

Electronic Supporting Information

Regioselective Living Polymerization of Allylcyclohexane and Precise Synthesis of Hydrocarbon Block Copolymers with Cyclic Units

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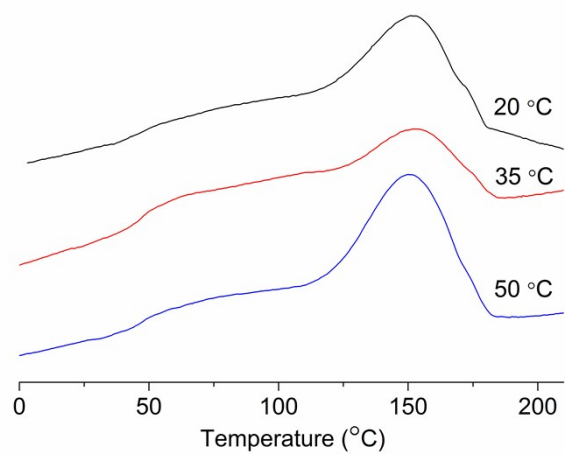


Figure S1. DSC curves of PACH produced by 1/Et₂AlCl at different temperatures.

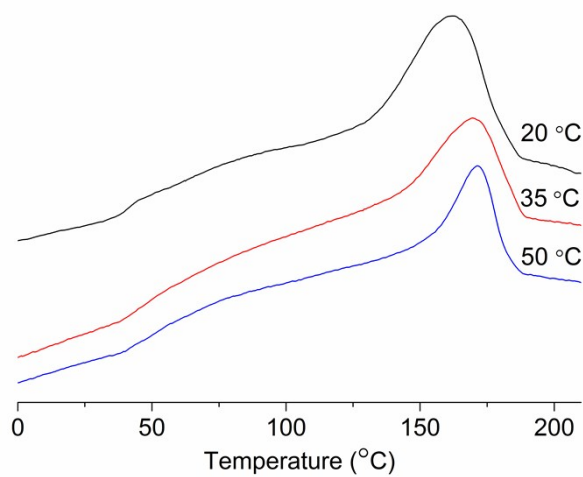


Figure S2. DSC curves of PACH produced by 1/MMAO at different temperatures.

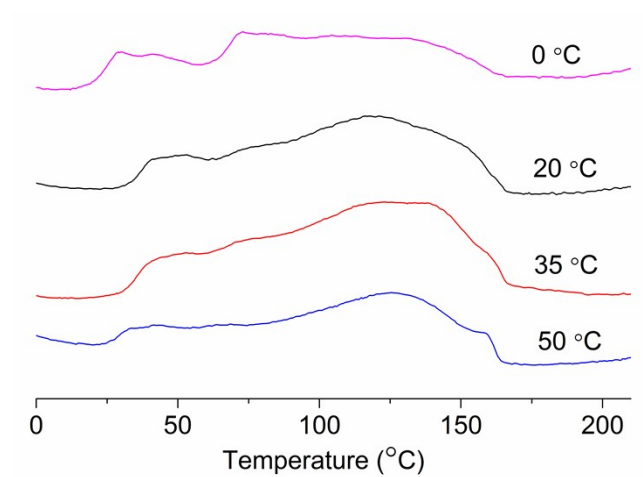


Figure S3. DSC curves of PACH produced by **2**/Et₂AlCl at different temperatures.

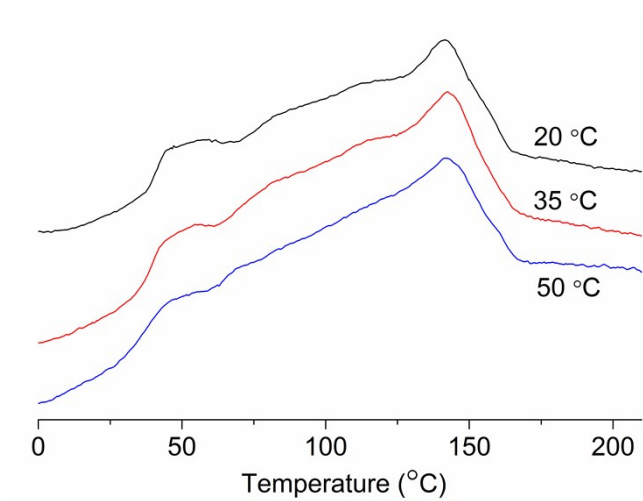


Figure S4. DSC curves of PACH produced by **2**/MMAO at different temperatures.

