

Supporting Information

of

Alternating Copolymerization of Ethylene with 7- Methylenebicyclo[4.1.0]heptane Promoted by Cobalt Complex. Highly Regulated Structure and Thermal Rearrangement of the Obtained Copolymer.

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Experimental Procedures

General Method

Ethylene and ethylene-d₄ (C₂D₄), anhydrous toluene and deuterated 1,1,2,2-tetrachloroethane (C₂D₂Cl₄) were used as received. Cobalt complex was prepared according to the reported procedure.¹ Modified methylaluminoxane (MMAO) was purchased from TOSOH FINECHEM Co. Ltd. and used as received. 7-Methylenebicyclo[4.1.0]heptane² and 7,7-dimethylbicyclo[4.1.0]heptane³ were prepared according to the reported procedure.

NMR spectra (¹H, ²H and ¹³C) were recorded on a Varian Mercury 300 or JEOL JNM-500 spectrometer where the chemical shifts were determined with respect to C₂D₂Cl₄ (δ 5.91) for ¹H and ²H, and C₂D₂Cl₄ (δ 74.2) for ¹³C. Gel permeation chromatography (GPC) was performed at 40 °C on a TOSOH HLC-8020 high-speed liquid chromatograph system equipped with a differential refractometer detector and a variable-wavelength UV-vis detector, using tetrahydrofuran as eluent at a flow rate of 0.6 mL min⁻¹ with TSKgel SuperHM-L and SuperHM-M columns. The molecular weights were calibrated based on polystyrene standards. DSC and TG were recorded on Seiko DSC6200R and Seiko TG/DTA6200R.

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1. Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; McTavish, S. J.; Redshaw, C.; Solan, G. A.; Strömberg, S.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 8728.
 2. Arora, S.; Binger, P. *Synthesis*, **1974**, 801.
 3. Corey, E. J.; Posner, G. H. *J. Am. Chem. Soc.* **1968**, *90*, 5615.

Copolymerization of Ethylene with 7-Methylenebicyclo[4.1.0]heptane

Typically, a toluene solution (3.7 mL) of Co complex (0.0083 mmol, 5 mg) and 7-methylenebicyclo[4.1.0]heptane (**1**) (1.66 mmol, 0.18 g) in a 25-mL Schlenk flask, was subjected to a freeze-pump-thaw cycle, and back-filled with ethylene. Toluene solution of MMAO (1.3 mL, 2.5 mmolAl) was added by a syringe, and the mixture was stirred for 1 h under ethylene flow (1 mL/min) at -40 °C. The reaction mixture was quenched by adding EtOH (ca. 1 mL). The produced polymer was isolated by pouring the reaction mixture into a large amount of HCl/methanol. Thus formed white precipitate was collected by filtration and dried in vacuo at room temperature. Yield = 0.18 g. ^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$): δ 0.46 (2H, s, CH), 1.15 (8H, br, CH_2), 1.26 (4H, br, CH_2), and 1.74 (2H, s, CH (cyclohexane)). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{C}_2\text{D}_2\text{Cl}_4$): δ 19.2 (CH), 19.5 (CH_2 (cyclohexane)), 22.7 (CH_2 (cyclohexane)), 23.0 (CH_2), 25.2 (C), 26.4 (CH_2), and 40.2 (CH_2).

