

Platinum catalyzed sequential hydroboration of decaborane: a facile approach to poly(alkenyldecaborane) with decaborane in mainchain

Xing-Hua Yu^a, Ke Cao^{a,*}, Yawen Huang^a, Junxiao Yang^{a,*}, Jing Li^b and Guanjun Chang^a

^a *School of Materials Science and Engineering & State Key Laboratory Cultivation Base for Nonmetal Composite and Functional Materials, Southwest University of Science and Technology, Mianyang, 621010, P. R. China*

^b *Research Center of Laser Fusion, China Academy of Engineering Physics, Mianyang, Sichuan, 621900, P. R. China*

Email: caoke@swust.edu.cn, yangjunxiao@swust.edu.cn

Context

1. General information
2. Experimental
3. Spectroscopic data for products
4. Copies of ^1H NMR, ^{11}B NMR and GPC

1. General information:

The materials were obtained from different commercial sources, and the toluene, benzene was dried and freshly distilled over sodium before used. All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on gel F254 plates. The silica gel (300 - 400 meshes) is used for column chromatography, and the distillation range of petroleum ether is 60-90°C. ^1H NMR and ^{11}B NMR spectra were recorded on the Bruker 400MHz or 600MHz instruments. All ^1H NMR spectral data are reported in *ppm* relative to tetramethylsilane (TMS) as internal standard, all ^{11}B NMR spectral data are referenced to external $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.00ppm) with a negative sign indicating an upfield shift. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) on a Wyatt DAWN HELEOS using tetrahydrofuran (THF) as an eluent under 38°C. Polymer solutions were prepared with ~5mg/mL concentrations in THF. A loop size of 50 μL was employed, and makes each injection size 0.25mg. Thermogravimetric analysis (TGA) was carried out on a Thermal Analysis SDT Q600 Simultaneous DTA-TGA under a constant flow of 99.999% argon, alumina tube, heated at 10 $^\circ\text{C}/\text{min}$.

2. Experimental

2.1 Synthesis of 6-hexenyldecaborane and 6-norbornenyldecaborane

The 6-hexenyldecaborane (HD) and 6-norbornenyldecaborane (ND) was synthesized according to the method reported by Sneddon and coworkers,^[1] and gave the isolated yield with 78% and 81%, respectively.

6-hexenyldecaborane. ^1H NMR (600MHz, CDCl_3 , ppm): δ 5.86-5.76 (m, 1H), 5.03-4.94 (m, 2H), 2.11-2.06 (dd, $J = 18\text{Hz}$, 6Hz, 2H), 1.59-1.54 (m, 2H), 1.50-1.43 (m, 2H), 1.37 (br, 2H), -1.77(brs, 2H), -2.05(brs, 2H).

6-norbornenyldecaborane. ^1H NMR (400MHz, CDCl_3 , ppm): δ 6.18 (brs, 1H), 6.03 (brs, 1H), 2.99-2.96 (d, $J = 18\text{Hz}$, 2H), 1.74-1.72 (m, 1H), 1.43-1.39 (m, 1H), 1.37 (brs, 1H), 1.28(brs, 2H), -1.52 (s, 2H), -2.02 (s, 2H).

