H); ^{13}C NMR ($CDCl_3$): δ (ppm) 14.8, 20.1, 27.0, 29.2, 29.4, 29.8, 29.9, 30.0, 30.4, 34.0, 34.1, 36.4, 37.5, 114.3, 139.4; EI/HRMS: $[M]^+$ calculated for $C_{26}H_{50}$: 362.3913, found: 362.3918. Elemental analysis calculated for $C_{26}H_{50}$: 86.10 C, 13.90 H; found 86.09 C, 13.91 H.

12-Pentyltricos-1,22-diene (4e). After purification, 11.48 g (98% yield) of a colorless liquid was collected. The following spectral properties were observed: ^1H NMR (CDCl_3): $\delta(\text{ppm})$ 0.90 (t, 3H), 1.23-1.41 (m, 41H), 2.04 (q, 4H), 4.97 (m, 4H), 5.82 (m, 2H); ^{13}C NMR (CDCl_3): $\delta(\text{ppm})$ 14.4, 23.0, 26.7, 27.0, 29.2, 29.4, 29.7, 29.8, 29.9, 30.0, 30.4, 32.7, 33.9, 34.0, 34.1, 37.7, 114.3, 139.4; EI/HRMS: $[\text{M}]^+$ calculated for $\text{C}_{28}\text{H}_{54}$: 390.4226, found: 390.4228. Elemental analysis calculated for $\text{C}_{28}\text{H}_{54}$: 86.07 C, 13.93 H; found 86.05 C, 13.96 H.

12-isopropyltricos-1,22-diene (4g). After purification, 4.25 g (99% yield) of a colorless liquid was collected. The following spectral properties were observed: ^1H NMR (CDCl_3): $\delta(\text{ppm})$ 0.85 (d, 6H), 1.30 (br, 33H), 1.71 (br, 1H), 2.08 (q, 4H), 4.97 (m, 4H), 5.85 (m, 2H); ^{13}C NMR (CDCl_3): $\delta(\text{ppm})$ 19.45, 28.04, 29.23, 29.43, 29.5, 29.79, 29.91, 29.97, 30.44, 30.82, 34.08, 43.97, 114.3, 139.42; EI/HRMS: $[\text{M}]^+$ calculated for $\text{C}_{26}\text{H}_{50}$: 362.3913, found: 362.3910. Elemental analysis calculated for $\text{C}_{26}\text{H}_{50}$: 86.10 C, 13.90 H; found 86.08 C, 13.91 H.

12-isobutyltricos-1,22-diene (4h). After purification, colorless oil was collected 1.423 g (76% yield). The following spectral properties were observed; ^1H NMR (CDCl_3): δ (ppm) 0.82 (d, 6H, CH_3), 1.25-1.41 (m, 34H, CH_2), 1.60 (m, 1H, CH), 2.02 (q, 4H, allyl CH_2), 4.95 (m, 4H, vinyl CH_2), 5.80 (m, 2H, vinyl CH); ^{13}C NMR (CDCl_3): δ (ppm) 23.23, 25.53, 26.70, 29.18, 29.39, 29.75, 29.87, 29.93, 30.39, 34.05, 35.14, 44.01, 114.29 (vinyl CH_2), 139.50 (vinyl CH); EI/HRMS: $[\text{M}]^+$ calculated for $\text{C}_{27}\text{H}_{52}$: 367.4100, found: 367.4069. Elemental analysis calculated for $\text{C}_{27}\text{H}_{52}$: 86.09 C, 13.91 H; found: 85.77 C, 14.09 H.

