Controlled Oligomerization in Water to Hyperbranched Ethylene Oligomers

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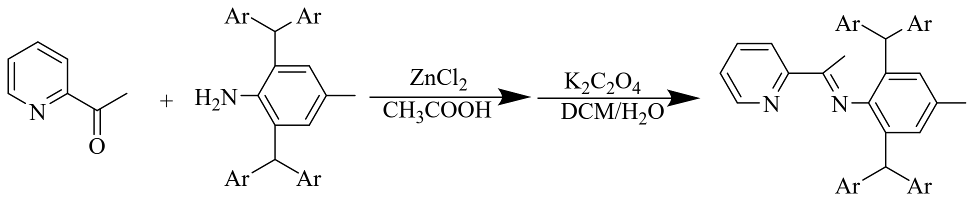
1. Experimental Sections

1.1 General Considerations

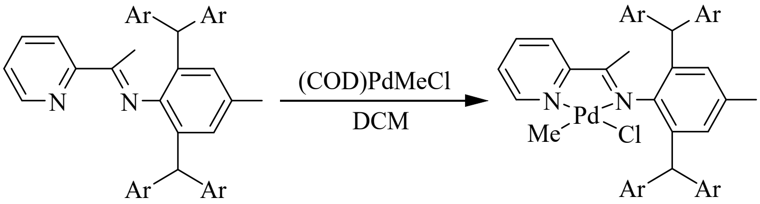
All chemicals were commercially sourced, except those whose synthesis is described. Deuterated solvents used for NMR were dried and distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded by a Bruker Ascend Tm 400 spectrometer or a JEOL JNM-ECZ600R 600 spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the ^{1}H and ^{13}C NMR spectra were referenced to the residual solvent; Coupling constants are in Hz.

1.2 Procedure for the Synthesis of Ligands L1-L5.



$ZnCl_2$ (0.2 g, 1.5 mmol) and 2-acetylpyridine (1.0 mmol), were suspended in glacial acetic acid (4 mL). Anilines (1.0 mmol) was added, and the reaction mixture was stirred and refluxed at 90 °C for 4 h. The solution was allowed to cool to room temperature, and a yellow solid precipitated. The solid was separated by filtration and washed with diethyl ether (5 × 5 mL), to remove remaining acetic acid. Drying under vacuum gave yellow, poorly soluble solid. Then the zinc was removed from the zinc pyridine-imine complex. The product of the previous step was suspended in methylene chloride (30 mL), and a solution of potassium oxalate (0.2 g, 1.2 mmol) in water (5 mL) was added. The reaction mixture was stirred vigorously for 1 h. The two phases were separated, and the organic layer was washed with water (3 × 20 mL) and dried with $MgSO_4$. After filtration, the solvent was removed under vacuum to afford the product as an yellow powder and dried under high vacuum. All the bulky arylamines used and ligands have been reported by us previously[1-4].

1.3 Procedure for the Synthesis of Palladium Complexes Pd1-Pd5.



A mixture of the ligand (1 mmol), Pd(COD)MeCl (265 mg, 1 mmol) in CH_2Cl_2 (20 mL) was stirred for overnight at room temperature. During stirring, the color of the solution was deepening. At the end of the reaction, the solution was concentrated to 2 mL. The product was crashed out with 20 ml ether and washed with ether (3 × 5 mL). Then dried under reduced pressure at room temperature for about 5 h. The pure compound was obtained as an orange or brown solid. These palladium complexes are all known compounds that have been reported by us[1-4].

1.4 A General Procedure for Formation of Polyethylene Oil within Water Using Pd Complexes

In a typical experiment, a 350 mL thick-walled pressurized glass reactor (supplied by Chemglass) was dried in an air blower at 60 °C for a minimum of 6 hours. The reactor was then charged with the complexes, 2 equivalents of NaBArF, and 1 mL of dichloromethane (DCM). After the solution was thoroughly mixed to achieve homogeneity, 20 mL of water (H2O) was added. Subsequently, the reactor was placed in an ultrasonic generator for 5 minutes. Following this, the reactor was connected to a medium-pressure polymerization line. With vigorous stirring, the reactor was pressurized and maintained at 4 atmospheres of ethylene. After 12 hours, the pressure in the reactor was released, and the resulting polyethylene oil was isolated and dried through extraction with hexane.