Copolymerization of C_2D_4 with 7-Methylenebicyclo[4.1.0]heptane

Typically, a toluene solution (3.7 mL) of Co complex (0.0083 mmol, 5 mg) and 7-methylenebicyclo[4.1.0]heptane (**1**) (1.66 mmol, 0.18 g) in a 25-mL Schlenk flask, was subjected to a freeze-pump-thaw cycle, and back-filled with C_2D_4 . Toluene solution of MMAO (1.3 mL, 2.5 mmolAl) was added by a syringe, and the mixture was stirred for 1 h under C_2D_4 atmosphere (1 atm) at -40 °C. The reaction mixture was quenched by adding EtOH (ca. 1 mL). The produced polymer was isolated by pouring the reaction mixture into a large amount of HCl/methanol. Thus formed white precipitate was collected by filtration and dried in vacuo at room temperature. Yield = 0.18 g. ^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$): δ 0.51 (2H, s, CH), 1.18 (6H, br, CH_2), 1.30 (2H, br, CH_2), and 1.79 (2H, s, CH (cyclohexane)). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{C}_2\text{D}_2\text{Cl}_4$): δ 19.1 (CH), 19.5 (CH_2 (cyclohexane)), 22.1 (CD_2), 22.7 (CH_2 (cyclohexane)), 25.0 (C), 26.1 (CH_2), and 39.1 (CD_2).

Homopolymerization of 7-methylenebicyclo[4.1.0]heptane at $-40\text{ }^{\circ}\text{C}$.

Typically, to a 25-mL Schlenk flask containing a toluene solution (3.7 mL) of Co complex (0.0083 mmol, 5 mg), 7-Methylenebicyclo[4.1.0]heptane (**1**) (1.66 mmol, 0.18 g), and a magnetic stirring bar under Ar, was added toluene solution of MMAO (1.3 mL, 2.5 mmolAl) by a syringe, and the mixture was stirred at $-40\text{ }^{\circ}\text{C}$ for 30 min. The reaction mixture was quenched by adding EtOH (ca. 1 mL). Pouring the reaction mixture into a large amount of HCl/methanol formed the polymer as a white precipitate, which was collected by filtration and dried in vacuo at room temperature. Yield = 0.028 g (16%)

Thermal Isomerization of **2**

A $\text{C}_2\text{D}_2\text{Cl}_4$ solution (0.5 mL) of **2** (0.05 g) was heated at $130\text{ }^{\circ}\text{C}$ for 12 h. The solution was subjected to NMR and GPC analyses directly. $M_n = 5800$, $M_w/M_n = 1.69$. ^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$): δ 1.9-2.2 (m, CH_2), 1.12 (br, CH), 1.9-2.2 (m, CH_2), 2.41 (m, CH (cis)), 2.75 (m, CH (trans)), and 5.09, 5.13 (s, CH=). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{C}_2\text{D}_2\text{Cl}_4$): δ 26.7 (CH_2 (cyclohexane)), 26.8 (CH_2 (cyclohexane)), 27.3 ($\text{CH}_2\text{CH=}$ (cis)), 27.3 ($\text{CH}_2\text{CH=}$ (trans)), 30.9 ($=\text{CCH}_2$ (cis)), 31.9 (CH_2 (cyclohexane)), 32.1 (CH_2 (cyclohexane)), 33.4 ($=\text{CCH}_2$ (trans)), 41.0 (CH (trans)), 45.4 (CH (cis)), 123.4 (CH=), and 144.8 ($=\text{C}$).

Preparation of 7,7-Dimethylbicyclo[4.1.0]heptane³

To a 25-mL Schlenk flask containing CuI (3.36 g, 17.5 mmol), Et_2O (70 mL), and a magnetic stirring bar, was added MeLi (35 mL, 1.0 M solution in ether) by a syringe under Ar at $-45\text{ }^{\circ}\text{C}$. The mixture was stirred for 10 min. An Et_2O solution (3.5 mL) of 7,7-dibromobicyclo[4.1.0]heptane (0.9 g, 3.5 mmol) was added to the mixture. After stirring for 1 h at $-45\text{ }^{\circ}\text{C}$ and for 18 h at $0\text{ }^{\circ}\text{C}$, MeI (3.5 mL, 56 mmol) was added to the mixture at $0\text{ }^{\circ}\text{C}$ and stirred for 16 h. The resulting mixture was poured into water (ca.