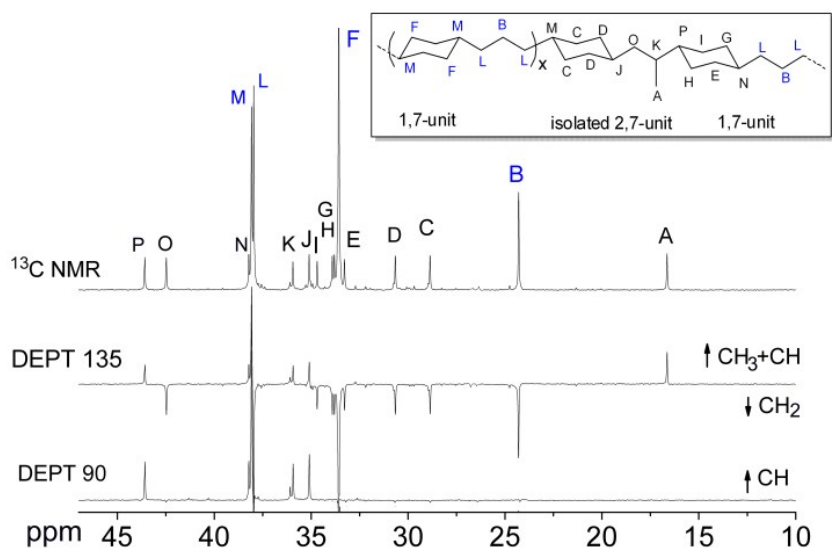


Table S1. Chemical shift assignments of ^{13}C NMR spectra of PACH.

Peak	DEPT	Chemical shift (ppm)	Assignment	References
A	P	16.64	CH_3	(1)
B	S	24.30	CH_2	(2)
C	S	28.87	CH_2	(3,4)
D	S	30.66	CH_2	(3,4)
E	S	33.29	CH_2	(2,3)
F	S	33.58	CH_2	(2)
G	S	33.81	CH_2	(2,3)
H	S	33.91	CH_2	(2,3)
I	S	34.70	CH_2	(2,3)
J	T	35.10	CH	(2,4)
K	T	36.10	CH	(2,3)
L	S	37.97	CH_2	(2)
M	T	38.08	CH	(2)
N	T	38.22	CH	(3,4)
O	S	42.48	CH_2	(1,4)
P	T	43.59	CH	(3,4)

The assignments of chemical shifts are referenced to the report in *Anal. Chem.* **1971**, *43*, 1245.

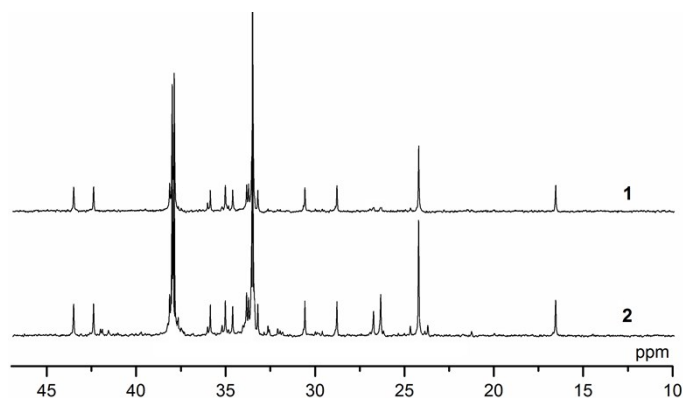


Figure S5. ^{13}C NMR spectra of PACH produced by catalysts **1** (entry 2) and **2** (entry 10).

Table S2. Allylcyclohexane living polymerization results at different times catalyzed by **1**/ Et_2AlCl at 20 °C.^a

Entry	Time (h)	Conv. (%)	M_n^b (kg/mol)	PDI ^b
1	0.5	32.3	6.2	1.18
2	1	45.7	9.1	1.16
3	1.5	62.7	12.9	1.15
4	2	70.3	14.1	1.15
5	3	76.6	15.9	1.15
6	6	86.0	17.3	1.15

^a Polymerization conditions: 20 μmol Ni, 1 mmol ACH, Al/Ni = 200, 8 mL toluene and 2 mL CH_2Cl_2 . ^b Determined by GPC in 1,2,4-trichlorobenzene at 150 °C.

References

- (1) McCord, E. F.; McLain, S. J.; Nelson, L. T. J.; Ittel, S. D.; Tempel, D. J.; Killian, C. M.; Johnson, L. K.; Brookhart, M. ^{13}C NMR Analysis of α -Olefin Enchainment in Poly(α -olefins) Produced with Nickel and Palladium α -Diimine Catalysts. *Macromolecules* **2007**, *40*, 410-420.
- (2) Takeuchi, D. Precise Isomerization Polymerization of Alkenylcyclohexanes: Stereoregular Polymers Containing Six-membered Rings along the Polymer Chain. *J. Am. Chem. Soc.* **2011**, *133*, 11106-11109.
- (3) Thuilliez, J.; Ricard, L.; Nief, F.; Boisson, F.; Boisson, C. Ansa-bis(fluorenyl)neodymium Catalysts for Cyclocopolymerization of Ethylene with Butadiene. *Macromolecules* **2009**, *42*, 3774.
- (4) Silva, L. C.; Wagener, K. B. Synthesis and Thermal Characterization of Precision Poly(*p*-cyclohexylene alkylene)s via Acyclic Diene Metathesis Polycondensation.

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