2.2 Synthesis of poly(6-hexenyldecaborane) (PHD)

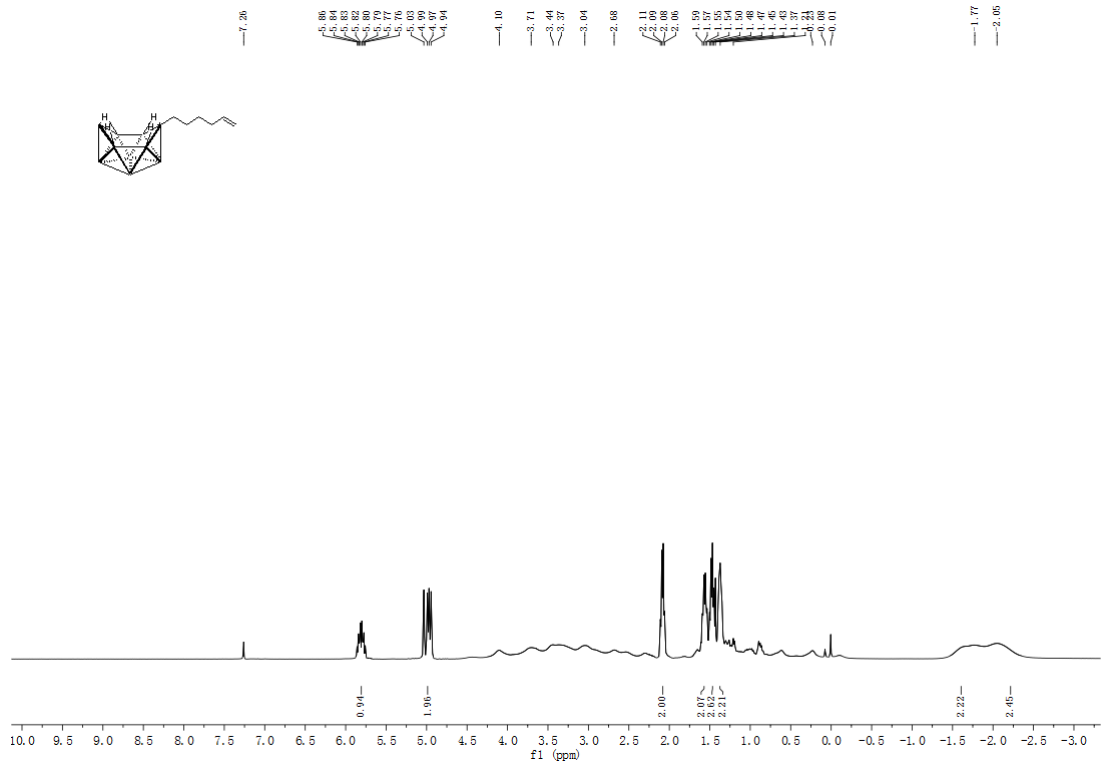
To a dried Schlenk tube was sequentially added 6-hexenyldecaborane (100 mg, 0.4854 mmol), PtBr₂ (17.2 mg, 0.0485 mmol) and 0.1mL freshly distilled benzene, then the mixture was stirred at 100°C under N₂ for 48h. After cooled to room temperature, the mixture was diluted with CH₂Cl₂ and filtered through a short silica gel column using CH₂Cl₂ as eluent to remove the catalyst. After evaporation of the solvent, the residue was added to *n*-hexane dropwise, and the polymer was precipitated, after centrifugation and dried under vacuum, the PHD was afforded as creamy white solid with 35% yield (35mg). ¹¹B NMR (192.5MHz, CDCl₃, ppm): δ 24.99, 10.59~8.97 (d), 1.33, -1.82~-2.48 (d), -33.64, -36.39, -38.41. ¹H NMR (400 MHz, CDCl₃, ppm): 1.56 (s, 4H), 1.40-1.36 (m, 4H), 1.30-1.27 (m, 4H), -1.59 (br, 3BHB), -2.05 (br, 1BHB).

