Supplementary Information For:

Ethylene/Allyl Monomer Cooligomerization by Nickel/Phosphine–Sulfonate Catalysts

Shingo Ito, Yusuke Ota, Kyoko Nozaki*

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.

General. All manipulations were carried out in a glovebox or using standard Schlenk and autoclave techniques under argon purified by passing through a hot column packed with BASF catalyst R3-11. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or a stainless steel cannula. NMR spectra were recorded on JEOL JNM-ECP500 (¹H: 500 MHz, ¹³C: 126 MHz, ³¹P: 202 MHz) or JEOL JNM-ECS400 (¹H: 400 MHz, ¹³C: 101 MHz) NMR spectrometers. Chemical shift values are expressed in parts per million (ppm) downfield form tetramethylsilane and are referenced to the resonance of residual solvent (δ 5.32 (CD₂Cl₂), and 5.91 (Cl₂CDCDCl₂) for ¹H NMR spectra and δ 77.2 (CDCl₃), 53.8 (CD₂Cl₂), and 74.6 (Cl₂CHCHCl₂) for ¹³C NMR spectra). Quantitative ¹³C NMR analyses of polymers were performed in a 5-mm probe on *ca*. 15 weight% solutions of the polymers and 0.05-M $Cr(acac)_3$ as a relaxation agent in 1,1,2,2-tetrachloroethane unlocked at 120 °C using a 90° pulse of 9.0 µs, a spectral width of 31 kHz, a relaxation time of 5–10 s, an acquisition time = 2 s, and inverse-gated decoupling^{1,2} with the number of FID's collected per sample of 5000-10000. Size exclusion chromatography (SEC) analyses were carried out with a Tosoh HLC-8121GPC/HT equipped with two SEC columns (Tosoh TSKgel GMH_{HR}-H(S)HT) by eluting the columns with 1,2-dichlorobenzene at 1 mL/min at 145 °C. Molecular weights were determined using narrow polystyrene standards and were corrected for polyethylene by universal calibration using the Mark–Houwink parameters of Rudin: $K = 1.75 \times 10^{-2} \text{ cm}^3/\text{g}$ and $\alpha = 0.67$ for polystyrene and K = 5.90×10^{-2} cm³/g and $\alpha = 0.69$ for LLDPE.³ X-ray crystallographic analyses were performed on a Rigaku Saturn724 CCD diffractometer.

Materials. Anhydrous toluene and CH_2Cl_2 was purchased from Kanto Chemical Co. Inc. and purified by the method of Pangborn *et al.*⁴ Ethylene (>99.9%) was purchased from Takachiho Chemical Industrial Co., Ltd., dried, and deoxygenated by passing through columns. The following reagents were prepared according to literature procedures: **1a**, ⁵ **1b**, ⁶ **1c**, ⁷ and NiMe₂(pyridine)₂, ⁸ NiMe₂(tmeda), ⁹ *N-tert*-butoxycarbonyl)allylamine.¹⁰

Electronic Supplementary Material (ESI) for Dalton Transactions This journal is © The Royal Society of Chemistry 2012

Preparation of 2a:



To a mixture of **1a** (270 mg, 0.79 mmol), Ni(cod)₂ (207 mg, 0.75 mmol), and 2,6-lutidine (0.45 mL) was added THF (30 mL), and the suspension was stirred at room temperature for 4 h. During that time, the suspension turned to dark orange solution. After adding allyl chloride (0.5 mL), the volatile matters were evaporated. The residual solid was dissolved in toluene (30 mL). To the mixture was added Me₃Al (1.0 M solution in hexane, 1.0 mL, 1.0 mmol), and the mixture was stirred for 10 min. The yellow solution was filtrated and pumped off. The residue solid was dissolved in THF then cooled to -30 °C. The formed yellow precipitates were collected and dried under reduced pressure to give 2a (210 mg, 0.39 mmol, 52%). ¹H NMR (500 MHz, CD₂Cl₂): δ –0.99 (d, J_{PH} = 6.0 Hz, 3H, H(1)), 1.19–1.53 (m, 8H, H(9), H(10), H(11)), 1.67–1.98 (m, 10H, H(9), H(10), H(11)), 2.08–2.20 (m, 2H, H(8)), 2.40–2.50 (m, 2H, 2H of H(9)), 3.78 (s, 6H, H(15)), 7.11 (d, J = 7.8 Hz, 2H, H(13)), 7.46 (t, J = 7.7 Hz, H(5) or H(6)), 7.50 (t, J = 7.7 Hz, H(5) or H(6)), 7.57 (t, J = 7.7 Hz, H(14)), 7.60 (t, J = 7.1 Hz, H(4)), 7.94–8.03 (m, 1H, H(7)); ¹³C NMR (101 MHz, CD₂Cl₂): δ –21.0 (d, J = 36 Hz, C(1)), 26.2 (2C, C(15)), 26.7 (C(11)), 27.5 (d, J = 10 Hz, C(10)), 27.8 (d, J = 12 Hz, C(10)), 28.9 (C(9)), 30.2 (C(9)), 35.1 (d, *J* = 25 Hz, 2C, C(8)), 122.9 (2C, C(13)), 124.5 (*J* = 25 Hz, C(3)), 127.7 (d, J = 6 Hz, C(7)), 129.5 (d, J = 4 Hz, C(5) or C(6)), 130.7 (C(5) or C(6)), 132.4(C(4)), 137.8 (C(14)), 150.4 (J = 10 Hz, C(2)), 159.1 (2C, C(12)); ³¹P NMR $(202 \text{ MHz}, CD_2Cl_2)$: δ 14.8; ESI-MS (m/z): 540.11 ([M+Li]⁺). HRMS-FAB (m/z): [M]+ calcd for C₂₆H₃₈NNiO₃PS, 533.1663; found, 533.1671. Anal. calcd for C₂₆H₃₈NNiO₃PS C, 58.44; H, 7.17; N, 2.62, found C, 57.95; H, 7.15; N, 2.59.

Preparation of 2b:



To a mixture of **1b** (80.3 mg, 0.02 mmol) and NiMe₂(pyridine)₂ (49.4 mg, 0.02 mmol) were added at -30 °C cold 2,6-lutidine (0.5 mL) and cold THF (2.0 mL). The solution was stirred for 10 min at

room temperature and then cooled to -30 °C. The formed yellow precipitates were collected, washed with diethyl ether, and dried under reduced pressure to give **2b** (78 mg, 0.134 mmol, 67%). ¹H NMR (500 MHz, CD₂Cl₂): δ –1.24 (d, J = 7.8 Hz, 3H, H(1)), 3.70 (s, 6H, H(14) or H(18)), 3.73 (s, 6H, H(14) or H(18)), 6.96–7.04 (m, 2H, H(10)), 7.06 (t, J = 7.6 Hz, 2H, H(12)), 7.11 (d, J = 7.8 Hz, 2H, H(16)), 7.22–7.32 (m, 2H, H(5) and H(6)), 7.38–7.48 (m, 1H, H(4)), 7.50–7.61 (m, 3H, H(11) and H(17)), 7.80–7.94 (m, 3H, H(7) and H(13)); ¹³C NMR (101 MHz, CD₂Cl₂): δ –16.2 (d, J = 35 Hz, C(1)), 25.3 (2C, C(18)), 54.6 (2C, C(14)), 110.7 (d, J = 5 Hz, 2C, C(10)), 116.0 (d, J = 52 Hz, 2C, C(8)), 120.7 (d, J = 11 Hz, 2C, C(12)), 122.0 (d, J = 3 Hz, 2C, C(16)), 126.3 (d, J = 8 Hz, C(7)), 126.7 (d, J = 40 Hz, C(3)), 128.1 (d, J = 6 Hz, C(6)), 129.5 (d, J = 2 Hz, C(4)), 132.6 (d, J = 2 Hz, 2C, C(15)), 160.1 (d, J = 2 Hz, 2C, C(9)); ³¹P NMR (162 MHz, CD₂Cl₂): δ 12.4.

Preparation of 2c:



