

Supporting Information of

Precise Isomerization Polymerization of
Alkenylcyclohexanes. Stereoregular Polymers
Containing Six-Membered Rings Along the
Polymer Chain

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Experimental Section (S2-S5)

Figures (S6-S8)

Experimental Section

General Method

Dry solvents were purchased and used as received. Diimine ligands,¹ PdCl(Me)(diimine)², NiBr₂(diimine)² and NaBARF³ were prepared according to the reported procedure. Vinylcyclohexane, allylcyclohexane, and MMAO were purchased and used as received. NMR (¹H and ¹³C) spectra were recorded on a Varian Mercury 300 or JEOL JNM-500 spectrometer. The peaks were referenced to CHCl₃ (δ 7.26) in the CDCl₃ solvent or C₂H₂Cl₄ (δ 5.91) in the C₂D₂Cl₄ solvent for ¹H and C₂D₂Cl₄ (δ 74.2) for ¹³C. Gel permeation chromatography (GPC) measurement was performed at 152 °C on a TOSOH HPLC-8121GPC/HT equipped with a FT-IR detector, using orthodichlorobenzene as eluent.

1. Monomer Synthesis

1) 4-Butenylcyclohexane (I-2)

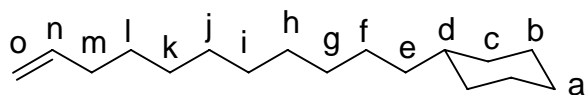
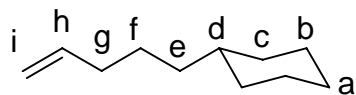
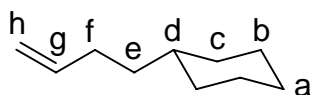
To a 100-mL two-necked round-bottomed flask containing allyl bromide (6.1 mL, 70.6 mmol) and dry ether (11.3 mL) was added ether solution (22.5 mL) of cyclohexylmagnesium bromide (70.6 mmol), prepared from cyclohexylmethyl bromide (12.5 g, 70.6 mmol) and magnesium (1.76 g), dropwise over a period of 40 min at 0 °C. After the reaction mixture was refluxed for 2 h, 1 M HCl (1.7 mL) and water (20 mL) was slowly added. The organic phase was extracted with ether, washed with water and brine, and was dried over MgSO₄. Volatile fraction was evaporated and the residue was distilled to afford butenylcyclohexane as colorless liquid (4.06 g, 41.6%, b.p. 176.5 °C). ¹H NMR (300 MHz, CDCl₃): δ 5.82 (m, 1H, H_g), 4.95 (m, 2H, H_h), 2.06 (m, 2H, H_f), 1.69 (m, 5H, H_a(equatorial), H_b(equatorial), H_c(equatorial)), 1.26 (m, 6H, H_a(axial), H_b(axial), H_d, H_e), 0.09 (m, 2H, H_c(axial)).

5-Pentenylcyclohexane (I-3) and 11-undecenylcyclohexane (I-9) were synthesized similarly by the reaction of cyclohexylmagnesium bromide and 5-

bromopentene and 11-bromoundecene, respectively.

5-Pentenylcyclohexane (**I-3**): ^1H NMR (300 MHz, CDCl_3): δ 5.81 (m, 1H, H_h), 4.95 (m, 2H, H_i), 2.04 (m, 2H, H_g), 1.68 and 1.5-0.8 (m, 17H, H_a - H_f).

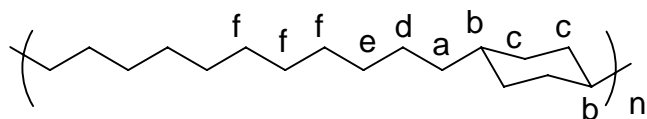
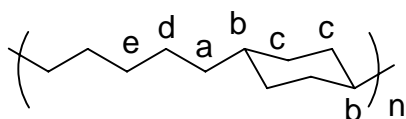
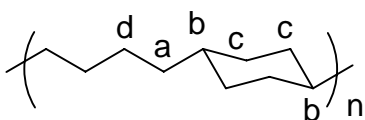
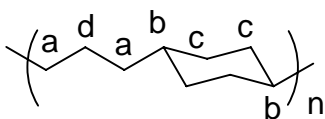
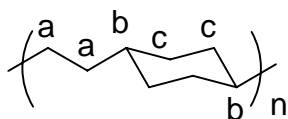
11-Undecenylcyclohexane (**I-9**): ^1H NMR (300 MHz, CDCl_3): δ 5.81 (m, 1H, H_o), 4.95 (m, 2H, H_n), 2.04 (m, 2H, H_m), 1.67 and 1.5-0.8 (m, 27H, H_a - H_l).



