

Supporting Information

**^{13}C NMR Analysis of α -Olefin Enchainment in
Poly(α -Olefins) Produced with Nickel and
Palladium α -Diimine Catalysts**

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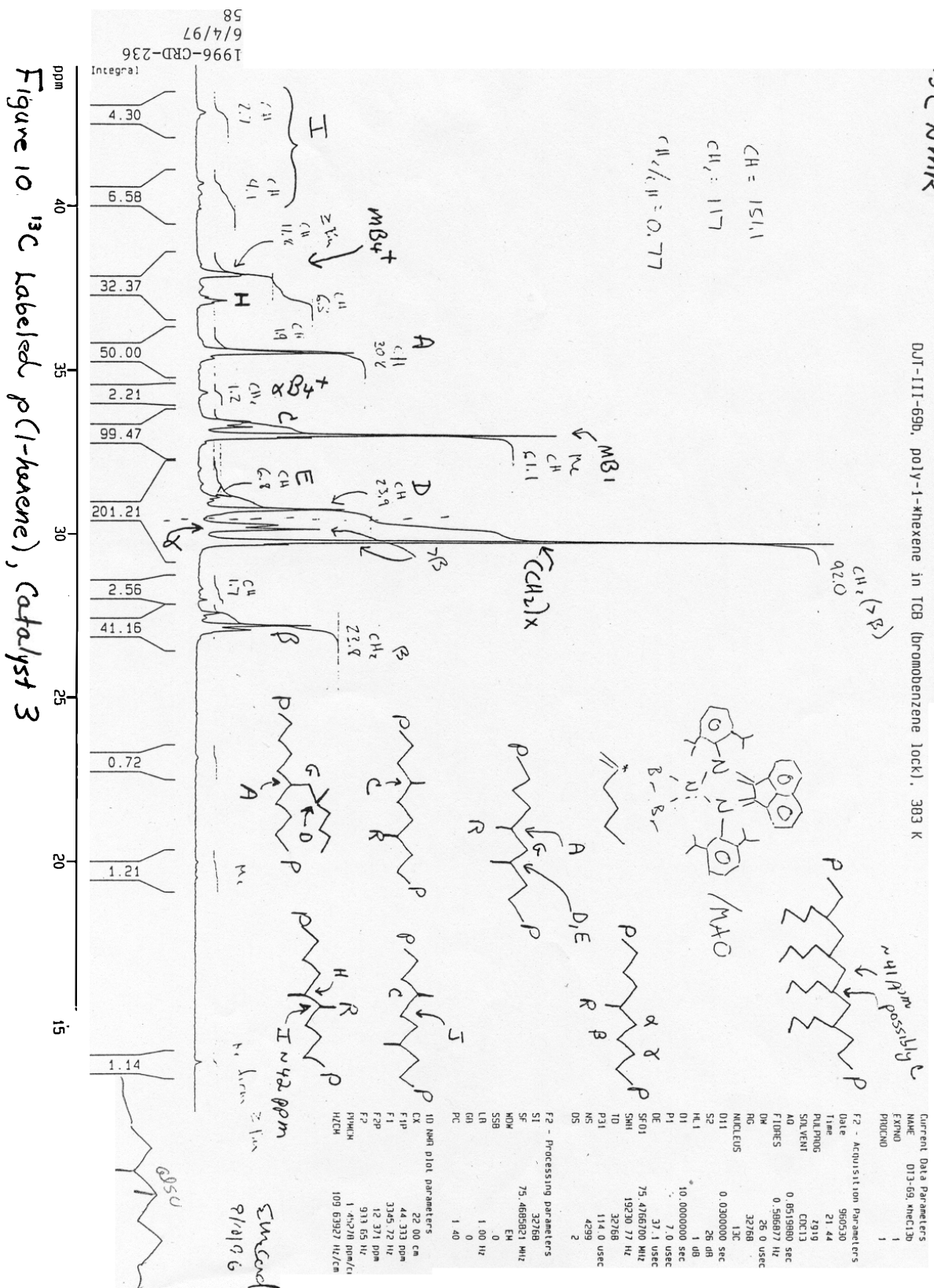
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6 pages