50 mL). Organic products were extracted with Et₂O, and the Et₂O layer was dried with MgSO₄. The volatile fraction was removed by evaporation to afford colorless oil (0.277 g). The ¹H NMR analysis indicated the formation of 7,7-dimethylbicyclo[4.1.0]heptane in ca. 80% purity. The compound was employed for thermal isomerization reaction without further purification. ¹H NMR (C₂D₂Cl₄): δ 0.45 (2H, d, *J* = 7.5 Hz, CH), 0.87 (3H, s, CH₃), 0.89 (3H, s, CH₃), 1.09 (4H, m, CH₂), 1.28 (2H, m, CH₂), and 1.74 (2H, m, CH₂). ¹³C{¹H} NMR (C₂D₂Cl₄): δ 15.7 (CH₃), 17.4 (C), 19.2 (CH), 19.5 (CH₂ (cyclohexane)), 21.5 (CH₂ (cyclohexane)), and 29.8 (CH₃).

Thermal Isomerization of 7,7-Dimethylbicyclo[4.1.0]heptane

C₂D₂Cl₄ solution (0.5 mL) of 7,7-dimethylbicyclo[4.1.0]heptane (0.05 g) was heated at 130 °C for 12 h. The solution was subjected to NMR analysis without isolation of the product. The main product was assigned by comparison of the NMR data with those of 1-isopropylcyclohexane reported by Apparau and Crandall (*J. Org. Chem.* **1984**, 49, 2125). ¹H NMR (C₂D₂Cl₄): δ 0.91 (6H, d, *J* = 7 Hz, CH₃), 1.47 (2H, m, CH₂), 1.54 (2H, m, CH₂), 1.86 (2H, s, CH₂), 1.92 (2H, s, CH₂), 2.07 (1H, m, *J* = 7 Hz, CH), and 5.31 (1H, s, =CH). ¹³C{¹H} NMR (C₂D₂Cl₄): δ 21.7 (CH₃), 23.2 (CH₂ (cyclohexane)), 23.5 (CH₂ (cyclohexane)), 25.6 (CH₂ (cyclohexane)), 26.3 (CH₂ (cyclohexane)), 35.5 (CH), 118.5 (=CH), and 143.8 (C=).

Preparation of 7,7-Dibutylbicyclo[4.1.0]heptane

To a 25-mL Schlenk flask containing CuI (3.36 g, 17.5 mmol), Et₂O (70 mL), and a magnetic stirring bar under Ar at –45 °C, was successively added n-BuLi (22 mL, 1.6 M solution in hexane) and Et₂O solution (3.5 mL) of 7,7-dibromobicyclo[4.1.0]heptane (0.9 g, 3.5 mmol) by a syringe. The mixture was stirred at –45 °C for 1 h and 0 °C for 18 h. n-BuI (6.4 mL, 56 mmol) was added to the mixture at 0 °C and stirred for 16 h. The mixture was poured into water, extracted with Et₂O, and dried with MgSO₄. The

volatile fraction was evaporated to afford colorless oil (0.7 g, ca. 70% purity by NMR). It was used for thermal isomerization reaction without further purification. ^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$): δ 0.45 (2H, s, CH), 0.81 (3H, s, CH_3), 0.85 (3H, s, CH_3), 1.1-1.4 (18H, m, CH_2), and 1.74 (2H, s, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{C}_2\text{D}_2\text{Cl}_4$): δ 14.7 (CH_3), 19.1 (CH), 19.5 (CH_2 (cyclohexane)), 22.7 (CH_2 (cyclohexane)), 23.8 (CH_3CH_2), 25.2 (C), 25.9 (CH_2C), 28.7 (CH_2), 28.8 (CH_2), and 39.3 (CH_2C).

