

Supporting Information Experimental Data

Unveiling the Hyperbolic Thermal Behavior of poly(*p*-phenylene alkylene)s

Nicolas F. Sauty, Lucas Caire da Silva, Robert Graf, Caitlyn Gallagher, and Kenneth B. Wagener*

The George and Josephine Butler Polymer Research Laboratory, Department of Chemistry and Center for Macromolecular Science and Engineering, University of Florida, Gainesville, FL 32611-7200.

* Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

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GENERAL INFORMATION

Reagents and Solvents

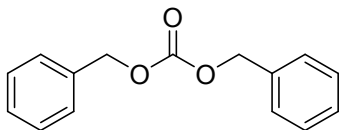
All reagents were obtained from commercial sources and used without further purification. Anhydrous tetrahydrofuran, diethyl ether and dichloromethane were obtained from a solvent purification system.

Instrumentation

All chemical shifts for ^1H NMR and ^{13}C NMR were referenced to the residue signals from CDCl_3 ($^1\text{H} = 7.27$ ppm, $^{13}\text{C} = 77.23$ ppm). All NMR spectra were recorded at room temperature. Gel permeation chromatography (GPC) was performed using Agilent 1100 Series HPLC System 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 at a rate of $10^\circ\text{C}/\text{min}$ with samples prepared in a hermetically sealed pan. Elemental analysis data were obtained on a combustion Analyzer. IR/ATR spectra were acquired on a Bruker Vertex 80v. Analytical thin-layer chromatography (TLC) was performed using aluminum supported silica plates with a 254 nm fluorescent indicator and pore size of 60 Å. Column chromatography was performed using ultrapure silica gel (40-63 μm , 230-400 mesh). The solid state NMR measurements were performed on a Bruker Avance 3 console at 700.21 MHz ^1H Larmor frequency with a commercial double resonance MAS probe supporting MAS rotors of 2.5mm outer diameter. All MAS experiments were performed at 25 kHz MAS spinning frequency (unless stated otherwise) and the rf nutation frequencies on both channels, ^1H and ^{13}C , have been adjusted to 100 kHz, corresponding to a 90° pulse length of 2.5 μs . For the ^1H MAS spectra, 16 transients of 4096 points with a dwell time of 5 μs were acquired. The phase sensitive REPT-HSQC correlation spectra were recorded with 80 experiments in the States-TPPI scheme and 4 rotor periods REDOR recoupling for excitation and reconversion. 400 – 1024 transients were acquired for each experiment for the indirect ^1H dimension applying SPINAL64 high power ^1H composite pulse decoupling during ^{13}C acquisition.

EXPERIMENTAL PROCEDURES AND ASSOCIATED DATA

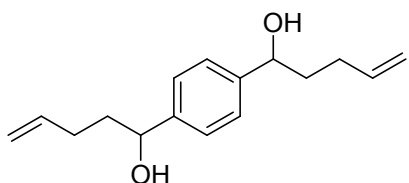
Dibenzyl carbonate



To a 1000 mL flame-dried round-bottomed flask, were introduced dry THF (500 mL) and benzyl alcohol (140 g, 1295 mmol, 2.1 equiv). The solution was cooled to 0 °C and sodium hydride (50.56 g, 1264 mmol, 2.05 equiv) was added in small portions over 2 hours. The suspension was then allowed to warm to room temperature and was stirred further for 2 hours. In a 2000 mL flame-dried round-bottomed flask, were added THF (1L) and 1,1'-carbonyldiimidazol (CDI) (100 g, 617 mmol, 1 equiv). Both suspensions were cooled to 0 °C and the phenylmethanolate solution was slowly added to the CDI suspension. The mixture was allowed to stir for an additional 4 hours and was then quenched with ammonium chloride. The heterogeneous mixture was extracted twice with diethyl ether and the combined organic layers were washed with water and brine, and dried over magnesium sulfate. Removal of the volatiles *in vacuo* afforded a yellow oil. Purification by column chromatography using hexanes/ethyl acetate (90:10) led to **3-22** as a colorless oil (149.5 g, 84%). ¹H NMR (300 MHz, Chloroform-d) δ (ppm) 7.43-7.30 (m, 10 H), 5.19 (s, 4 H); ¹³C NMR (125 MHz, Chloroform-d, 50 °C) δ (ppm) 155.0, 135.1, 128.5, 128.2, 69.6; Elemental analysis: calculated: C 74.36%, H 5.82%, found: C 74.54%, H 5.94%. FT-IR (cm⁻¹): 2981, 1740, 1498, 1455, 1391, 1239, 944, 909, 825, 788, 738, 695.

General procedures for the monomer synthesis

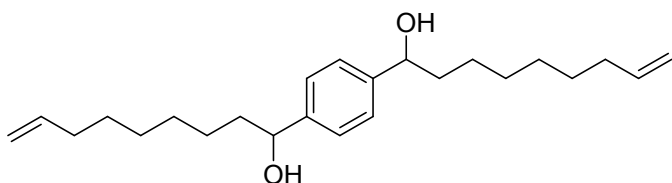
1,1'-(1,4-phenylene)bis(pent-4-en-1-ol)