2. Figures

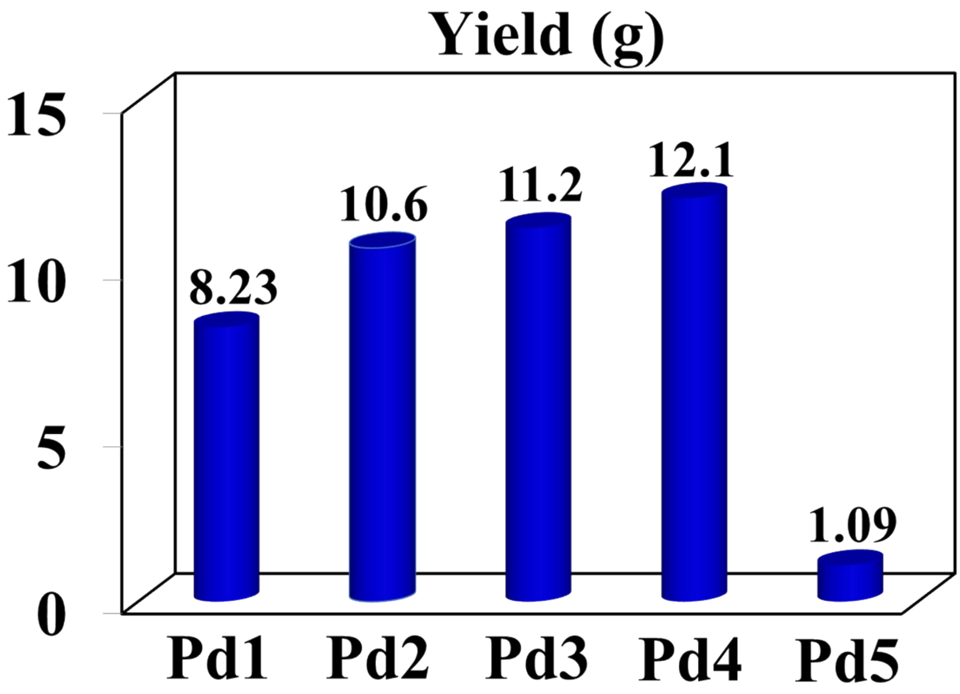


Figure S1. The yields of the ethylene aqueous polymerization by **Pd1-Pd5**.

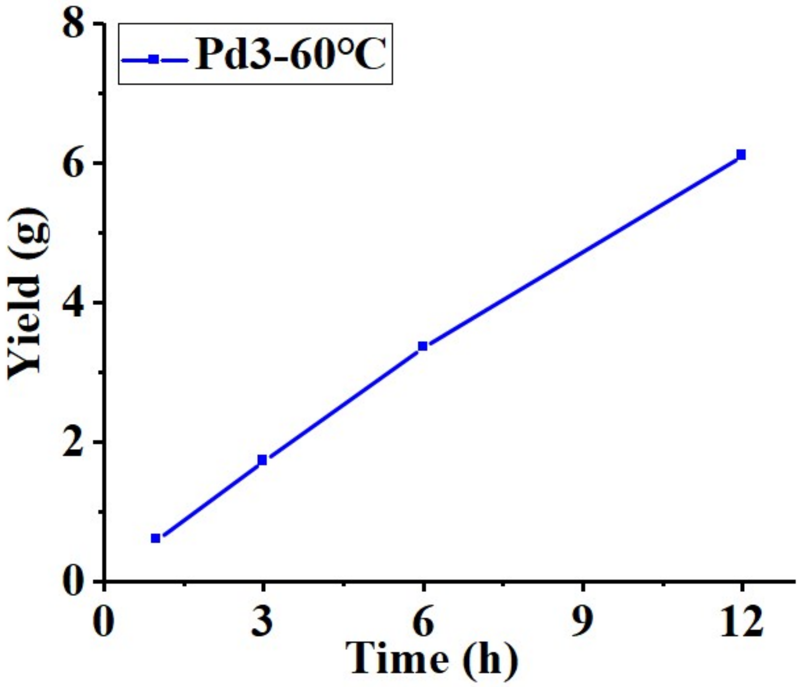


Figure S2. The yield plot of **Pd3** over time at 60 °C.

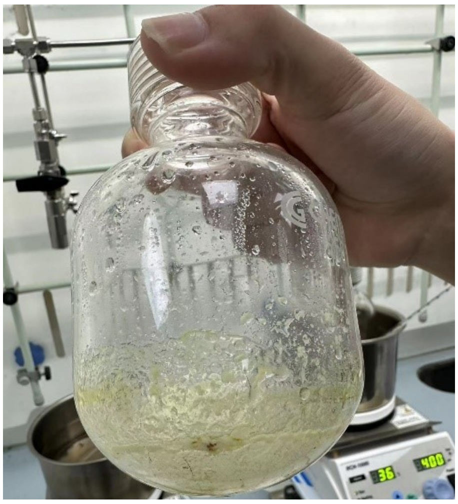


Figure S3. The state of the product obtained by **Pd5** catalyzing ethylene polymerization in water

3. ^{1}H and ^{13}C NMR of Representative Ethylene Oligomers.