^{13}C NMR Spectrum of ^{13}C -labeled poly(1-hexene)

DUT-III-69b, poly-1-hexene in TCB (bromobenzene lock), 383 K



Detailed synthesis of ^{13}C -labeled 1-hexene

$\text{CH}_3(\text{CH}_2)_3^{13}\text{CO}_2\text{H}$. A two-necked 500 mL round bottom flask containing a stir bar and equipped with a Schlenk arm was fitted with two rubber septa and flame-dried under vacuum. After cooling, 200 mL of ether was added and the flask was cooled to *ca.* $-15\text{ }^\circ\text{C}$ in a dry ice/isopropanol bath. One of the septa was replaced with a Schlenk adapter connected to a T-tube with rubber tubing. The T-tube was connected to a lecture bottle equipped with a regulator pressurized with 99% $^{13}\text{CO}_2$ purchased from Cambridge Isotope Laboratories. The third branch of the T-tube was fitted with a balloon secured over a small piece of tubing with copper wire. The entire apparatus up to the regulator was evacuated and carefully back-filled with the labeled gas until the ether became saturated and the balloon remained slightly inflated. A 2.0 M solution of butyl magnesium chloride in ether (Aldrich) was slowly added via syringe to the dissolved $^{13}\text{CO}_2$ with rapid stirring. The gas was continually introduced into the flask as the balloon became deflated. After addition of 100 mL of Grignard reagent (0.20 mol), the cylinder was closed off and the flask was warmed to room temperature. The balloon became inflated, presumably from unreacted $^{13}\text{CO}_2$, so the flask was cooled back to $0\text{ }^\circ\text{C}$ and additional Grignard reagent was added. This process was repeated until the balloon remained deflated at room temperature. A total of *ca.* 130 mL (0.26 mol) of Grignard reagent was added, yielding a thick white suspension. Workup began with addition of 5% H_2SO_4 to the reaction mixture cooled to $0\text{ }^\circ\text{C}$ until the solution became acidic. The ether layer was separated, washed with brine, and dried over Na_2SO_4 . The ether was removed under aspirator vacuum and then under high vacuum to yield 27 g of clean

product (92%). ^1H NMR (CDCl_3 , 250 MHz) δ 2.33 (dt, 2H, $J_{\text{CH}} = 7.3$ Hz, $J = 7.3$ Hz), 1.67-1.52 (m, 2H), 1.43-1.27 (m, 2H), 0.90 (t, 3H, $J = 7.2$ Hz), shift for acidic hydrogen not observed.

$\text{CH}_3(\text{CH}_2)_3^{13}\text{CH}_2\text{OH}$. A three-necked 2000 mL round bottom flask was equipped with an addition funnel and 2 rubber septa. The apparatus was flame-dried and charged with 24.88 g (0.6228 mol) of LiAlH_4 in the glove box. The apparatus was placed under argon and the flask was filled with 600 mL of ether, fitted with a mechanical stirrer, and cooled to 0 °C. Labeled valeric acid from above was added dropwise over a two hour period to this stirring suspension as a 1 M solution in ether (56.7 g, 0.550 mol/500 mL ether). Upon complete addition, the reaction was stirred at 0 °C for an additional one hour and was then allowed to warm to room temperature. Workup included careful addition of 25 mL of water, followed by 25 mL of 10% NaOH, and 75 mL more water. The clear ether solution was filtered away from the resulting aluminum salts through Celite® and the salts were washed with about 100 mL more ether. The solution was washed with brine, dried over Na_2SO_4 , and concentrated. This concentrate was distilled to give 44.5 g of labeled 1-pentanol (89 %). ^1H NMR (CDCl_3 , 250 MHz) δ 3.60 (d of br t, 2H, $J_{\text{CH}} = 140$ Hz), 1.60-1.25 (2 m, 6H total), 0.93-0.82 (m, 3H), hydroxyl proton not observed.