In a three-necked flame-dried round-bottomed flask, were introduced freshly ground magnesium turnings (2.16 g, 89 mmol) and diethyl ether (45 mL). The heterogeneous mixture was stirred and 0.2 mL of 1,2-dibromoethane was added. The solution became cloudy shortly after that, and was refluxed for 1 hour. The mixture was cooled to about 35 °C, and 4-bromo-but-1-ene (6 g, 4.51 mL, 44.5 mmol) was added dropwise with a syringe pump at the minimal rate that sustained a reflux. After 4 hours, the mixture was allowed to cool to room temperature. In a two-necked flame-dried round-bottomed flask, were introduced terephthalaldehyde (2.39 g, 17.8 mmol) and THF (50 mL). The clear solution was cooled to 0 °C, and the previously prepared Grignard reagent was injected slowly while maintaining the temperature at 0 °C. The mixture thickened to the point that magnetic stirring

became impossible for a while. After 30 minutes, the mixture was allowed to warm to room temperature and was stirred for 2 hours. After that, the reaction was quenched with ammonium chloride at 0 °C, and the organic components were extracted with diethyl ether. The combined organic fractions were washed with 1 M HCl once and twice with brine. The ether solution was dried with anhydrous magnesium sulfate and the solvents were removed *in vacuo*. The crude was purified by column chromatography using hexanes/ethyl acetate (70:30), and the desired product was obtained as a white solid. Yield = 3.29 g (75%). ¹H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.30 (s, 4H), 5.83 (m, 2H), 5.00 (m, 4H), 4.67 (dd, 2H), 2.22-2.00 (m, 4H), 2.00-1.69 (m, 4H); ¹³C NMR (75 MHz, Chloroform-*d*) δ (ppm) 143.9, 138.1, 126.0, 115.0, 73.7, 38.0, 30.0; IR ν_{max} = cm⁻¹; Elemental analysis: calculated: C 78.01%, H 9.00%, O 12.99%, found: C 77.87%, H 8.96%.

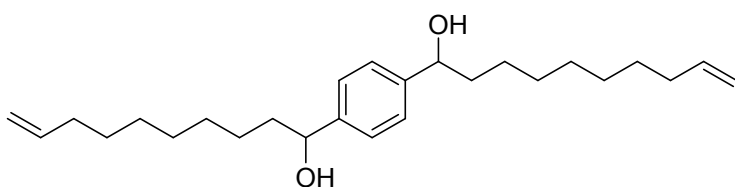
1,1'-(1,4-phenylene)bis(non-8-en-1-ol)



Yield = 4.31 g (81%); ¹H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.29 (s, 4 H), 5.77 (m, 2 H), 4.94 (m, 4 H), 4.60 (dd 2 H), 2.00 (qd, 4 H), 1.90 (m, 2 H), 1.71 (m, 4 H), 1.43-1.12 (m, 12 H); ¹³C

NMR (75 MHz, Chloroform-*d*) δ (ppm) 144.0, 139.1, 125.8, 114.1, 74.4, 39.0, 33.7, 29.3, 29.0, 28.8, 25.8; Elemental analysis: calculated: C 80.39%, H 10.68%, O 8.92%, found: C 80.47%, H 10.77%.

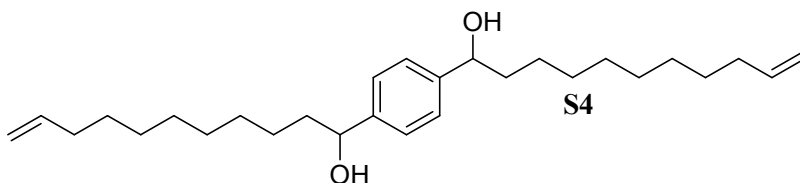
1,1'-(1,4-phenylene)bis(dec-9-en-1-ol)



Yield = 3.76 g (75%); ¹H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.29 (s, 4 H), 5.77 (m, 2 H), 5.94 (m, 4 H), 4.60 (dd, 2 H), 2.00 (qd, 4 H), 1.91 (m, 2 H),

1.72 (m, 4 H), 1.44-1.16 (m, 20 H); ¹³C NMR (75 MHz, Chloroform-*d*) δ (ppm) 144.1, 139.1, 125.9, 114.1, 74.4, 39.0, 33.7, 29.3, 29.0, 28.8, 25.8; Elemental analysis: calculated: C 80.77%, H 10.95%, O 8.28%, found: C 80.87%, H 11.02%.

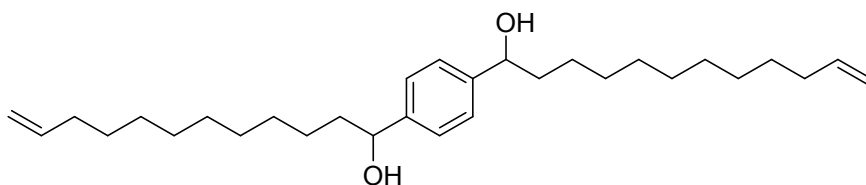
1,1'-(1,4-phenylene)bis(undec-10-en-1-ol)



Yield = 2.87 g (79%); ¹H NMR (300MHz,

Chloroform-*d*) δ (ppm) 7.29 (s, 4 H), 5.79 (m, 2 H), 4.95 (m, 4 H), 4.63 (dd, 2 H), 2.02 (q, 4 H), 1.83 (m, 6 H), 1.47 - 1.11 (br, 24 H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 144.1, 139.2, 125.9, 114.1, 74.4, 39.1, 33.8, 29.57, 29.54, 29.48, 29.1, 28.9, 25.9; Elemental analysis: calculated: C 81.10%, H 11.18%, O 7.72%, found: C 80.91%, H 11.09%. FT-IR (cm^{-1}): 3355, 2980, 2915, 2849, 1641, 1464, 1426, 1241, 1207, 1127, 1100, 1069, 1033, 1010, 995, 953, 923, 835, 792, 723, 638.

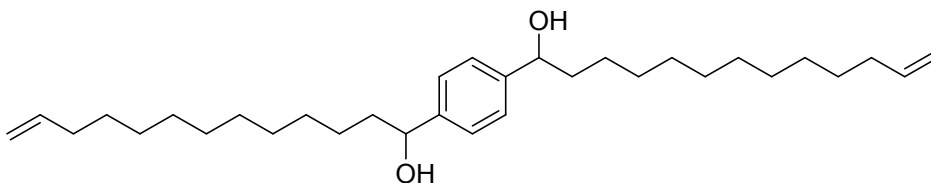
1,1'-(1,4-phenylene)bis(dodec-11-en-1-ol)



Yield = 7.14 g (82%);
 ^1H NMR (300MHz,
 Chloroform-*d*) δ
 (ppm) 7.29 (s, 4 H),
 5.79 (m, 2 H), 4.95

(m, 4 H), 4.63 (dd, 2 H), 2.02 (q, 4 H), 1.83 (m, 6 H), 1.47 - 1.11 (br, 28 H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 144.1, 139.2, 125.9, 114.1, 74.4, 39.1, 33.8, 29.57, 29.54, 29.48, 29.1, 28.9, 25.9; Elemental analysis: calculated: C 81.39%, H 11.38%, O 7.23%, found: C 81.16%, H 11.55%.