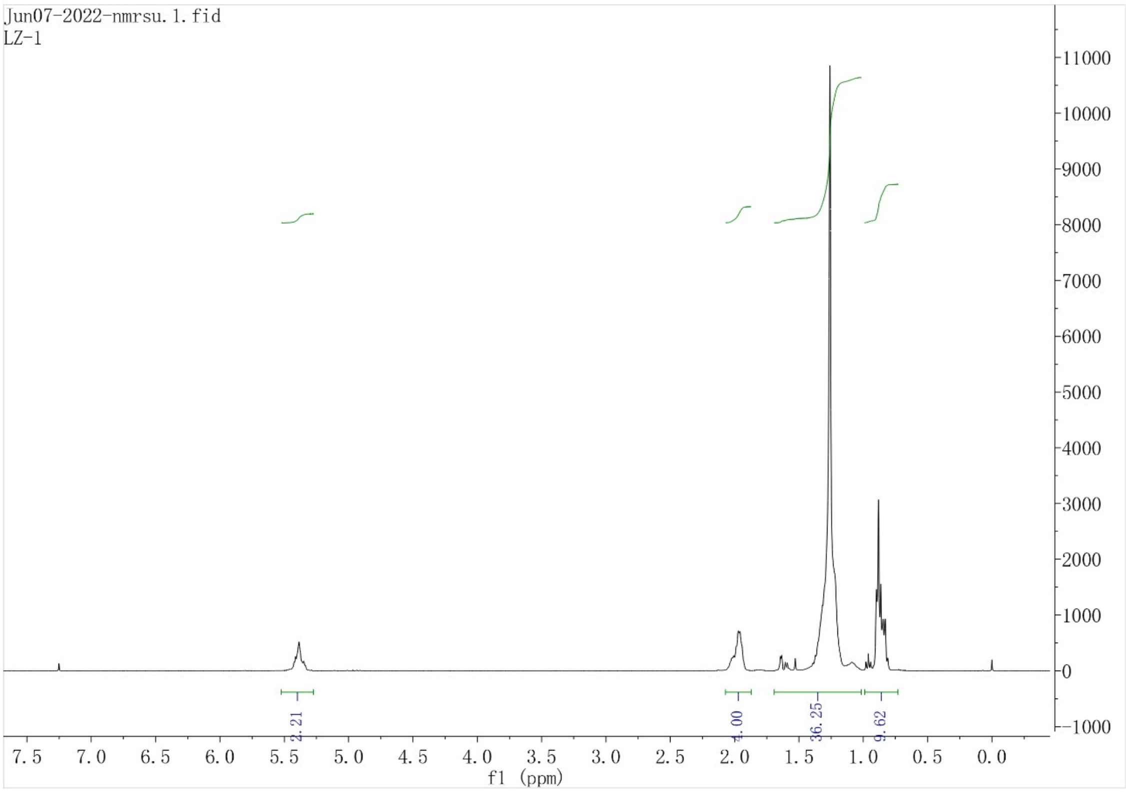


Figure S4. ^{1}H NMR spectrum of the oligomer from table 1, entry 1 ($CDCl_3$, 20 ^{o}C).