12-tert-butyltricos-1,22-diene (4i). After purification, 3.70 g (99% yield) of a colorless liquid was collected. The following spectral properties were observed: ^1H NMR (CDCl_3): $\delta(\text{ppm})$ 0.86 (s, 9H), 1.30 (br, 33H), 2.05 (q, 4H), 4.97 (m, 4H), 5.85 (m, 2H); ^{13}C NMR (CDCl_3): $\delta(\text{ppm})$ 28.04, 29.2, 29.42, 29.77, 29.91, 30.34, 30.6,

31.81, 34.08, 49.01, 114.3, 139.44; EI/HRMS: $[M]^+$ calculated for $C_{27}H_{52}$: 376.4069, found: 376.4070. Elemental analysis calculated for $C_{27}H_{52}$: 86.09 C, 13.91 H; found 86.11 C, 13.89 H.

tricos-1,22-dien-12-ylcyclohexane (4j). After purification, 4.25 g (99% yield) of a colorless liquid was collected. The following spectral properties were observed: 1H NMR ($CDCl_3$): δ (ppm) 1.03-1.75 (br, 44H), 2.04 (q, 4H), 4.97 (m, 4H), 5.84 (m, 2H); ^{13}C NMR ($CDCl_3$): δ (ppm) 27.21, 27.26, 28.06, 29.19, 29.4, 29.76, 29.89, 29.94, 30.03, 30.42, 31.03, 34.07, 40.4, 43.54, 114.29, 139.47; EI/HRMS: $[M]^+$ calculated for $C_{29}H_{54}$: 402.4226, found: 402.4230. Elemental analysis calculated for $C_{29}H_{54}$: 86.49 C, 13.51 H; found 86.50 C, 13.49 H.

12-adamantyltricos-1,22-diene (4k). After purification, colorless oil was collected 0.491 g (98.0 % yield). The following spectral properties were observed; δ (ppm), 1.28 (m, 28H, CH_2), 1.65 (m, 1H, CH), 1.95 (m, 11H, CH_2 and CH), 2.05(q, 4H, allyl CH_2), 4.98 (m, 4H, vinyl CH_2), 5.83 (m, 2H, vinyl CH) ; ^{13}C NMR ($CDCl_3$): δ (ppm), 29.04, 29.19, 29.40, 29.75, 29.91, 30.36, 30.58, 34.06, 35.90, 37.69, 40.11, 49.46, 114.29 (vinyl CH_2), 139.50 (vinyl CH); EI/HRMS: $[M]^+$ calculated for $C_{34}H_{58}$: 454.4539, found: 454.4539. Elemental analysis calculated for $C_{34}H_{58}$: 87.15 C, 12.85 H, found: 86.96 C, 13.06 H.

General Polymerization Conditions. All glassware was flame dried under vacuum prior to use. Monomers were dried over K mirror and degassed prior to polymerization. All metathesis reactions were initiated in the bulk, inside an argon atmosphere drybox. Monomer was placed in a 50 mL round-bottomed flask equipped with a magnetic stirbar. Grubbs first generation catalyst (400:1 monomer:catalyst) was added to the flask, and the flask was then fitted with a Schlenk adapter equipped with a vacuum valve. The reaction was monitored by formation of ethylene gas as a

moderate observed bubbling. The sealed reaction vessel was removed from the drybox and immediately placed on the vacuum line. The reaction vessel was then exposed to intermittent vacuum. After 4 h, the polymerization was exposed to full vacuum (10^{-4} torr) for 96 h at 45-50 °C. The reaction vessel was then cooled to room temperature, exposed to air, and 50 mL of a mixture of ethyl vinyl ether in toluene 1% v/v was added. The polymer/toluene solution was precipitated in methanol by dropwise addition of the solution to a beaker containing 1500 mL of acidic methanol (1 M), yielding pure **5c-(propyl)**, **5e-(pentyl)**, **5g-(iso-propyl)**, **5h-(sec-butyl)**, **5i-(tert-butyl)**, **5j-(cyclohexyl)**, and **5k-(adamantyl)** polymers, respectively.