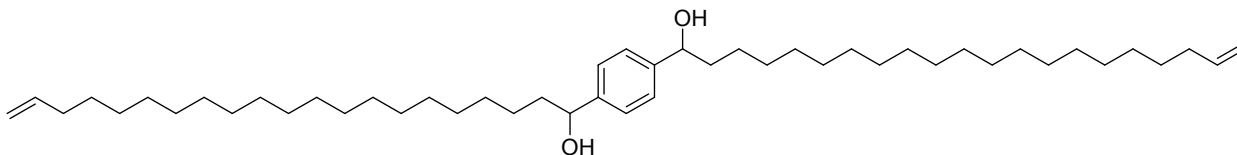
1,1'-(1,4-phenylene)bis(tridec-12-en-1-ol)



Yield = 2.78 g
 (79%); ^1H
 NMR
 (300MHz,
 Chloroform-*d*)

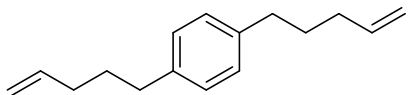
δ (ppm) 7.29 (s, 4 H), 5.79 (m, 2 H), 4.95 (m, 4 H), 4.63 (dd, 2 H), 2.02 (q, 4 H), 1.83 (m, 6 H), 1.47 - 1.11 (br, 32 H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 144.1, 139.2, 125.9, 114.1, 74.4, 39.1, 33.8, 29.57, 29.54, 29.48, 29.1, 28.9, 25.9; Elemental analysis: calculated: C 81.64%, H 11.56%, O 6.80%, found: C 81.93%, H 11.46%.

1,1'-(1,4-phenylene)bis(henic-20-en-1-ol)



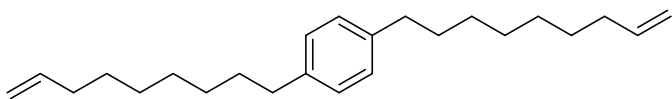
Yield = 3.31 g (64%); ^1H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.30 (s, 4 H), 5.78 (m, 2 H), 4.93 (m, 4 H), 4.65 (dd, 2 H), 2.00 (q, 4 H), 1.83-1.59 (m, 6 H), 1.40-1.13 (m, 64 H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 144.1, 139.2, 126.0, 114.0, 74.4, 39.1, 33.8, 29.7, 29.5, 29.2, 29.0, 25.9; Elemental analysis: calculated: C 82.93%, H 12.47%, O 4.60%, found: C 82.67%, H 12.50%.

1,4-di(pent-4-en-1-yl)benzene



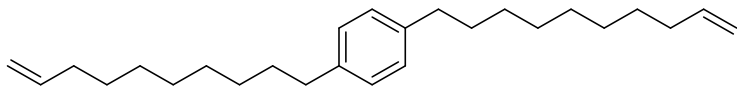
In a three-necked flame-dried round-bottomed flask, were introduced anhydrous FeCl_3 (g, 10 mol%), and 1,2-dichloroethane (mL). The mixture was allowed to stir for 10 minutes. TMSD (g, mL, mmol) was added to the catalyst solution followed by 1,1'-(1,4-phenylene)bis(pent-4-en-1-ol) (g, mmol). The solution was stirred for 1.5 hours. After completion of the reaction, water was added and the aqueous phase was extracted with diethyl ether. The combined organic layers were washed with brine and dried with anhydrous magnesium sulfate. The solvents were removed *in vacuo*, affording a clear crude oil. The desired product was obtained after purification by column chromatography using hexanes as eluent. Yield = 1.60 g (56%). ^1H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.11 (s, 4 H), 5.86 (m, 2 H), 5.02 (m, 4 H), 2.61 (t, 4 H), 2.12 (q, 4 H), 1.73 (quin, 4 H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 139.7, 138.6, 128.3, 114.6, 34.9, 33.3, 30.7; Elemental analysis: calculated: C 89.65%, H 10.35%, found: C 89.74%, H 10.43%. FT-IR (cm^{-1}): 2928, 2856, 1640, 1513, 1440, 990, 908, 803, 632.

1,4-di(non-8-en-1-yl)benzene



Yield = 2.67 g (84%); ^1H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.08 (s, 4 H), 5.80 (m, 2 H), 4.96 (m, 4 H), 2.56 (t, 4 H), 2.02 (q, 4 H), 1.59 (quin, 4 H), 1.43-1.20 (m, 16 H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 140.0, 139.2, 128.2, 114.1, 35.6, 33.8, 31.6, 29.4, 29.3, 29.1, 28.9; Elemental analysis: calculated: C 88.27%, H 11.73%, found: C 88.42%, H 11.80%. FT-IR (cm^{-1}): 2924, 2853, 1640, 1513, 1462, 992, 908, 820, 723, 634.

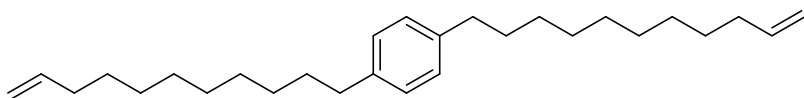
1,4-di(dec-9-en-1-yl)benzene



Yield = 2.54 g (91%); ^1H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.08 (s, 4 H), 5.81 (m, 2 H), 4.96 (m, 4 H), 2.56 (t, 4 H), 2.03 (q, 4 H), 1.58 (quin, 4 H), 1.43-1.20 (m, 20 H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 140.0, 139.2, 128.2, 114.1, 35.6,

33.8, 31.6, 29.5, 29.4, 29.2, 29.0; Elemental analysis: calculated: C 88.06%, H 11.94%, found: C 88.12%, H 12.02%. FT-IR (cm⁻¹): 2923, 2853, 1640, 1513, 1463, 991, 908, 818, 721, 635.