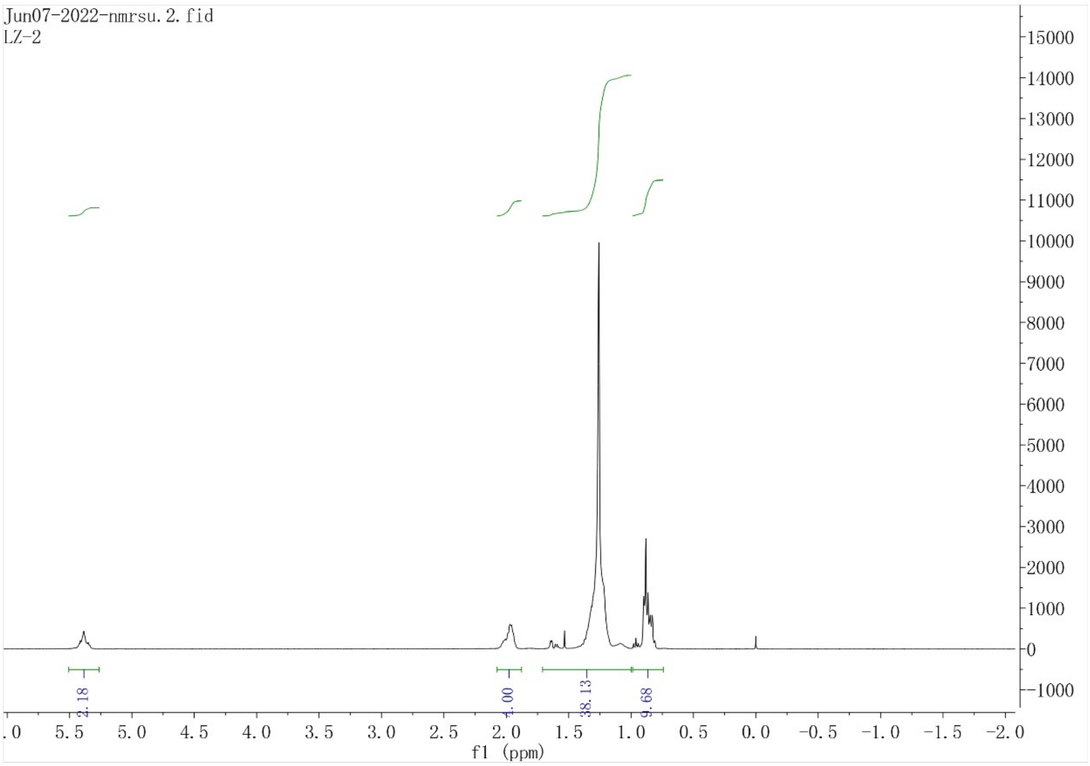


Figure S5. ^{1}H NMR spectrum of the oligomer from table 1, entry 2 ($CDCl_3$, 20 °C).

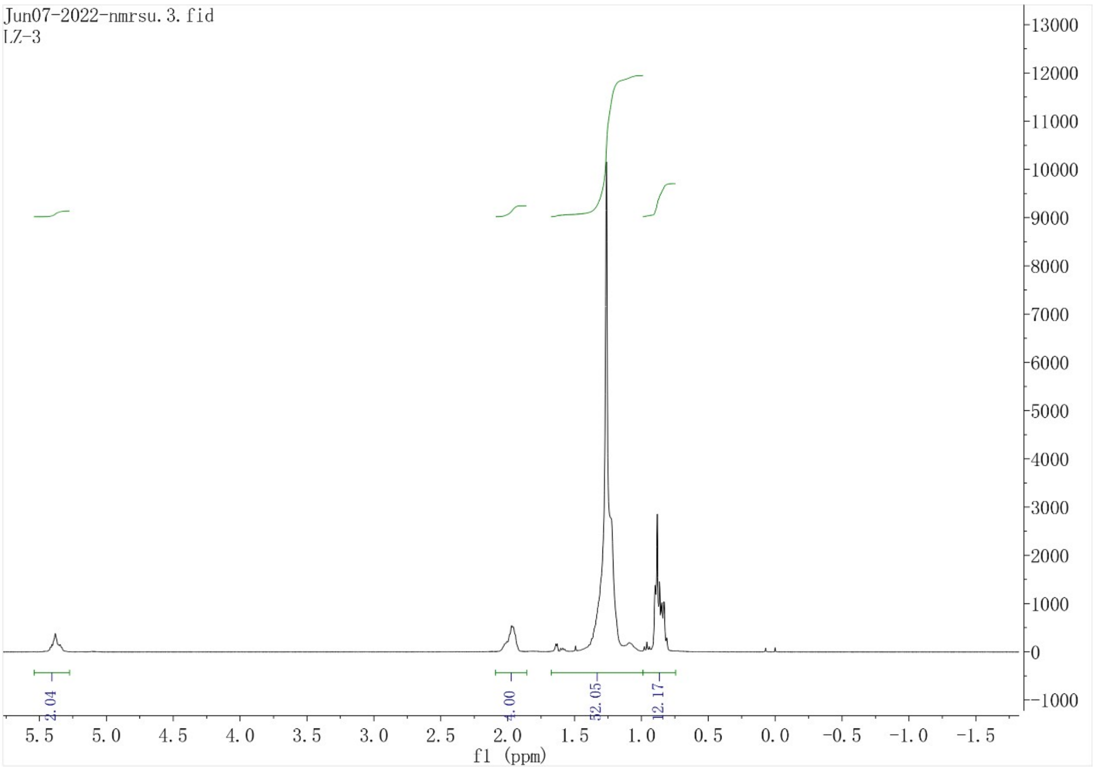


Figure S6. ^{1}H NMR spectrum of the oligomer from table 1, entry 3 ($CDCl_3$, 20 °C).