$\text{CH}_3(\text{CH}_2)_3^{13}\text{CHO}$. Oxidation of the labeled alcohol was accomplished using Swern conditions.¹ A flame-dried three-necked 2000 mL round bottom flask was fitted with a mechanical stirrer, thermometer, and addition funnel. The flask was charged with 700 mL of CH_2Cl_2 and cooled to -78 °C. With stirring, 150 mL of a 2.0 M solution of

oxalyl chloride in CH_2Cl_2 was added (0.300 mol). After 5 minutes, 43.0 mL (0.60 mol) of DMSO in 45 mL of CH_2Cl_2 was added through the addition funnel at a rate such that the solution temperature did not exceed $-60\text{ }^\circ\text{C}$. The labeled pentanol from above was added dropwise after 5 minutes (30.0 mL, 0.273 mol/ 30 mL CH_2Cl_2) and the reaction was allowed to stir for an additional 15 minutes. Diisopropylethylamine was added through the addition funnel (240 mL, 1.38 mol) at a dropwise rate so as to maintain a temperature below $-60\text{ }^\circ\text{C}$. Stirring was continued at this temperature for 15 more minutes and the reaction was then allowed to warm to room temperature. The resulting product mixture was washed in two fractions with water, 10% HCl (2x, until aqueous layer was acidic), water, saturated aqueous NaHCO_3 , water, and brine. The fractions were combined and dried over Na_2SO_4 overnight. Analysis of this crude solution by GC indicated that only CH_2Cl_2 , dimethyl sulfide, pentanal, and a small amount of remaining pentanol were present (24:1 aldehyde to alcohol). The bulk of the solvent was removed at room temperature by careful distillation under reduced pressure and the remaining yellow/orange liquid was vacuum transferred into another flask. Failure to do this results in significant trimerization and oligomerization upon heating. The remainder of the solvent was distilled away at reduced pressure followed by the product ($50\text{ }^\circ\text{C}$ at 114 mm Hg). The distillate was vacuum transferred into a tared flask for storage. Yield = 13.7 g (58%). ^1H NMR (CDCl_3 , 250 MHz) δ 9.73 (dt, 1H, $J_{\text{CH}} = 170\text{ Hz}$, $J = 1.8\text{ Hz}$), 2.39 (dtd, 2H, $J_{\text{CH}} = 7.3\text{ Hz}$, $J = 6.2, 1.8\text{ Hz}$), 1.66-1.52 (m, 2H), 1.41-1.25 (m, 2H), 0.90 (t, 3H, 7.3 Hz).

$\text{CH}_3(\text{CH}_2)_3^{13}\text{CH}=\text{CH}_2$. The Wittig reaction was carried out in DMSO solvent to make isolation more efficient.² A 500 mL three necked round bottom flask was equipped

with a stir bar, a condenser with Schlenk adapter, an addition funnel, and a rubber septum. The flask was charged with 4.35 g (0.172 mol) of NaH in the glove box. Under an argon atmosphere, 100 mL of DMSO was added via syringe and the flask was warmed to 75 °C to facilitate reaction to give dimethyl anion. Upon complete consumption of NaH the flask was cooled to 0 °C and a warmed (*ca.* 50 °C) 0.35 M solution of methyltriphenylphosphonium-bromide in DMSO was added via cannula. This mixture was warmed to room temperature and labeled aldehyde from above was slowly added through the addition funnel. The reaction was stirred for 30 minutes and the product was distilled off at ambient pressure. This crude mixture contained mostly 1-hexene, a small amount of CH₂Cl₂ from the previous preparation, benzene, and dimethyl sulfide. Benzene and dimethyl sulfide are presumed to form from Na reduction of triphenylphosphine oxide and DMSO. The desired product was isolated through distillation but retained some impurities according to the GC trace. Almost all remaining impurities except benzene were removed by stirring over Na/K alloy followed by vacuum transfer. Yield = 9.22 g (63.7%) GC analysis indicated that benzene accounted for approximately 1% of the isolated liquid. ¹H NMR (CDCl₃, 200 MHz) δ 5.80 (dm, 1H, *J*_{CH} = 152 Hz), 5.03-4.47 (m, 2H), 2.10-1.95 (m, 2H), 1.40-1.25 (m, 4H), 0.93-0.83 (m, 3H).

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