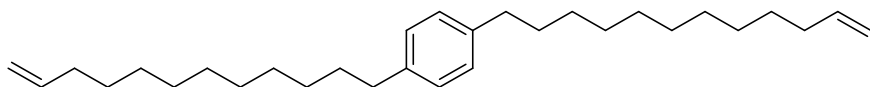
1,4-di(undec-10-en-1-yl)benzene



Yield = 1.85 g (89%); ¹H NMR (300 MHz, Chloroform-*d*) δ (ppm)

7.07 (s, 4 H), 5.80 (m, 2 H), 4.95 (m, 4 H), 2.55 (t, 4 H), 2.03 (q, 4 H), 1.58 (quin, 4 H), 1.43-1.20 (m, 24 H); ¹³C NMR (75 MHz, Chloroform-*d*) δ (ppm) 140.0, 139.2, 128.2, 114.1, 35.6, 33.8, 31.6, 29.54, 29.52, 29.50, 29.4, 29.1, 28.9; Elemental analysis: calculated: C 87.88%, H 12.12%, found: C 88.00%, H 12.24%. FT-IR (cm⁻¹): 2980, 2923, 2852, 1640, 1513, 1462, 991, 908, 817, 721, 634.

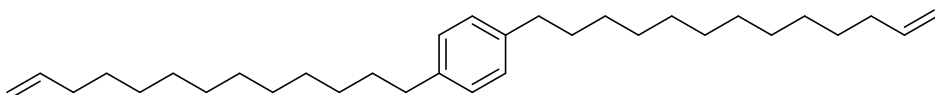
1,4-di(dodec-11-en-1-yl)benzene



Yield = 4.79 g (92%); ¹H NMR (300 MHz, Chloroform-*d*) δ

(ppm) 7.08 (s, 4 H), 5.81 (m, 2 H), 4.96 (m, 4 H), 2.55 (t, 4 H), 2.03 (q, 4 H), 1.58 (quin, 4 H), 1.43-1.20 (m, 28 H); ¹³C NMR (75 MHz, Chloroform-*d*) δ (ppm) 140.1, 139.2, 128.2, 114.1, 35.6, 33.8, 31.6, 29.6, 29.5, 29.4, 29.1, 28.9; Elemental analysis: calculated: C 87.73%, H 12.27%, found: C 87.93%, H 12.45%. FT-IR (cm⁻¹): 2980, 2923, 2852, 1640, 1513, 1463, 1153, 991, 908, 817, 721, 633.

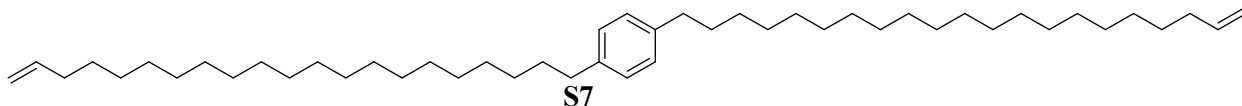
1,4-di(tridec-12-en-1-yl)benzene



Yield = 1.24 g (87%); ¹H NMR (300

MHz, Chloroform-*d*) δ (ppm) δ (ppm) 7.07 (s, 4 H), 5.80 (m, 2 H), 4.95 (m, 4 H), 2.55 (t, 4 H), 2.03 (q, 4 H), 1.58 (quin, 4 H), 1.40-1.18 (m, 32 H); ¹³C NMR (75 MHz, Chloroform-*d*) δ (ppm) 140.0, 139.2, 128.2, 114.1, 35.6, 33.8, 31.6, 29.7, 29.62, 29.55, 29.53, 29.4, 29.2, 29.0; Elemental analysis: calculated: C 87.59%, H 12.41%, found: C 87.54%, H 12.39%. FT-IR (cm⁻¹): 2980, 2915, 2848, 1641, 1516, 1470, 1120, 991, 913, 831, 767, 720, 644.

1,4-di(henicos-20-en-1-yl)benzene

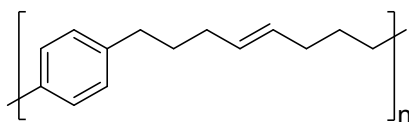


S7

Yield = 1.19 g (78%); ^1H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.06 (s, 4 H), 5.80 (m, 2 H), 4.95 (m, 4 H), 2.54 (m, 4 H), 2.02 (m, 4 H), 1.57 (m, 4 H), 1.42-1.13 (m, 64 H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 140.0, 139.2, 128.2, 114.0, 35.6, 33.8, 31.6, 29.7, 29.65, 29.62, 29.55, 29.52, 29.4, 29.2, 29.0; Elemental analysis: calculated: C 86.93%, H 13.07%, found: C 86.74%, H 13.11%. FT-IR (cm^{-1}): 2980, 2912, 2847, 1641, 1516, 1471, 1383, 1252, 1152, 991, 956, 913, 832, 729, 719, 645.

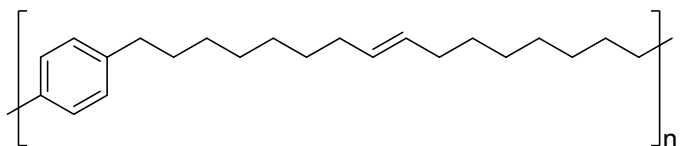
General procedure for the ADMET polymerization.

poly(*p*-phenylene oct-4-en-1-ylene)