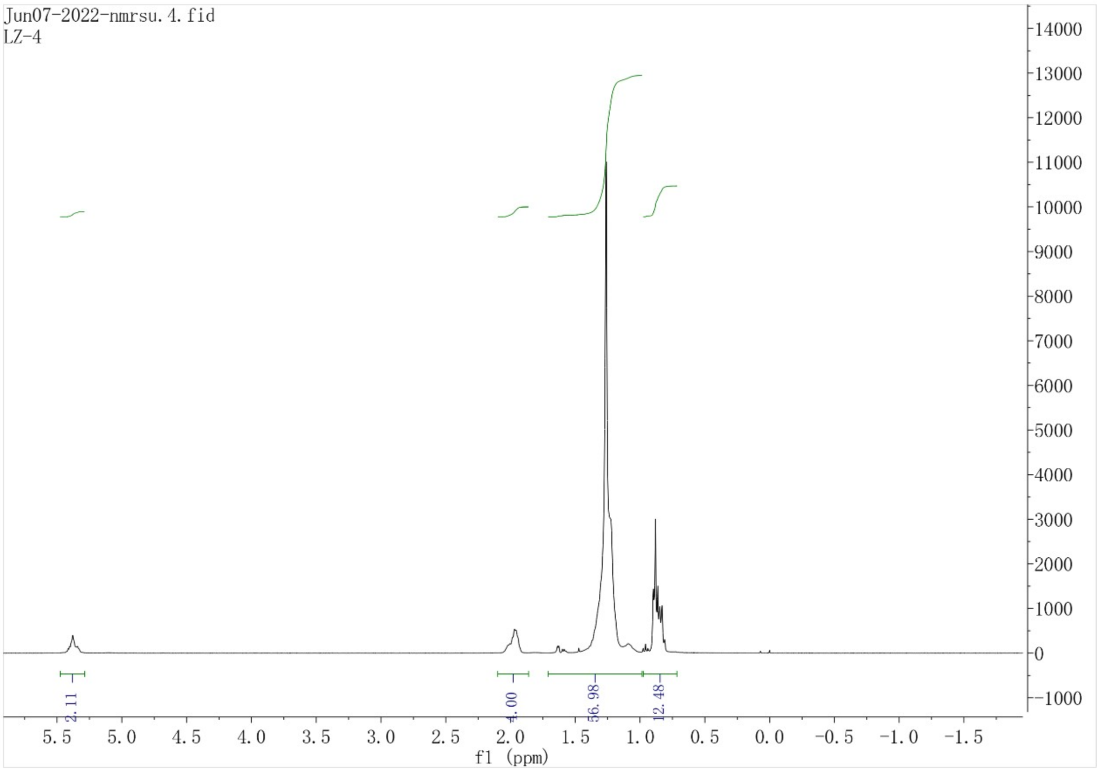


Figure S7. ^{1}H NMR spectrum of the oligomer from table 1, entry 4 ($CDCl_3$, 20 ^{o}C).

