

Supporting Information

2,3-*exo*-Diheterotactic Dicyclopentadiene Oligomers: An X-Ray Powder Diffraction Study of a Challenging Multiphase Case

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Additional Files

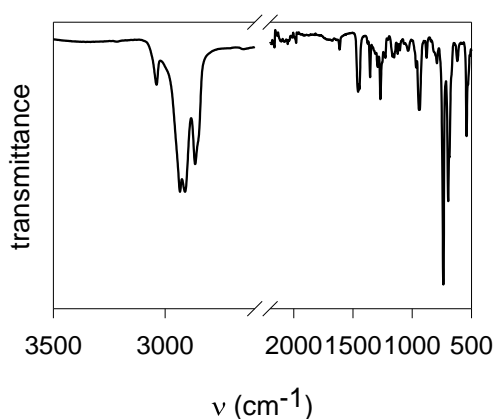
This supplemental file “FTIR_NMR.pdf” contains the FTIR, and ^1H and ^{13}C NMR spectra.

The supplemental file “WAXS_SEC_files.zip” contains experimental X-ray pattern, and SEC mass distribution in x-y text format.

The supplemental file “cif_files.zip” contains crystal structures of DCPD oligomers and polymer in .cif format.

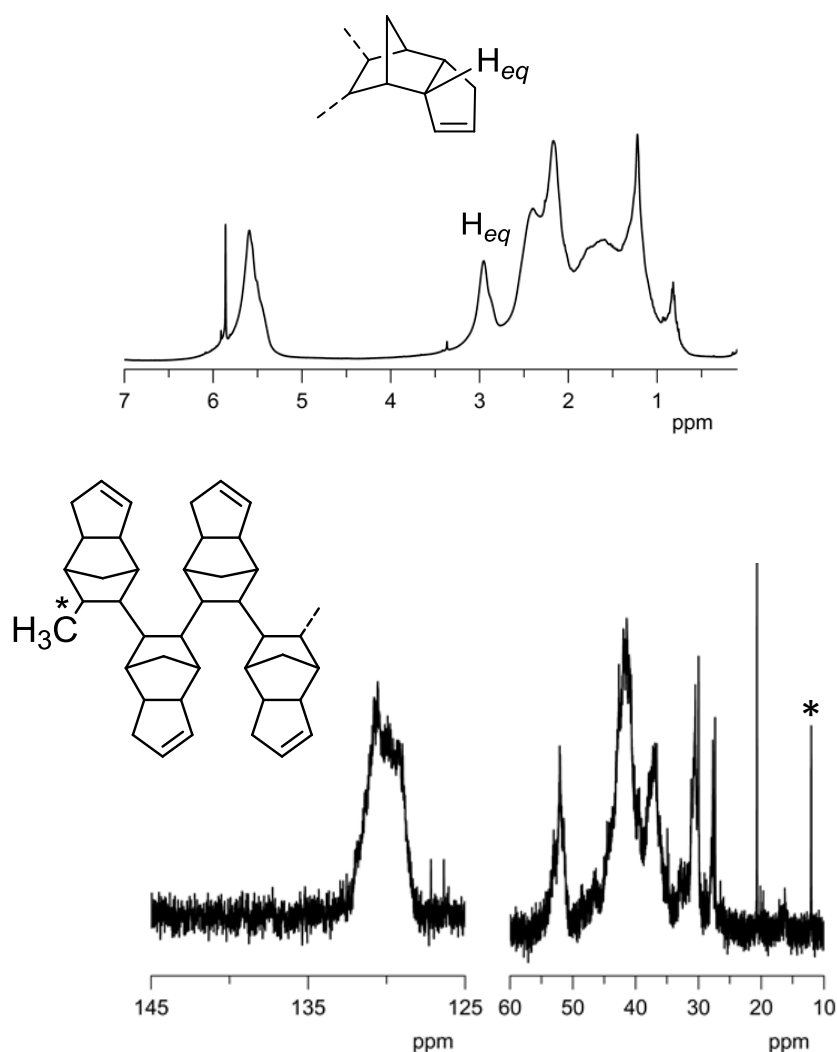
The supplemental file “tinker4.2_files.zip” contains TINKER 4.2 input files .key and .xyz for energy calculations on the crystal structures of DCPD oligomers and polymer. Please note that the most recent version of TINKER (actually 8.5) can deal with the provided input files, but the results of the calculations are wrong. In this newer version the mechanism “GROUP and GROUP-SELECT” is either broken or simply acts differently from the version of TINKER used in this work.

Figure S1. FTIR spectra of DCPD sample obtained with Cr1/MAO.



FTIR spectra of DCPD oligomers show the characteristic absorption bands at 3038 (s), 2933–2865 (s) 1613 (w), 1457 (m), 942 (m), 737 (s) and 696 (s) cm^{-1} . The presence of bands at 3038 and 1613 cm^{-1} and the absence of any band at about 1580 cm^{-1} indicate that all the bicycloheptene double bonds were consumed during the oligomerization. The remaining unsaturations are entirely due to the cyclopentene double bond: the bands at 3038 and 1613 cm^{-1} are characteristic of the olefinic $=\text{C}-\text{H}$ stretching vibration and $\text{C}=\text{C}$ stretching vibration, respectively. The absorption peak at 942 cm^{-1} is assigned to the bending of the $\text{C}-\text{H}$ bonds in the ring system of norbornene, thus confirming that also the oligomerization of DCPD occurs through a 2,3-addition rather than via ROMP (see Ref. 20 in the manuscript).

Figure S2. ^1H (top) and ^{13}C NMR (bottom) spectra of DCPD sample obtained with **Cr1**/MAO.



Fine microstructural analysis by ^{13}C NMR was difficult because of the broadness of several overlapping peaks. However, further insights by ^{13}C NMR indicated an average molecular length of roughly 24 monomers, very different from the SEC outcome, through still in the range of oligomers. This estimation was obtained through the evaluation of the ratio $I(\text{C}_{\text{DCPD}})/[10 I(\text{C}_{\text{CH}_3})]$ where $I(\text{C}_{\text{DCPD}})$ is the total area of the DCPD carbon atoms in the NMR spectrum, $I(\text{C}_{\text{CH}_3})$ is the area of the signal at about 12 ppm due to the methyl group, and “10” is the number of carbon atoms in a DCPD monomer unit.