To a flame-dried Schlenk tube equipped with a magnetic stirrer, were added dibenzyl carbonate (10 mL) and 1,4-di(pent-4-en-1-yl)benzene (0.214 mg, 1 mmol). The mixture was degassed for 45 minutes by bubbling argon. After that, Grubbs 1st generation catalyst (8.2 mg, 0.5 mol%) was added, and the resulting homogeneous mixture was stirred under vacuum for 30 min. The temperature was raised to 50 °C for 1 hour, after which the temperature was set to 80 °C. After 24 hours, another load of catalyst (8.2 mg, 0.5 mol%) was added and the polymerization was pursued at 80 °C for another 24 hours. The polymerization reaction was then allowed to cool to room temperature and ethyl vinyl ether (0.25 mL) was added to deactivate the catalyst. The solvent was carefully removed from the reaction vessel and xylenes (5 mL) was added to dissolve the polymer. The polymer was collected by precipitating in cold methanol (500 mL at -40 °C) twice. Yield = 194 mg. ^1H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.06 (s, 4 H), 5.42 (m, 2H) 2.56 (t, 4 H), 2.01 (m, 4 H), 1.65 (quin, 4 H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 139.8, 130.3, 128.3, 35.0, 32.2, 31.4; Elemental analysis: calculated: C 90.26%, H 9.74%, found: C 90.00%, H 9.66%; $\bar{M}_n = 24,000$ g/mol, $\bar{M}_w = 61,000$ g/mol, $T_g = -36$ °C, $T_m = 61$ °C, $T_{95\%} = 228$ °C, $T_{50\%} = 401$ °C. FT-IR (cm^{-1}): 2981, 2913, 2852, 1513, 1437, 1383, 1252, 1153, 1079, 1021, 965, 804.

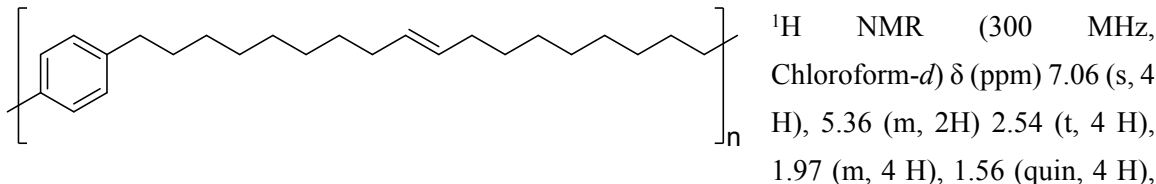
poly(*p*-phenylene hexadec-8-en-1-ylene)



^1H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.07 (s, 4 H), 5.36 (m, 2H) 2.54 (t, 4 H), 1.96 (m, 4 H), 1.57 (quin, 4 H), 1.36-1.14 (br, 20 H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 140.0, 130.3, 128.3, 35.6, 31.7, 29.7, 29.6, 29.5; Elemental analysis: calculated: C 88.52%, H 11.48%, found: C 88.72%, H 11.59%; $\bar{M}_n = 55,000$ g/mol, $\bar{M}_w = 125,000$

g/mol, $T_g = -61\text{ }^\circ\text{C}$, $T_m = 45\text{ }^\circ\text{C}$, $T_{95\%} = 380\text{ }^\circ\text{C}$, $T_{50\%} = 411\text{ }^\circ\text{C}$. FT-IR (cm^{-1}): 2981, 2918, 2850, 1465, 1383, 1252, 1152, 1074, 963, 827.

poly(*p*-phenylene octadec-9-en-1-ylene)

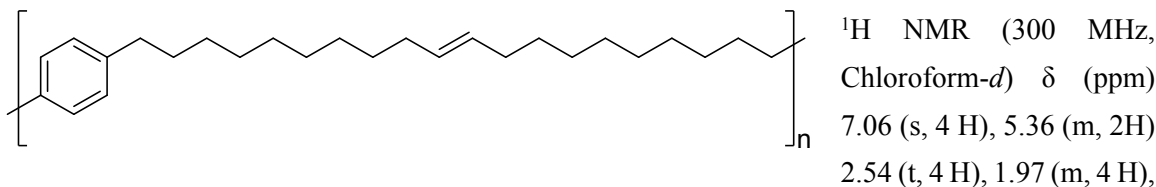


1.35-1.13 (br, 20 H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 140.0, 130.3, 128.3, 35.6, 31.7, 29.7, 29.6, 29.5; Elemental analysis: calculated: C 88.27%, H 11.73%, found: C 88.27%, H 11.87%;

$\bar{M}_n = 50,000\text{ g/mol}$, $\bar{M}_w = 100,000\text{ g/mol}$, $T_g = -43\text{ }^\circ\text{C}$, $T_m = 60\text{ }^\circ\text{C}$, $T_{95\%} = 387\text{ }^\circ\text{C}$, $T_{50\%} = 412\text{ }^\circ\text{C}$.

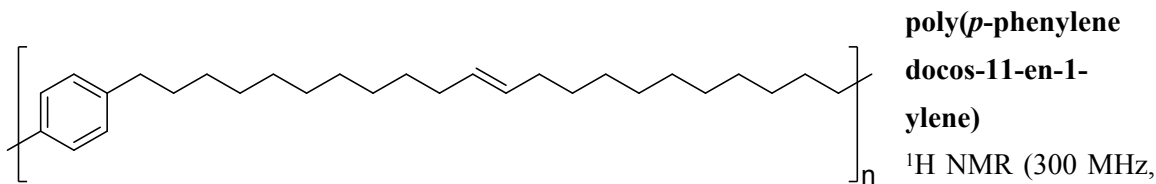
FT-IR (cm^{-1}): 2981, 2917, 2849, 1515, 1469, 1383, 1252, 1152, 1072, 963, 821, 719.

poly(*p*-phenylene icos-10-en-1-ylene)



1.57 (quin, 4 H), 1.35-1.13 (br, 24 H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 140.0, 130.3, 128.3, 35.6, 31.7, 29.7, 29.6, 29.5; Elemental analysis: calculated: C 88.06%, H 11.94%, found: C