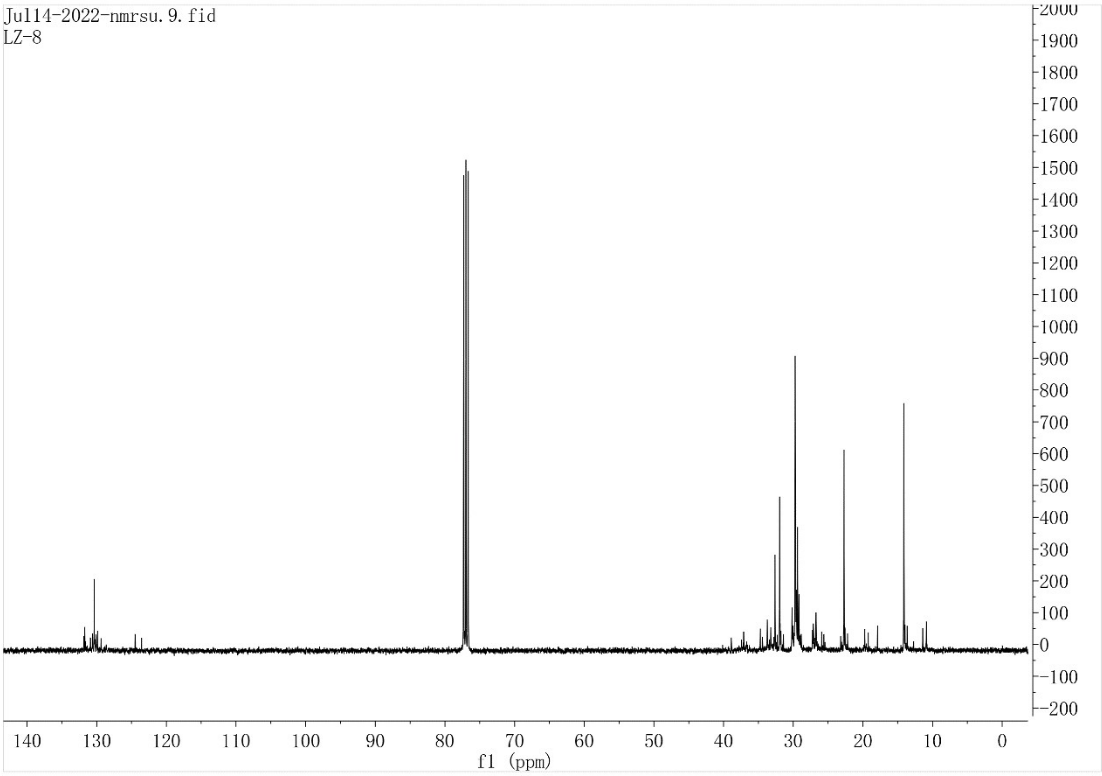


Figure S8. ^{13}C NMR spectrum of the oligomer from table 1, entry 4 ($CDCl_3$, 20 ^{o}C).

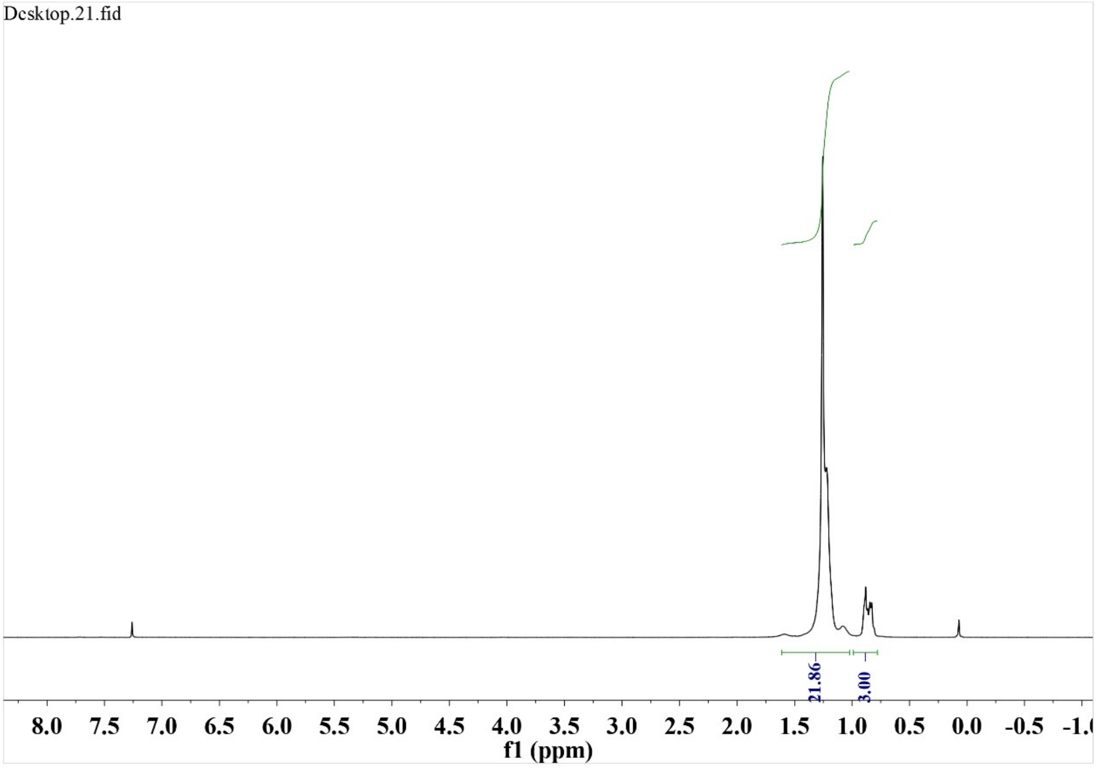


Figure S9. ^{1}H NMR spectrum of the polymer from table 1, entry 5 ($CDCl_3$, 20 °C).