2.3 Synthesis of poly(6-norbornenyldecaborane) (PND)

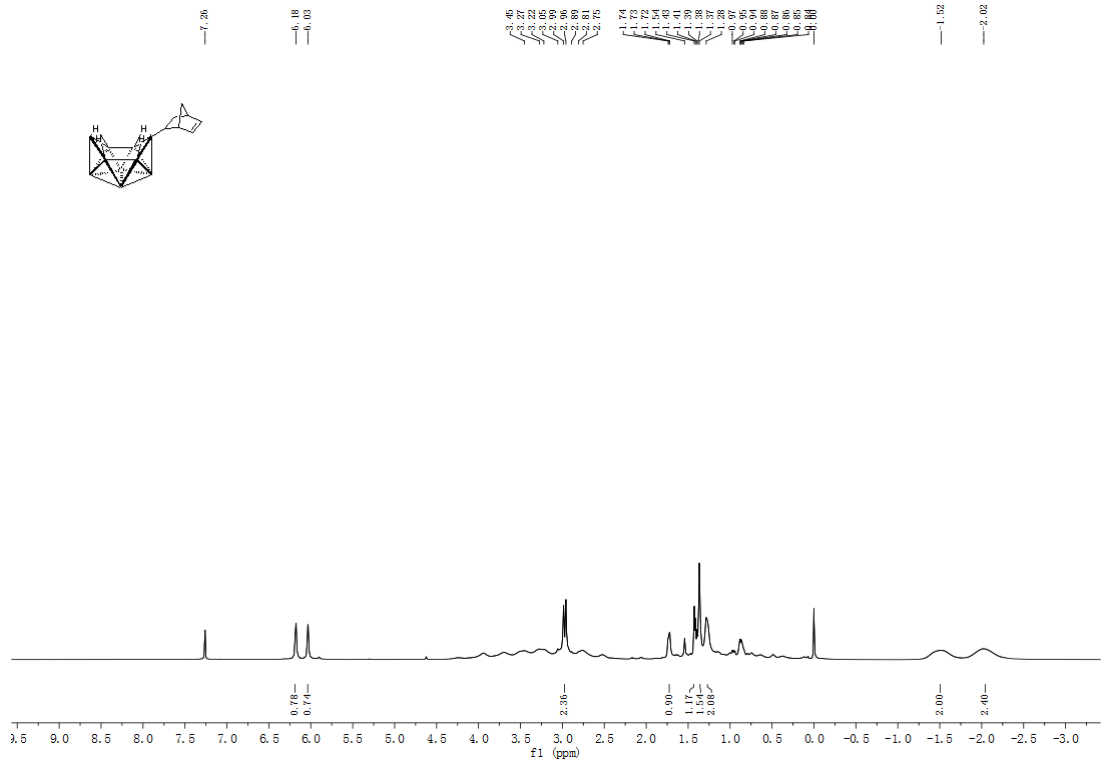
poly(6-norbornenyldecaborane) was synthesized in a similar manner as described for PHD with 0.5mL benzene, and the PND was obtained as creamy white solid with 55% yield (55mg). ¹¹B NMR (192.5MHz, CDCl₃, ppm): δ 27.42, 12.84, 10.36, 8.85, 1.35, -3.19, -33.87, -36.56~-38.33. ¹H NMR (400 MHz, CDCl₃, ppm): 2.48 (m, 2H), 1.73-1.43 (m, 6H), 1.27 (m, 2H), -1.62 (br, 2BHB), -2.04 (br, 2BHB).