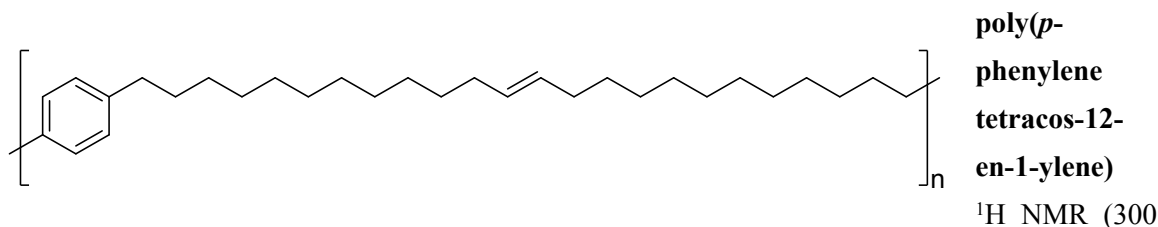
88.24%, H 11.95%; $\bar{M}_n = 78,000\text{ g/mol}$, $\bar{M}_w = 123,000\text{ g/mol}$, $T_g = -44\text{ }^\circ\text{C}$, $T_m = 63\text{ }^\circ\text{C}$, $T_{95\%} = 391\text{ }^\circ\text{C}$, $T_{50\%} = 415\text{ }^\circ\text{C}$. FT-IR (cm^{-1}): 2981, 2916, 2850, 1514, 1469, 1383, 1252, 1152, 1072, 963, 823, 755, 719.



^1H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.07 (s, 4 H), 5.37 (m, 2H) 2.54 (t, 4 H), 1.96 (m, 4 H), 1.57 (quin, 4 H), 1.38-1.17 (br, 28 H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ (ppm) 140.0, 130.3, 128.2, 35.6, 31.6, 29.7, 29.6, 29.5;

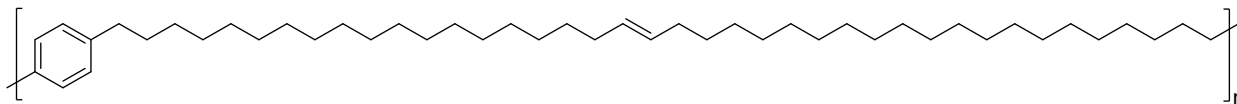
Elemental analysis: calculated: C 87.88%, H 12.12%, found: C 87.66%, H 12.06%; $\bar{M}_n = 65,000$

g/mol, $\bar{M}_w = 109,000$ g/mol, $T_g = -40$ °C, $T_m = 67$ °C, $T_{95\%} = 391$ °C, $T_{50\%} = 414$ °C. FT-IR (cm⁻¹): 2917, 2849, 1516, 1469, 1351, 1120, 1019, 964, 806, 766, 719.



MHz, Chloroform-*d*) δ (ppm) 7.06 (s, 4 H), 5.37 (m, 2H) 2.55 (t, 4 H), 1.97 (m, 4 H), 1.56 (quin, 4 H), 1.37-1.13 (br, 32 H); ¹³C NMR (75 MHz, Chloroform-*d*) δ (ppm) 140.1, 130.4, 128.1, 35.7, 31.6, 29.7, 29.6, 29.5; Elemental analysis: calculated: C 87.73%, H 12.27%, found: C 87.65%, H 12.19%; $\bar{M}_n = 88,000$ g/mol, $\bar{M}_w = 157,000$ g/mol, $T_g = -38$ °C, $T_m = 74$ °C, $T_{95\%} = 392$ °C, $T_{50\%} = 416$ °C. FT-IR (cm⁻¹): 2981, 2916, 2849, 1515, 1469, 1383, 1252, 1153, 963, 820, 718.

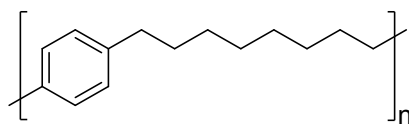
poly(*p*-phenylene tetracont-20-en-1-ylen)



¹H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.06 (s, 4 H), 5.36 (m, 2H) 2.54 (t, 4 H), 1.95 (m, 4 H), 1.57 (quin, 4 H), 1.36-1.11 (br, 64 H); ¹³C NMR (75 MHz, Chloroform-*d*) δ (ppm) 140.0, 130.3, 128.2, 35.6, 31.6, 29.7; Elemental analysis: calculated: C 86.99%, H 13.01%, found: C 87.09%, H 12.98%; $T_g = -13$ °C, $T_m = 88$ °C, $T_{95\%} = 390$ °C, $T_{50\%} = 416$ °C. FT-IR (cm⁻¹): 2981, 2915, 2848, 1516, 1471, 1383, 1252, 1152, 963, 808, 717.

General procedure for the exhaustive hydrogenation

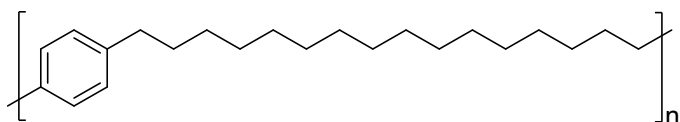
poly(*p*-phenylene octylene)



In a three-necked flame-dried round-bottomed flask equipped with a condenser and magnetic stir bar, were introduced poly(*p*-phenylene oct-4-en-1-ylen) (mg) and 3 *p*-xylene (mL). After complete dissolution of the polymer, tripropylamine (3 equiv.) and *p*-toluenesulfonylhydrazide (3 equiv.) were added and the mixture was refluxed for 3 hours. After cooling of the solution, tripropylamine (3 equiv.) and *p*-toluenesulfonylhydrazide (3 equiv.) were added and the mixture was refluxed for another 3 hours.