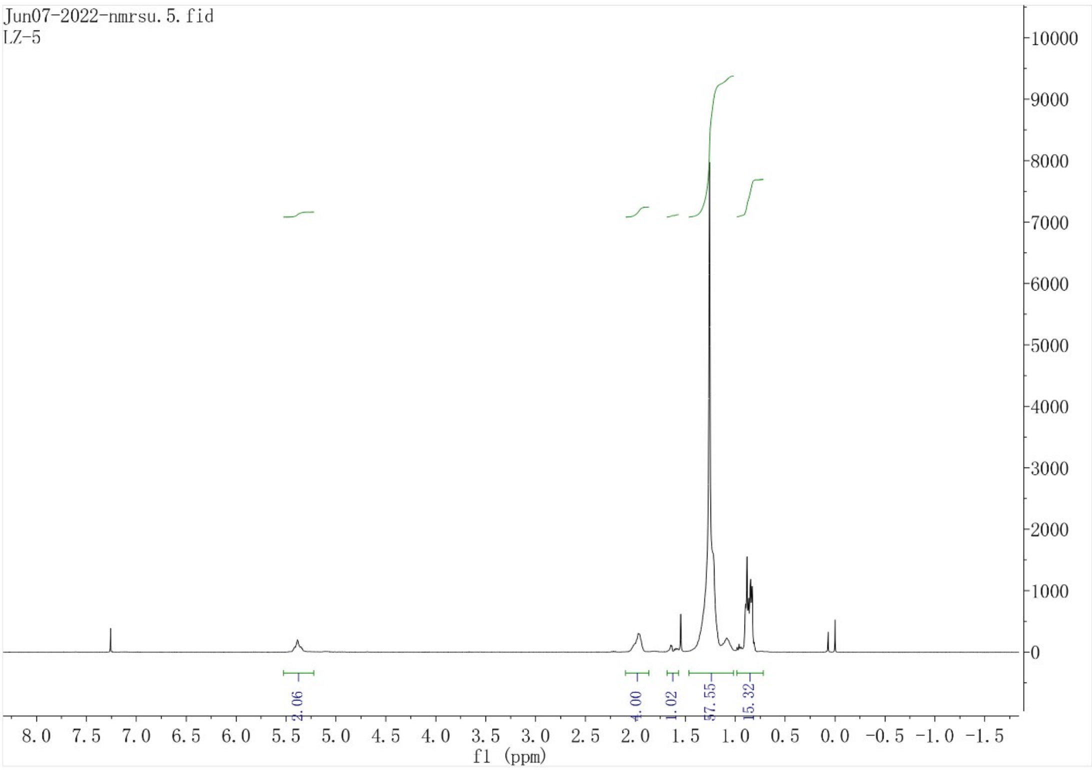


Figure S10. ^{1}H NMR spectrum of the oligomer from table 1, entry 6 ($CDCl_3$, 20 °C).