Polymerization of 2-propyltricos-1,22-diene (4c) to give 5c-(propyl). After purification, 980 mg (98% yield) of material was collected. The following spectral properties were observed: ^1H NMR (CDCl_3): $\delta(\text{ppm})$ 0.88 (t, 3H), 1.27 (br, 30H), 1.55 (s, 1H), 1.98 (br, 3H), 5.39 (br, 2H); ^{13}C NMR (CDCl_3): $\delta(\text{ppm})$ 14.79, 20.07, 26.95, 27.46, 29.43, 29.57, 29.79, 29.92, 29.96, 30.41, 32.85, 33.96, 36.37, 37.44, 130.12, 130.58; GPC data (THF vs. polystyrene standards): $\overline{M}_w = 41,200$ g/mol; P.D.I. ($\overline{M}_w / \overline{M}_n$) = 1.7

Polymerization of 12-pentyltricos-1,22-diene (4e) to give 5e-(pentyl). After purification, 970 mg (97% yield) of material was collected. The following spectral properties were observed: ^1H NMR (CDCl_3): $\delta(\text{ppm})$ 0.89 (t, 3H), 1.27 (br, 32H), 1.55 (s, 1H), 1.98 (br, 3H), 5.39 (br, 2H); ^{13}C NMR (CDCl_3): $\delta(\text{ppm})$ 14.36, 22.95, 26.61, 26.96, 27.46, 29.36, 29.44, 29.57, 29.62, 29.68, 29.79, 29.82, 29.92, 29.96, 30.03, 30.4, 32.63, 32.85, 33.89, 33.96, 37.66, 130.11, 130.58; GPC data (THF vs. polystyrene standards): $\overline{M}_w = 45,100$ g/mol; P.D.I. ($\overline{M}_w / \overline{M}_n$) = 1.8

Polymerization of 12-isopropyltricos-1,22-diene (4g) to give 5g-(iso-propyl). After purification, 960 mg (96% yield) of material was collected. The following spectral properties were observed: ^1H NMR (CDCl_3): $\delta(\text{ppm})$ 0.84 (d, 6H),

1.28 (br, 32H), 1.69 (br, 1H), 1.98 (br, 4H), 5.40 (br, 2H); ^{13}C NMR (CDCl_3): $\delta(\text{ppm})$ 19.43, 28.01, 29.38, 29.44, 29.58, 29.8, 29.94, 29.97, 30.44, 30.74, 32.86, 43.91, 130.09, 130.56; GPC data (THF vs. polystyrene standards): $\overline{M}_w = 45,500$ g/mol; P.D.I. ($\overline{M}_w / \overline{M}_n$) = 1.7

Polymerization of 12-isobutyltricos-1,22-diene (4h) to give 5h-(*sec*-butyl).

After purification 967 mg (96% yield) of material was collected. The following spectral properties were observed; ^1H NMR (CDCl_3): δ (ppm) 0.82 (d, CH_3), 1.23-1.34 (m, CH_2), 1.62 (m, CH), 1.98 (m, allyl CH_2), 5.40 (m, vinyl CH); ^{13}C NMR (CDCl_3): δ (ppm) 23.24, 25.53, 26.72, 27.46, 29.18, 29.44, 29.92, 29.96, 30.42, 32.86, 34.12, 35.15, 44.09, 130.58 (vinyl CH); GPC data (THF vs. polystyrene standards): $\overline{M}_w = 43,000$ g/mol; P.D.I. ($\overline{M}_w / \overline{M}_n$) = 1.6

Polymerization of 12-*tert*-butyltricos-1,22-diene (4i) to give 5i-(*tert*-butyl).

After purification, 915 mg (92% yield) of material was collected. The following spectral properties were observed: ^1H NMR (CDCl_3): $\delta(\text{ppm})$ 0.85 (s, 8H), 1.02 (br, 2H), 1.28 (br, 26H), 1.98 (br, 4H), 5.40 (br, 2H); ^{13}C NMR (CDCl_3): $\delta(\text{ppm})$ 28.07, 29.47, 29.60, 29.81, 29.85, 29.94, 30.05, 30.35, 30.63, 31.82, 32.87, 34.12, 49.05, 130.12, 130.58; GPC data (THF vs. polystyrene standards): $\overline{M}_w = 30,600$ g/mol; P.D.I. ($\overline{M}_w / \overline{M}_n$) = 1.7