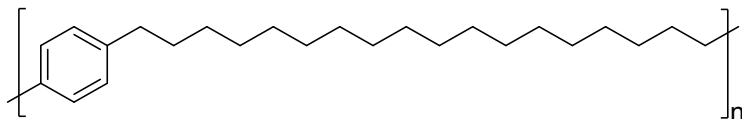
After cooling, the solution was added to cold methanol (500 mL at -40 °C) to precipitate the hydrogenated polymer. The polymer was dissolved in xylenes (10 mL) and precipitated in cold methanol. ¹H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.06 (s, 4 H), 2.54 (t, 4 H), 1.57 (quin, 4 H), 1.37-1.21 (br, 8 H); ¹³C NMR (75 MHz, Chloroform-*d*) δ (ppm) 140.0, 128.2, 35.6, 31.6, 29.5, 29.4; Elemental analysis: calculated: C 89.29%, H 10.71%, found: C 89.59%, H 10.75%; $T_g = -31$ °C, $T_m = 85$ °C, $T_{95\%} = 389$ °C, $T_{50\%} = 404$ °C.

poly(*p*-phenylene hexadecylene)



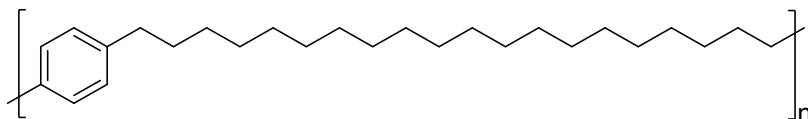
¹H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.06 (s, 4 H), 2.54 (t, 4 H), 1.57 (q, 4 H), 1.38-1.14 (br, 24 H); ¹³C NMR (75 MHz, Chloroform-*d*) δ (ppm) 140.0, 128.2, 35.6, 31.6, 29.7, 29.6, 29.4; $T_g = -23$, $T_m = 96$ °C, $T_{95\%} = 374$ °C, $T_{50\%} = 417$ °C.

poly(*p*-phenylene octadecylene)



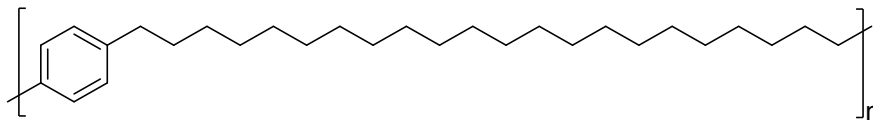
¹H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.06 (s, 4 H), 2.55 (t, 4 H), 1.57 (q, 4 H), 1.36-1.12 (br, 28 H); ¹³C NMR (75 MHz, Chloroform-*d*) δ (ppm) 140.0, 128.1, 35.6, 31.6, 29.7, 29.6, 29.5; $T_g = -14$, $T_m = 99$ °C, $T_{95\%} = 393$ °C, $T_{50\%} = 419$ °C.

poly(*p*-phenylene icosylene)



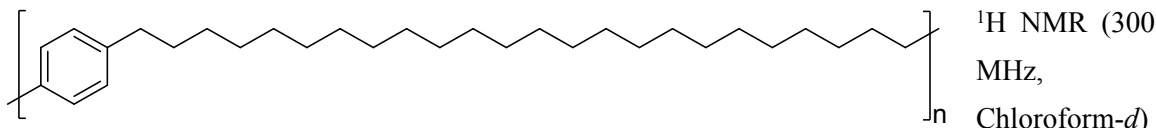
¹H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.07 (s, 4 H), 2.54 (t, 4 H), 1.57 (q, 4 H), 1.37-1.11 (br, 32 H); ¹³C NMR (75 MHz, Chloroform-*d*) δ (ppm) 140.1, 128.2, 35.6, 31.6, 29.7, 29.6, 29.5; $T_g = -11$, $T_m = 101$ °C, $T_{95\%} = 386$ °C, $T_{50\%} = 418$ °C.

poly(*p*-phenylene docosylene)



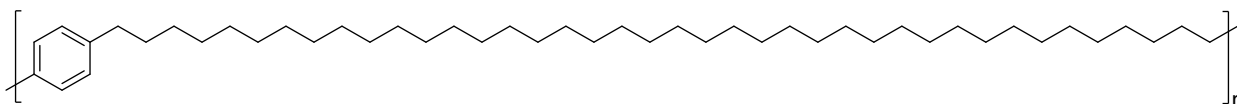
¹H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.06 (s, 4 H), 2.55 (t, 4 H), 1.56 (q, 4 H), 1.36-1.12 (br, 36 H); ¹³C NMR (75 MHz, Chloroform-*d*) δ (ppm) 140.0, 128.1, 35.7, 31.6, 29.7, 29.6, 29.4; $T_g = -7$, $T_m = 101$ °C, $T_{95\%} = 389$ °C, $T_{50\%} = 419$ °C.

poly(*p*-phenylene tetracosylene)



δ (ppm) 7.07 (s, 4 H), 2.56 (t, 4 H), 1.57 (q, 4 H), 1.37-1.14 (br, 40 H); ¹³C NMR (75 MHz, Chloroform-*d*) δ (ppm) 140.1, 128.0, 35.6, 31.6, 29.7, 29.6, 29.4; $T_g = -7$, $T_m = 101$ °C, $T_{95\%} = 383$ °C, $T_{50\%} = 418$ °C.

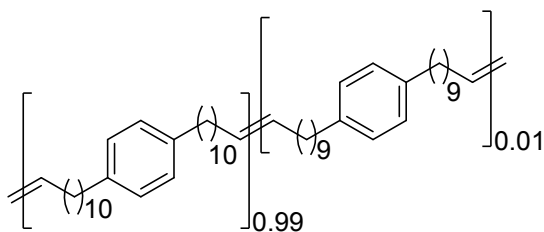
poly(*p*-phenylene tetracontylene)



¹H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.06 (s, 4 H), 2.56 (t, 4 H), 1.56 (q, 4 H), 1.36-1.11 (br, 72 H); ¹³C NMR (75 MHz, Chloroform-*d*) δ (ppm) 140.0, 128.1, 35.6, 31.6, 29.7, 29.6; $T_g = -8$, $T_m = 107$ °C, $T_{95\%} = 389$ °C, $T_{50\%} = 418$ °C.