Copies of ¹HNMR/¹¹BNMR/GPC

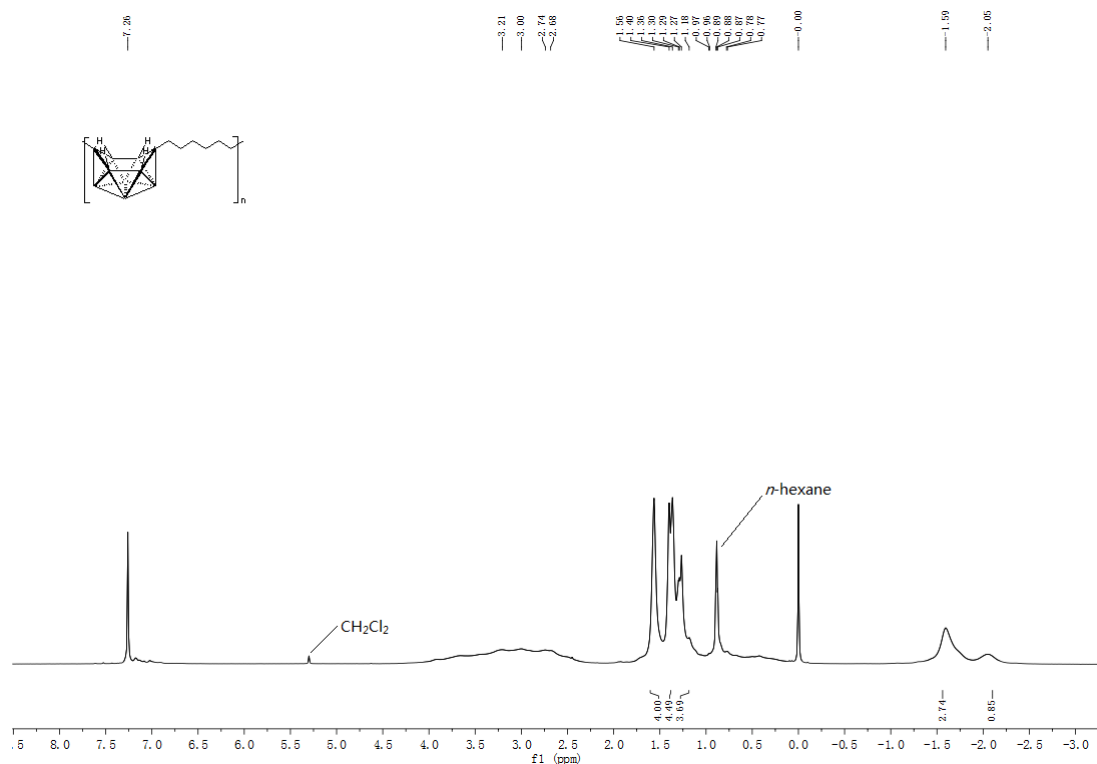
¹HNMR of HD



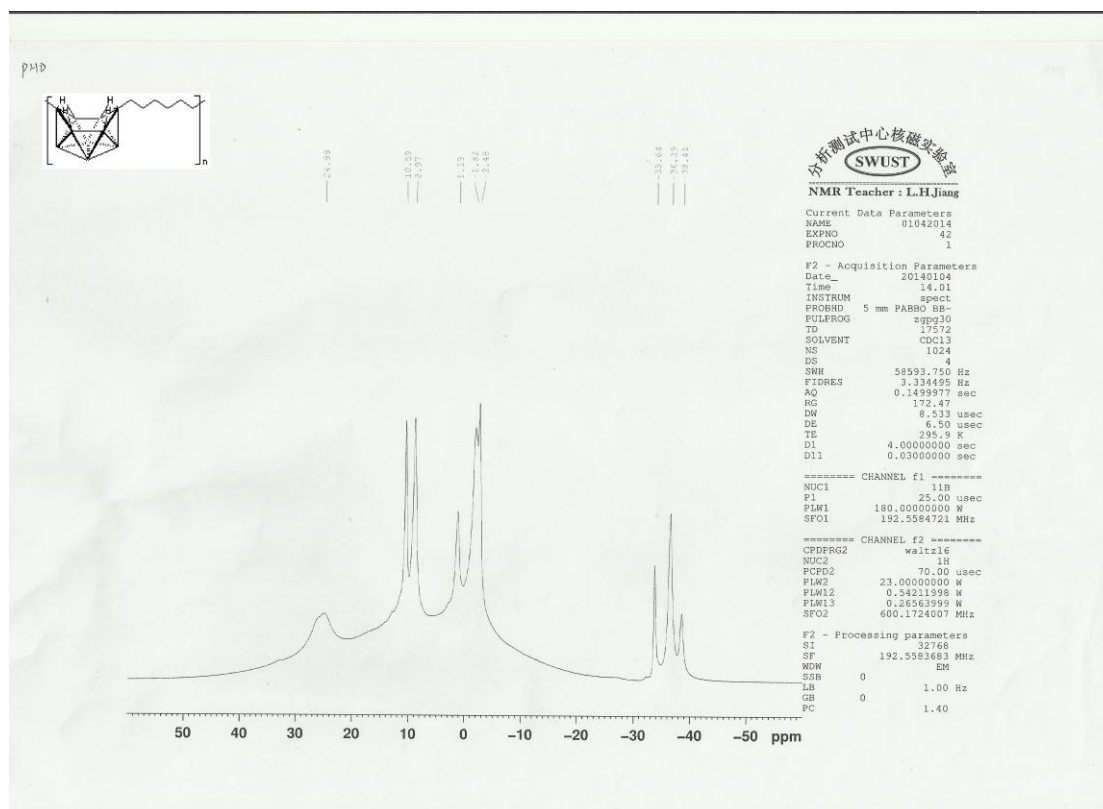
¹HNMR of ND



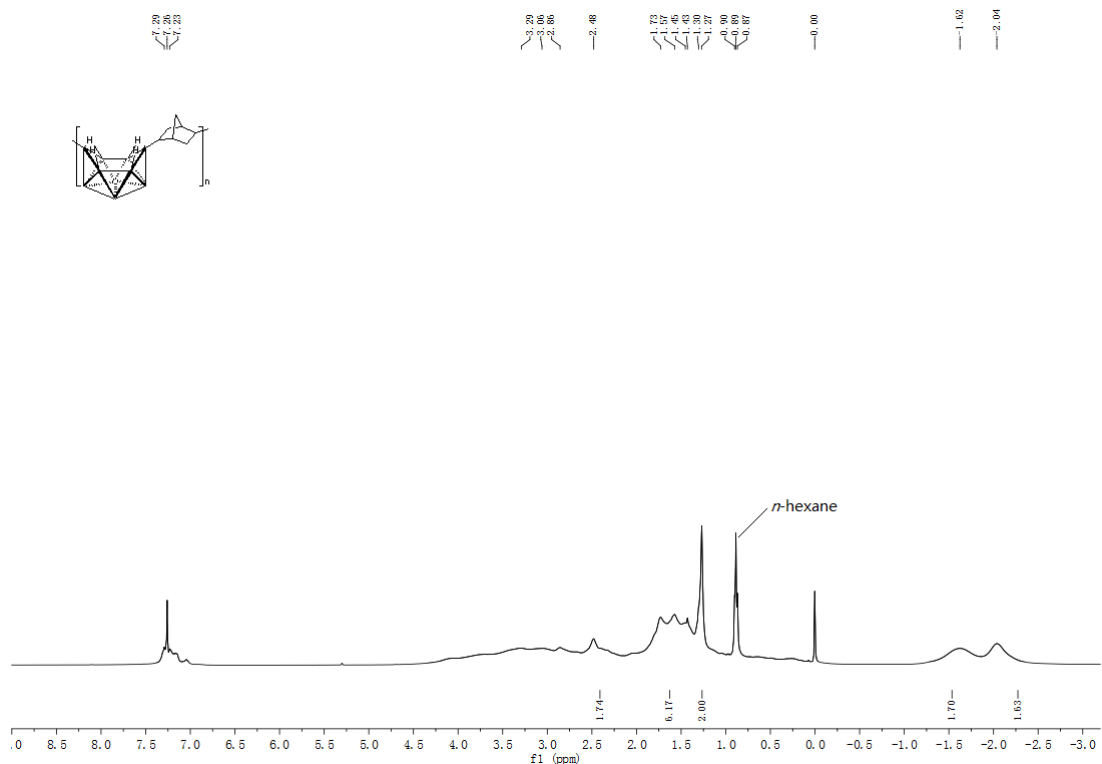