Polymerization of tricos-1,22-dien-12-ylcyclohexane (4j) to give 5j-(cyclohexyl). After purification, 938 mg (94% yield) of material was collected. The following spectral properties were observed: ^1H NMR (CDCl_3): $\delta(\text{ppm})$ 1.27 (br, 40H), 1.53-1.71 (m, 5), 1.98 (br, 4H), 5.39 (br, 2H); ^{13}C NMR (CDCl_3): $\delta(\text{ppm})$ 27.22, 27.27, 28.09, 29.45, 29.58, 29.80, 29.95, 29.97, 30.04, 30.45, 31.05, 32.87, 40.41, 43.56, 130.11, 130.57; GPC data (THF vs. polystyrene standards): $\overline{M}_w = 32,500$ g/mol; P.D.I. ($\overline{M}_w / \overline{M}_n$) = 1.6

Polymerization of 12-adamantyltricos-1,22-diene (4k) to give 5k-(adamantyl). After purification, 292 mg (95%) The following spectral properties were observed; ^1H NMR (CDCl_3): $\delta(\text{ppm})$, 1.27 (m, CH_2), 1.56 (m, CH), 1.65 (m, CH_2 and CH in adamantyl branch), 1.94 (m, allyl CH_2), 5.38 (m, vinyl CH); ^{13}C NMR (CDCl_3): $\delta(\text{ppm})$ 29.04, 29.45, 29.80, 29.94, 30.01, 30.39, 30.61, 32.86, 35.91, 37.70, 40.12, 130.58 (vinyl CH); GPC data (THF vs. polystyrene standards): $\overline{M}_w = 64,000$ g/mol; P.D.I. ($\overline{M}_w / \overline{M}_n$) = 1.7

General hydrogenation methodology using diimide. A solution of unsaturated polymer (~1.0 g) was dissolved in xylenes (30 mL) in a 350 mL three-neck round bottomed flask. Tripropyl amine (3.79 g, 26.3 mmol) was added via syringe followed by addition of *p*-toluenesulfonhydrazide (4.33 g, 23.3 mmol) using a powder funnel. The reaction mixture was heated to 135°C for 2 hours. The reaction was monitored by the produced nitrogen observed through a mineral oil bubbler. When production of nitrogen gas was ceased, the solution was cooled to room temperature, and a second batch of tripropyl amine (3.79 g, 26.3 mmol) and *p*-toluenesulfonhydrazide (4.33 g, 23.3 mmol) was added. The reaction mixture was heated to 135°C for 2 h, and its performance was monitored by the evolution of nitrogen gas. Precipitation of the crude mixtures into acidic methanol (1M HCl), followed by filtration afforded the saturated polymers **6c-(propyl)**, **6e-(pentyl)**, **6g-(iso-propyl)**, **6h-(sec-butyl)**, **6i-(tert-butyl)**, **6j-(cyclohexyl)**, and **6k-(adamantyl)**.

Hydrogenation of 5c-(propyl) to give 6c-(propyl). After precipitation, 912 mg (91% yield) of material was collected. The following spectral properties were observed: ^1H NMR (CDCl_3): $\delta(\text{ppm})$ 0.89 (t, 3H), 1.27 (br, 36H); ^{13}C NMR (CDCl_3): $\delta(\text{ppm})$ 14.80, 20.07, 26.94, 29.99, 30.42, 33.93, 36.37, 37.42; GPC data (THF vs.

polystyrene standards): $\overline{M}_w = 41,400$ g/mol; P.D.I. ($\overline{M}_w / \overline{M}_n$) = 1.7; DSC Results: Melting Temperature Data: $T_m = 12$ °C, $\Delta h_m = 60$ J/g

Hydrogenation of 5e-(pentyl) to give 6e-(pentyl). After precipitation, 860 mg (86% yield) of material was collected. The following spectral properties were observed: ^1H NMR (CDCl_3): $\delta(\text{ppm})$ 0.88 (t, 3H,), 1.26 (br, 41H); ^{13}C NMR (CDCl_3): $\delta(\text{ppm})$ 14.80, 22.97, 26.62, 26.94, 29.99, 30.41, 33.89, 33.93, 37.64; GPC data (THF vs. polystyrene standards): $\overline{M}_w = 45,800$ g/mol; P.D.I. ($\overline{M}_w / \overline{M}_n$) = 1.8; DSC Results: Melting Temperature Data: $T_m = 14$ °C, $\Delta h_m = 58$ J/g