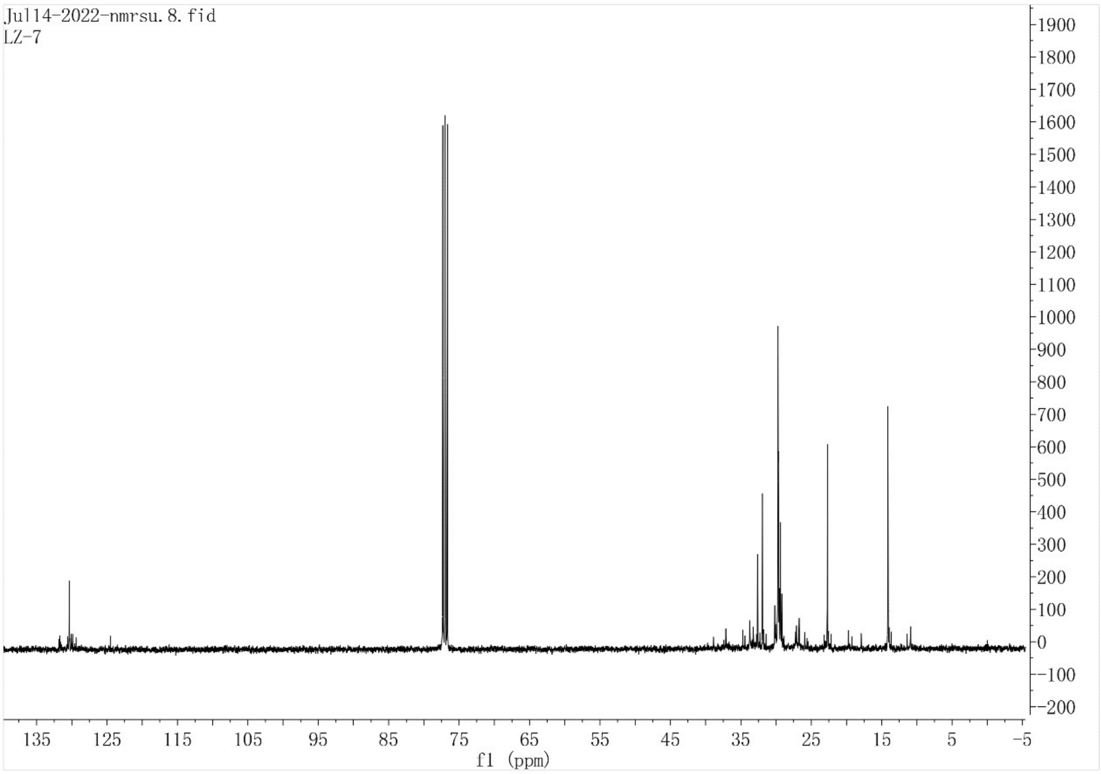


Figure S11. ^{13}C NMR spectrum of the oligomer from table 1, entry 6 ($CDCl_3$, 20 ^{o}C).

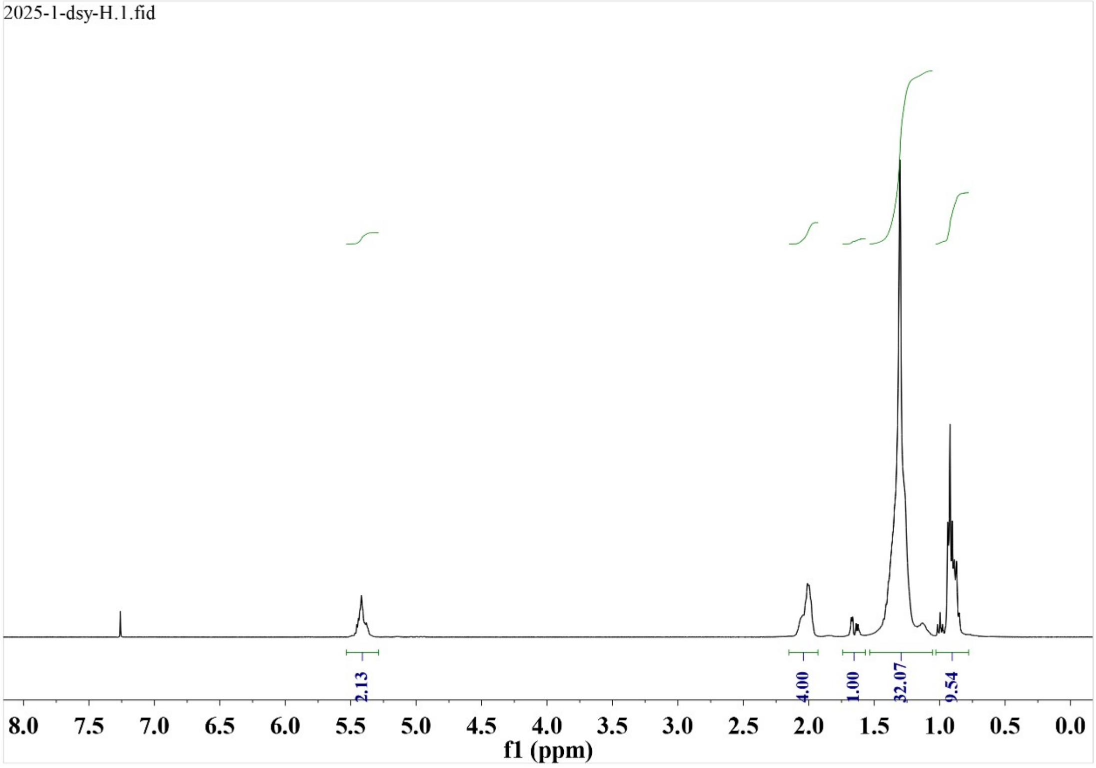


Figure S12. ^{1}H NMR spectrum of the oligomer from table 1, entry 7 ($CDCl_3$, 20 ^{o}C).

4. References

1. Z. Yan, H. Bi, B. Ding, H. Wang, G. Xu and S. Dai, *New J. Chem.* **2022**, ***46***, 8669-8678.
2. Z. Yan, S. Li and S. Dai, *Chin. J. Syn. Chem.*, 2021, **29**, 1033-1044.
3. X. Wu, G. Xu, W. Lu, Z. Y. Li and S. Dai, *Eur. Polym. J.*, 2022, **177**, 111495.
4. S. Li and S. Dai, *J. Catal.* 2021, **393**, 51-59.