Thermal Isomerization of 7,7-Dibutylbicyclo[4.1.0]heptane

$\text{C}_2\text{D}_2\text{Cl}_4$ solution (0.5 mL) of 7,7-dimethylbicyclo[4.1.0]heptane (0.1 g) was heated at 130 °C for 12 h. The solution was subjected to NMR analysis without isolation of the product. The main product was assigned to be (*E*)-5-cyclohexyl-4-nonene by comparison of the NMR results with the reported data of (*E*)- and (*Z*)-2-cyclohexyl-2-butene (Bangerter, F.; Karpf, M.; Meier, L. A.; Rys, P.; Skrabal, P. *J. Am. Chem. Soc.* **1998**, *120*, 10653 (Supporting Information)). ^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$): δ 0.81 (6H, t, $J = 7$ Hz, CH_3), 1.10 (2H, m, CH_2 (cyclohexane)), 1.20 (10H, m, CH_2), 1.50 (2H, m, CH_2 (cyclohexane)), 1.73 (4H, m, $=\text{C}-\text{CH}_2$), 1.92 (3H, m, CH, $\text{CH}_2-\text{CH}=\text{}$), and 5.28 (1H, s, $\text{CH}=\text{}$). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{C}_2\text{D}_2\text{Cl}_4$): δ 14.5 (CH_3), 23.2 (CH_3CH_2), 23.4 (CH_2), 23.5 (CH_2), 24.3 ($\text{CH}_2\text{CH}=\text{}$), 25.7 (CH_2 (cyclohexane)), 30.2 ($=\text{CCH}_2$), 33.6 (CH_2 (cyclohexane)), 47.9 (CH), 122.1 ($\text{CH}=\text{}$), and 140.0 ($=\text{C}$).

Table 1. Copolymerization of ethylene with 7-methylenebicyclo[4.1.0]heptane (**1**) by Co complexes

run	solvent / mL	temp. / °C	time / min	yield / g
1	5	-40	60	0.18
2	5	-40	120	0.17
3	5	-40	10	0.105
4	2.5	-40	60	0.16
5	5	0	60	0.068
6	5	0	120	0.051
7	5	r.t.	30	0.014
8	5	r.t.	60	0.033

Reaction conditions: Co complex = 5 mg (0.0083 mmol), **1** = 0.18 g (1.66 mmol), ethylene = 1 atm

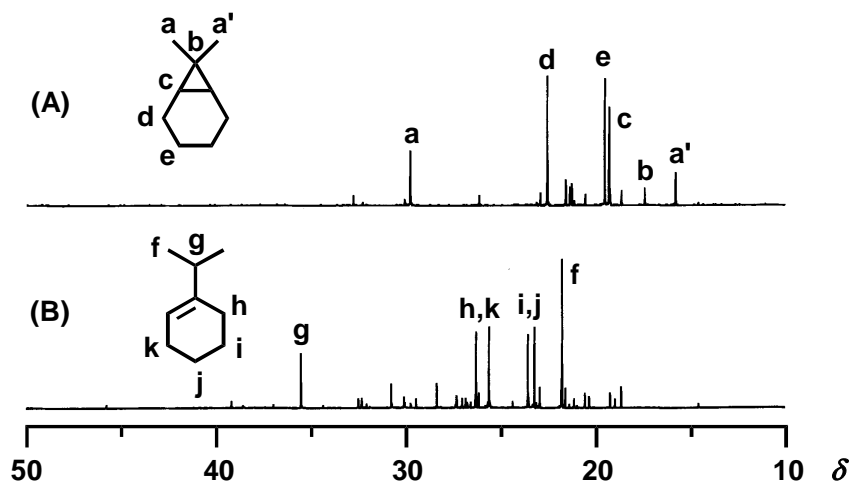


Figure 1. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of (A) 7,7-dimethylbicyclo[4.1.0]heptane and (B) the product after heating the solution at 130 °C for 12 h.