Hydrogenation of 5g-(iso-propyl) to give 6g-(iso-propyl). After precipitation, 985 mg (99% yield) of material was collected. The following spectral properties were observed: ^1H NMR (CDCl_3): $\delta(\text{ppm})$ 0.84 (br, 6H,), 1.28 (br, 43H), 1.69 (br, 1H); ^{13}C NMR (CDCl_3): $\delta(\text{ppm})$ 19.46, 28.03, 29.48, 29.99, 30.45, 30.80, 43.96; GPC data (THF vs. polystyrene standards): $\overline{M}_w = 46,000$ g/mol; P.D.I. ($\overline{M}_w / \overline{M}_n$) = 1.7; DSC Results: Melting Temperature Data: $T_m = 11$ °C, $\Delta h_m = 37$ J/g

Hydrogenation of 5h-(sec-butyl) to give 6h-(sec-butyl). After precipitation, 900 mg (90% yield) of material was collected. The following spectral properties were observed: ^1H NMR (CDCl_3): $\delta(\text{ppm})$ 0.86 (d, CH_3), 1.23-1.34 (m, CH_2), 1.62 (m, CH); ^{13}C NMR (CDCl_3): δ (ppm) 23.24, 25.53, 26.72, 27.46, 29.18, 29.44, 29.92, 29.96, 30.42, 32.86, 34.12, 35.15; GPC data (THF vs. polystyrene standards): $\overline{M}_w = 27,000$ g/mol; P.D.I. ($\overline{M}_w / \overline{M}_n$) = 1.9; DSC Results: Melting Temperature Data: $T_m = 9$ °C, $\Delta h_m = 43$ J/g

Hydrogenation of 5i-(tert-butyl) to give 6i-(tert-butyl). After precipitation, 895 mg (90% yield) of material was collected. The following spectral properties were observed: ^1H NMR (CDCl_3): $\delta(\text{ppm})$ 0.85 (s, 9H,), 1.01 (br, 3H), 1.27 (br, 36H); ^{13}C

NMR (CDCl₃): δ (ppm) 28.06, 29.99, 30.33, 30.61, 31.80, 34.11, 49.02; GPC data (THF vs. polystyrene standards): $\overline{M}_w = 32,100$ g/mol; P.D.I. ($\overline{M}_w / \overline{M}_n$) = 1.7; DSC Results: Melting Temperature Data: $T_m = 13$ °C, $\Delta h_m = 50$ J/g

Hydrogenation of 5j-(cyclohexyl) to give 6j-(cyclohexyl). After precipitation, 950 mg (95% yield) of material was collected. The following spectral properties were observed: ¹H NMR (CDCl₃): δ (ppm) 1.27 (br, 14H), 1.53-1.74 (m, 2H); ¹³C NMR (CDCl₃): δ (ppm) 27.21, 27.26, 28.06, 29.99, 30.03, 30.44, 31.03, 40.41, 43.53; GPC data (THF vs. polystyrene standards): $\overline{M}_w = 33,600$ g/mol; P.D.I. ($\overline{M}_w / \overline{M}_n$) = 1.6; DSC Results: Melting Temperature Data: $T_m = 9$ °C, $\Delta h_m = 37$ J/g

Hydrogenation of 5k-(adamantyl) to give 6k-(adamantyl). After precipitation, 200 mg (95% yield) of material was collected. The following spectral properties were observed; ¹H NMR (CDCl₃): δ (ppm), 1.27 (m, CH₂), 1.51 (m, CH), 1.65 (m, CH₂ and CH in adamantyl branch), ¹³C NMR (CDCl₃): δ (ppm), 28.10, 29.20, 29.30, 29.99, 30.00, 30.80, 31.30, 38.10, 40.70, 47.60; GPC data (THF vs. polystyrene standards): $\overline{M}_w = 70,000$ g/mol; P.D.I. ($\overline{M}_w / \overline{M}_n$) = 1.3; DSC Results: Melting Temperature Data: $T_m = -8$ & 17 °C, $\Delta h_m = 2$ & 8 J/g