2) Polymerization of alkenylcyclohexanes

Typically, to a 25-mL Schlenk flask containing a CH_2Cl_2 solution (1.5 mL) of Pd complex **1** (0.010 mmol, 6.6 mg) was added NaBARF (0.012 mmol, 10.6 mg) under Ar. After stirring for several minutes, allylcyclohexane (**I-1**, 0.37 g, 3.0 mmol) was added and the reaction mixture was stirred at room temperature. The polymer precipitates in a few minutes. After 20-min reaction, the reaction mixture was poured into large amount of dichloromethane (ca. 50 mL). A solid formed was collected and dried in vacuo at 25 °C to give poly-**I-1**. (0.32 g, 86% yield, M_n = 18000, M_w/M_n = 2.48). ^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$): δ 1.71 (d, 4H, H_c), 1.28 (s, 2H, H_b), 1.15 (s, 6H, H_a and H_d), 0.88 (s, 4H, H_e). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$): δ 38.3 (C_b), 38.1 (C_a), 33.8 (C_c), 24.4 (C_d).

Other alkenylcyclohexanes are polymerized similarly.



Poly-I-0: $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$): δ 38.6 (C_b), 35.0 (C_a), 33.8 (C_c).

Poly-I-2: $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$): δ 38.3 (C_b), 37.7 (C_a), 33.8 (C_c), 27.5 (C_d).

Poly-I-3: ^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$): δ 1.71 (d, 4H, H_c), 1.27 and 1.16 (s, 12H, H_a , H_b , H_d , H_e), 0.88 (s, 4H, H_c). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$): δ 38.3 (C_b), 37.7 (C_a), 33.8 (C_c), 30.6 (C_e), 27.1 (C_d).

Poly-I-9: ^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$): δ 1.71 (d, 4H, H_c), 1.27 and 1.16 (s, 20H, H_b , H_d , H_e , H_f), 0.88 (s, 4H, H_c). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$): δ 38.3 (C_b), 37.7 (C_a), 33.9 (C_c), 30.2 (C_e), 29.8 (C_f), 27.0 (C_d).

For kinetic study, the above polymerization was conducted at 0 °C in the presence of naphthalene as inner standard. The portion of the reaction mixture was periodically taken out from the flask and subjected to ^1H NMR to determine conversion of **I-1**.

References.