Statistical Polymers:

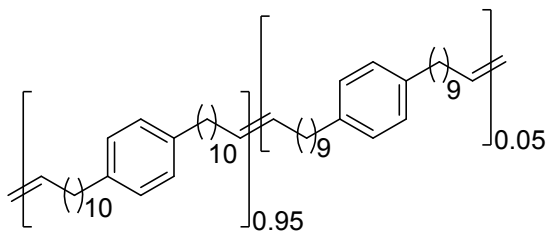
P1



¹H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.07 (s, 4 H), 5.37 (m, 2 H), 2.54 (t, 4 H), 1.96 (m, 4 H), 1.57 (quin, 4 H), 1.38-1.17 (br, 27.98 H); ¹³C NMR (75 MHz, Chloroform-*d*) δ (ppm) 140.0, 130.3, 128.2, 35.6, 31.6, 29.7, 29.6, 29.5; $\bar{M}_n =$

34,000 g/mol, $\bar{M}_w = 87,000$ g/mol, $T_g = -7$, $T_m = 101$ °C, $T_{95\%} = 387$ °C, $T_{50\%} = 411$ °C.

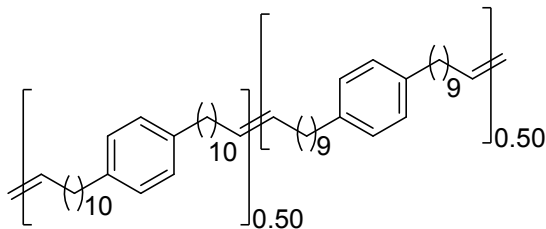
P2



¹H NMR (300 MHz, Chloroform-*d*) δ (ppm) 7.07 (s, 4 H), 5.37 (m, 2 H), 2.54 (t, 4 H), 1.96 (m, 4 H), 1.57 (quin, 4 H), 1.38-1.17 (br, 27.08 H); ¹³C NMR (75 MHz, Chloroform-*d*) δ (ppm) 140.0, 130.3, 128.2, 35.6, 31.6, 29.7, 29.6, 29.5; $\bar{M}_n =$

51,000 g/mol, $\bar{M}_w = 122,000$ g/mol, $T_g = -9$, $T_m = 99$ °C, $T_{95\%} = 389$ °C, $T_{50\%} = 413$ °C.

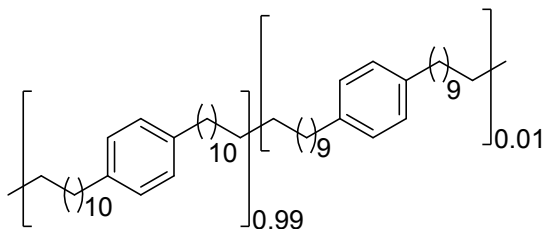
P3



$^1\text{H NMR}$ (300 MHz, Chloroform-*d*) δ (ppm) 7.07 (s, 4 H), 5.37 (m, 2 H) 2.54 (t, 4 H), 1.96 (m, 4 H), 1.57 (quin, 4 H), 1.38-1.17 (br, 27.08 H); $^{13}\text{C NMR}$ (75 MHz, Chloroform-*d*) δ (ppm) 140.0, 130.3, 128.2, 35.6, 31.6, 29.7, 29.6, 29.5; $\bar{M}_n =$

46,000 g/mol, $\bar{M}_w = 121,000$ g/mol, $T_g = -9$, $T_m = 91$ °C, $T_{95\%} = 386$ °C, $T_{50\%} = 407$ °C.

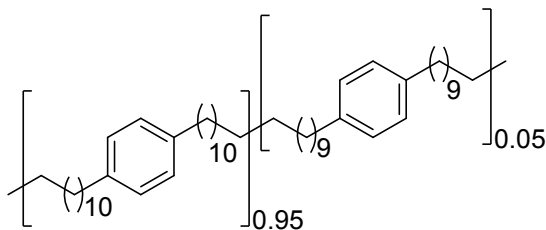
PPP21.98*



$^1\text{H NMR}$ (300 MHz, Chloroform-*d*) δ (ppm) 7.06 (s, 4 H), 2.55 (t, 4 H), 1.56 (q, 4 H), 1.36-1.12 (br, 35.98 H); $^{13}\text{C NMR}$ (75 MHz, Chloroform-*d*) δ (ppm) 140.0, 128.1, 35.7, 31.6, 29.7, 29.6, 29.4; $T_g = -7$, $T_m = 101$ °C, $T_{95\%} = 391$ °C, $T_{50\%} = 410$

°C. FT-IR (cm^{-1}): 2981, 2913, 1472, 1383, 1252, 1152, 1074, 954, 807.

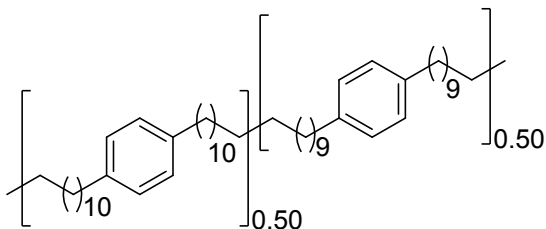
PPP21.9*



$^1\text{H NMR}$ (300 MHz, Chloroform-*d*) δ (ppm) 7.06 (s, 4 H), 2.55 (t, 4 H), 1.56 (q, 4 H), 1.36-1.12 (br, 35.90 H); $^{13}\text{C NMR}$ (75 MHz, Chloroform-*d*) δ (ppm) 140.0, 128.1, 35.7, 31.6, 29.7, 29.6, 29.4; $T_g = -9$, $T_m = 99$ °C, $T_{95\%} = 385$ °C, $T_{50\%} = 414$ °C.

FT-IR (cm^{-1}): 2981, 2913, 1472, 1383, 1252, 1152, 1074, 954, 807.

PPP21*



$^1\text{H NMR}$ (300 MHz, Chloroform-*d*) δ (ppm) 7.06 (s, 4 H), 2.55 (t, 4 H), 1.56 (q, 4 H), 1.36-1.12 (br, 35.50 H); $^{13}\text{C NMR}$ (75 MHz, Chloroform-*d*) δ (ppm) 140.0, 128.1, 35.7, 31.6, 29.7, 29.6, 29.4;

$T_g = -10$, $T_m = 91$ °C, $T_{95\%} = 387$ °C, $T_{50\%} = 411$ °C. FT-IR (cm^{-1}): 2981, 2915, 2848, 1515, 1470, 1153, 955, 819, 718.