¹H NMR of PHD



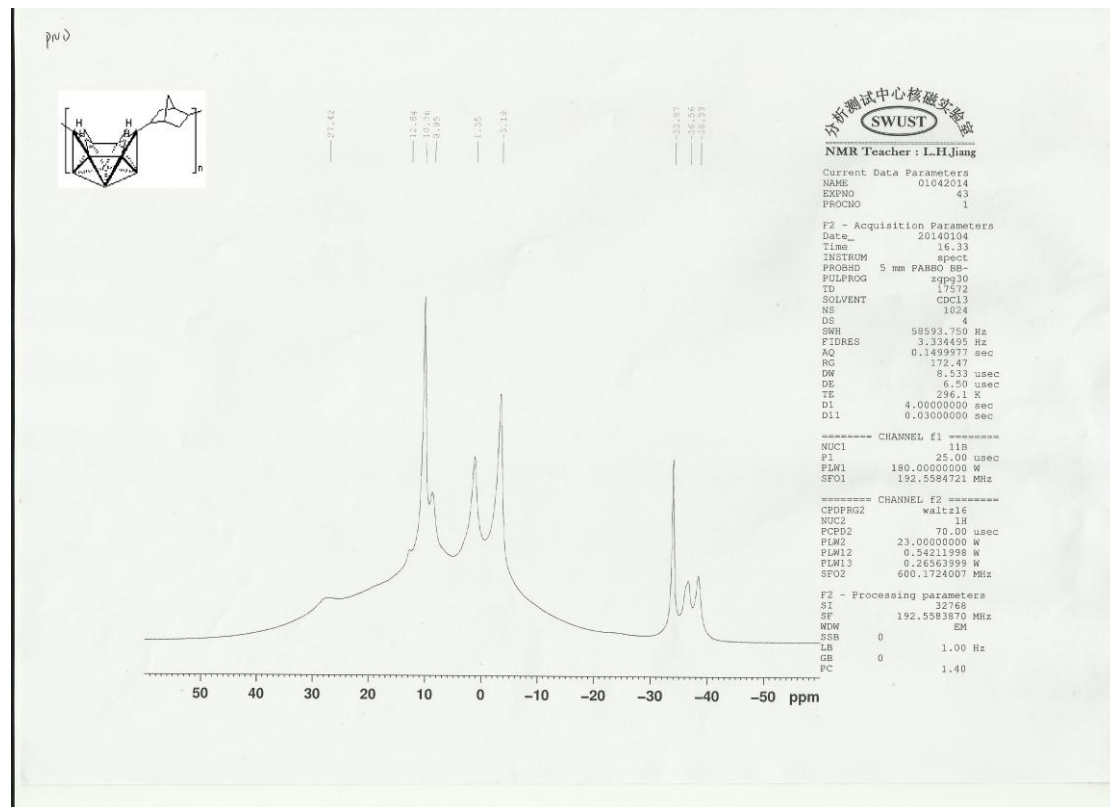
¹¹B NMR of PHD



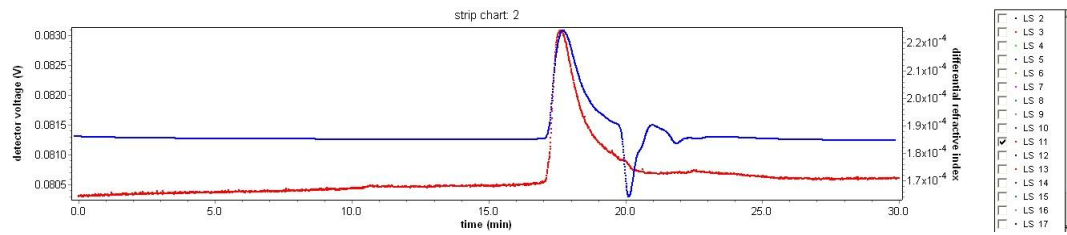
¹H NMR of PND



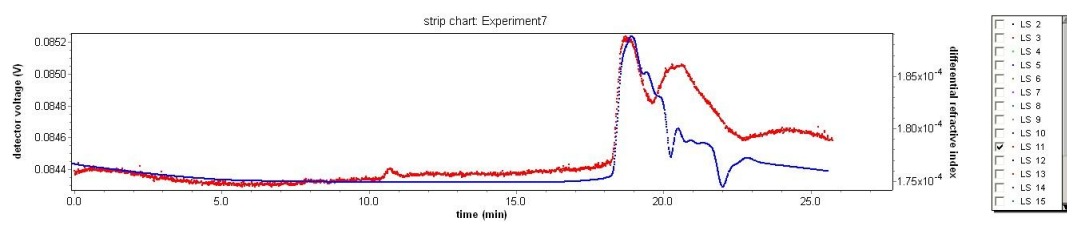
¹¹B NMR of PND



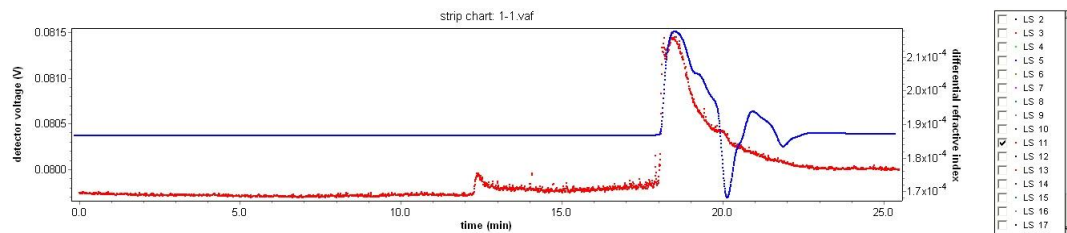
GPC of PHD with 10mol% PtBr₂



GPC of PND with 5mol% PtBr₂



GPC of PND with 10mol% PtBr₂



GPC of PND with 15mol% PtBr₂