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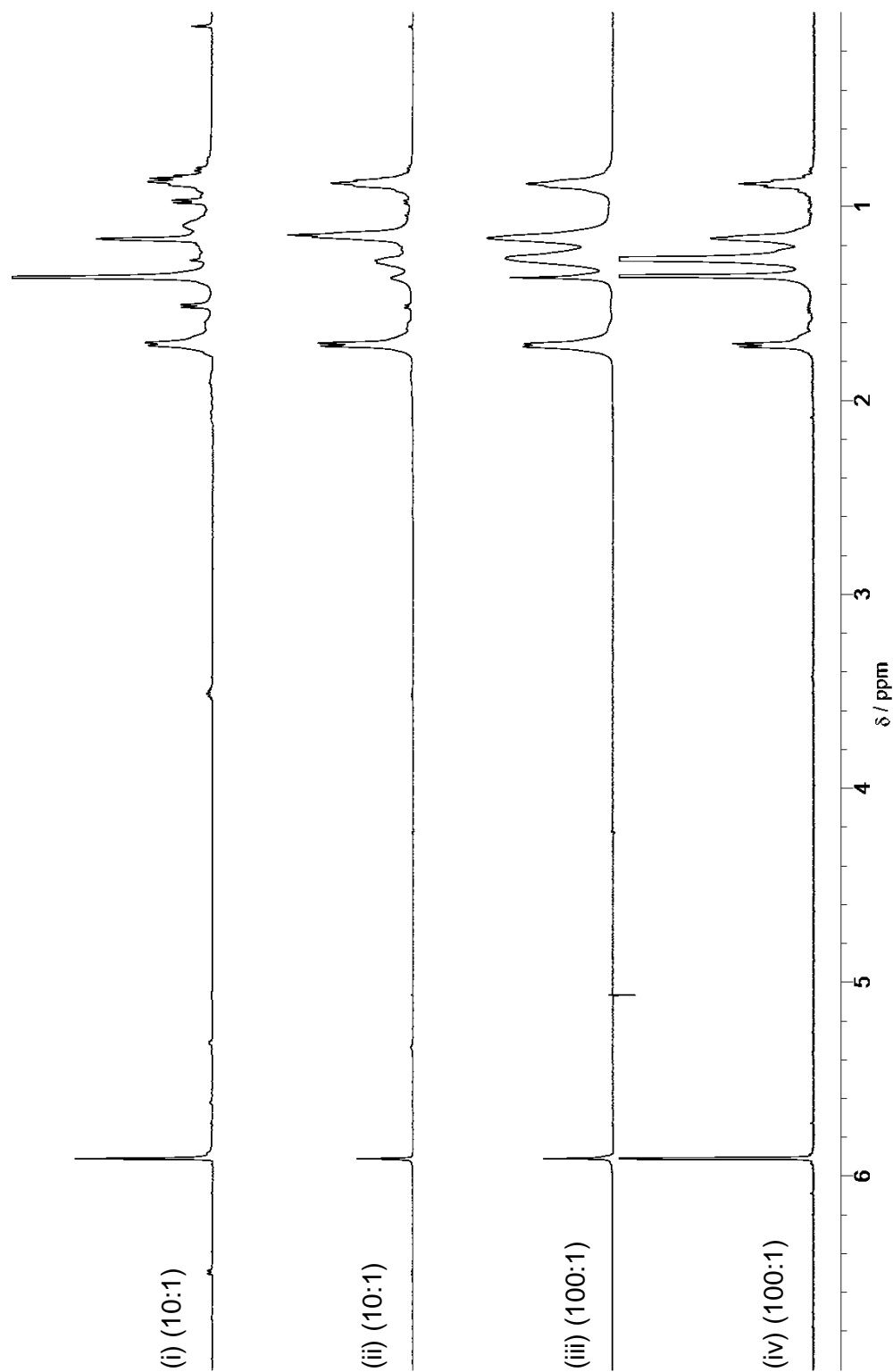


Figure S-1. ^1H NMR spectra ($\text{C}_2\text{D}_2\text{Cl}_4$ at $130\text{ }^\circ\text{C}$) of (i) poly-I-0, (ii) poly-I-1, (iii) poly-I-3, and (iv) poly-I-9. Ratios in parentheses corresponds to the initial monomer-to-Pd molar ratio of the polymerization reaction.