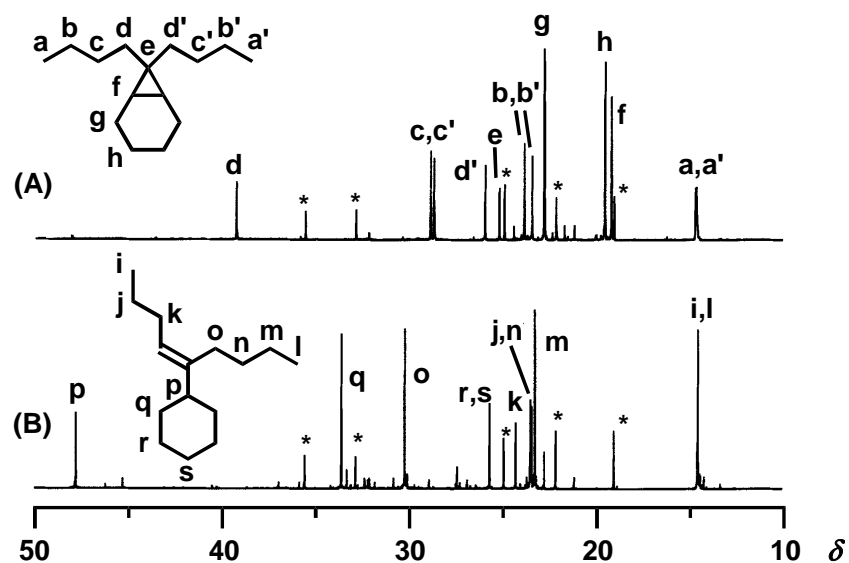


Figure 2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of (A) 7,7-dibutylbicyclo[4.1.0]heptane and (B) the product after heating the solution at 130 °C for 12 h. The peaks with asterisks are due to impurities.

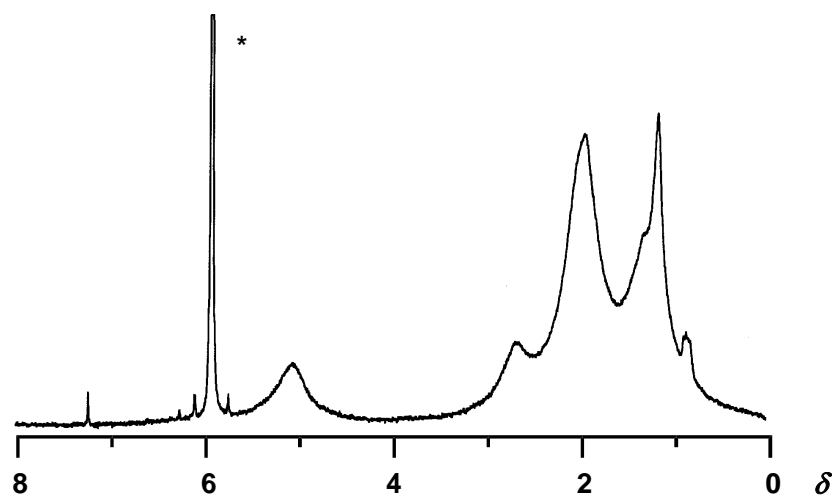


Figure 3. ^2H NMR spectrum of **3-d** in CHCl_3 at room temperature. The peak with asterisk is due to solvent ($\text{C}_2\text{D}_2\text{Cl}_4$).

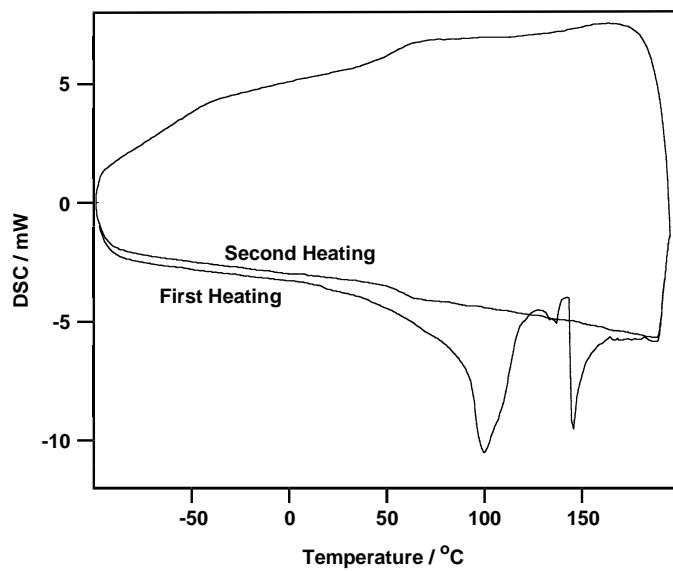


Figure 4. DSC chart of **2**.