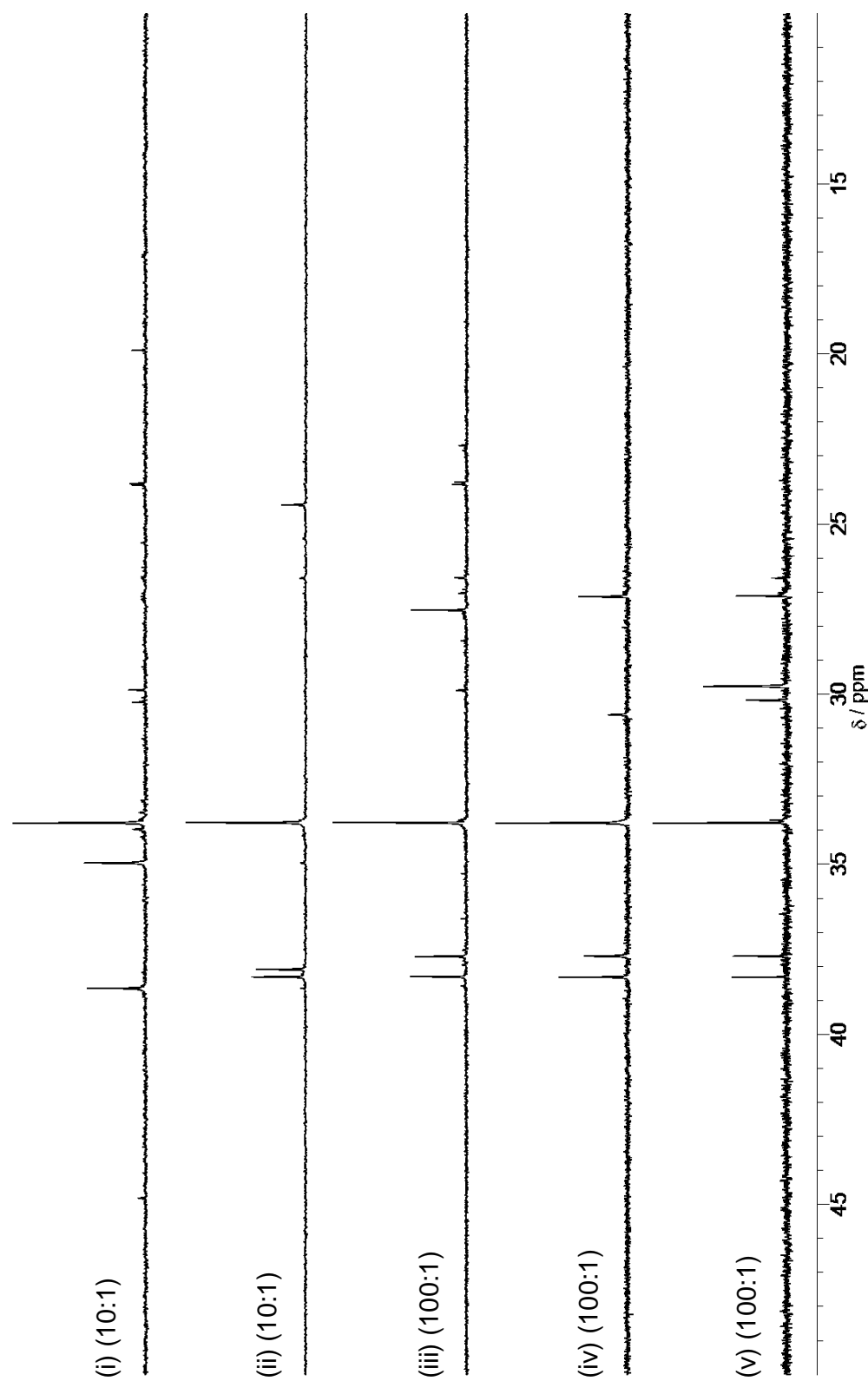


Figure S-2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra ($\text{C}_2\text{D}_2\text{Cl}_4$ at $130\text{ }^\circ\text{C}$) of (i) poly-I-0, (ii) poly-I-1, (iii) poly-I-2, (iv) poly-I-3, and (v) poly-I-9. Ratios in parentheses corresponds to the initial monomer-to-Pd molar ratio of the polymerization reaction.

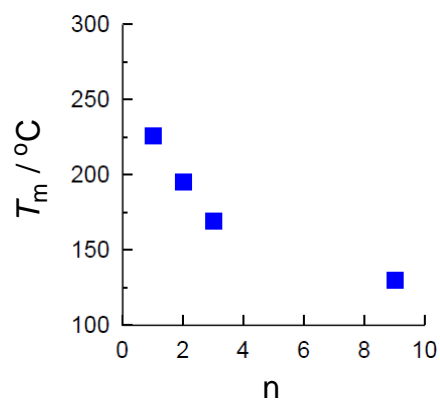


Figure S-3. Relationship between length of oligomethylene spacers (n) and melting point of poly-**I-n**.

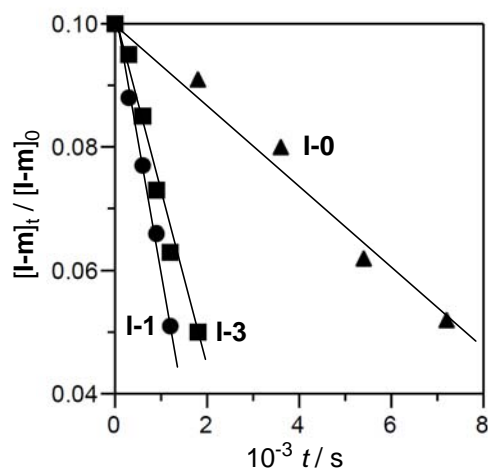


Figure S-4. Zeroth-order plots of the polymerization of **I-0** (triangle), **I-1** (circle), and **I-3** (square) by **1/NaBARF** at 0 °C ($[\mathbf{1}]_0 = 2.0 \text{ mM}$, $[\mathbf{I-m}]_0 = 0.20 \text{ M}$).