To a mixture of 1c (122.6 mg, 0.2 mmol) and NiMe₂(tmeda) (41.8 mg, 0.2 mmol) were added at -30 °C cold lutidine (0.5 mL) and cold THF (2.0 mL). The solution was stirred at room temperature for 10 min. The solution was concentrated and reprecipitated by hexane. The formed yellow precipitates were collected, washed with diethyl ether, and dried under reduced pressure to give 2c (123 mg, 0.155 mmol, 77%). ¹H NMR (500 MHz, CD₂Cl₂): δ –1.20 (3H, d, J_{P-H} = 6.2 Hz, H(1)), 2.57 (3H, s, H(18) or H(22)), 3.01 (3H, s, H(18) or H(22)), 3.11 (3H, s, H(18) or H(22)), 3.52 (3H, s, H(18) or H(22)), 3.57 (3H, s, H(18) or H(22)), 3.62 (3H, s, H(18) or H(22)), 5.77 (1H, d, J = 8.0 Hz), 6.30 (1H, d, J = 7.3 Hz), 6.63 (2H, dd, J = 18.4, 8.4 Hz), 6.75 (1H, t, J = 8.0 Hz), 6.92–7.51 (m), 7.92 (1H, m, H(7)); ¹³C NMR (126 MHz, CDCl₃): δ –15.3 (d, J = 32 Hz, C(1)), 23.8 (C(22)), 25.5 (C(22')), 53.7 (C(18)), 53.8 (C(18')), 54.5 (C(18")), 54.6 (C(18"')), 101.5 (C(16)), 102.1 (C(16')), 103.5 (C(16")), 103.7 (C(16")), 116.2, 116.8, 119.5, 120.6, 121.2, 123.7 (d, *J* = 36 Hz), 125.2, 125.3, 125.4 (d, J = 12 Hz), 126.4 (d, J = 4 Hz), 126.6 (d, J = 7 Hz), 127.9, 128.1, 129.2, 129.3, 129.5, 130.8, 133.2 (d, J = 7 Hz), 133.5, 134.0, 136.2, 137.4, 137.8, 140.5 (d, J = 16 Hz), [signals from 116.2 to 140.5 were not fully characterized], 147.1 (d, J = 14 Hz, C(2)), 155.0, 156.4, 156.7, 157.6, 157.8, 159.2 (C(15) and (C(19)); ³¹P NMR (202 MHz, CD₂Cl₂): δ 16.2. HRMS-FAB (*m/z*): [M]⁺ calcd for C₄₂H₄₂NNiO₇PS, 793.1773; found, 793.1790.

A Procedure for Ethylene Homopolymerization by 2a. To a 50-mL autoclave containing catalyst 2a (10.5 mg, 0.02 mmol) was transferred CH_2Cl_2 (15.0 mL) under argon atmosphere. After being charged with ethylene (3.0 MPa), the autoclave was stirred at 30 °C for 3 h. After cooling to room temperature, methanol (30 mL) was added into the autoclave. The polymer was isolated by filtration, washed with methanol, and dried under vacuum at 60 °C. The polymer was analyzed by SEC analysis for its molecular weight and by ¹H and ¹³C NMR analysis for its structures.

A General Procedure for the Copolymerization of Ethylene and Allyl Monomers 3. To a 50-mL autoclave containing catalyst 2a (10.5 mg, 0.02 mmol) were transferred CH_2Cl_2 (12.0 mL) and allyl monomer 3 (3.0 mL) under argon atmosphere. After being charged with ethylene (3.0 MPa), the autoclave was stirred at 30 °C for 3 h. After cooling to room temperature, methanol (30 mL) was added into the autoclave. The polymer was isolated by filtration, washed with methanol, and dried under vacuum at 60 °C. The polymer was analyzed by SEC analysis for its molecular weight and by ¹H and ¹³C NMR analysis for its structures.

Reference

- (1) (a) Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. Science 1999, 283, 2059–2062. (b)
- Cotts, P. M.; Guan, Z.; McCord. E.; McLain, S. Macromolecules 2000, 33, 6945-6952.
- (2) Randall, J. C.; Ruff, C. J.; Kelchtermans, M.; Gregory, B. H. *Macromolecules* **1992**, *25*, 2624–2633.
- (3) V. Grinshpun, A. Rudin, Makrom. Chem., Rapid Commun., 1985, 6, 219–223.
- (4) A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics*, 1996, **15**, 1518–1520.
- (5) S. Ito, K. Munakata, A. Nakamura, K. Nozaki, J. Am. Chem. Soc., 2009, 131, 14606–14607.
- (6) T. Kochi, S. Noda, K. Yoshimura, K. Nozaki, J. Am. Chem. Soc., 2007, 129, 8948-8949.
- (7) (a) K. M. Skupov, P. R. Marella, M. Simard, G. P. A. Yap, N. Allen, D. Conner, B. L. Goodall, J.
 P. Claverie, *Macromol. Rapid Commun.*, 2007, 28, 2033–2038. (b) N. T. Allen, T. C. Kirk, B. L.
 Goodall, EP 176254572A2 (2007); *Chem. Abstr.* 2007, 249480.
- (8) J. Cámpora, M. del Mar Conejo, K. Mereiter, P. Palma, C. Pérez, M. L. Reyes, C. Ruiz, C. J. Organomet. Chem., 2003, 683, 220–239.
- (9) W. Kaschube, K. R. Pörschke, W. Günther, J. Organomet. Chem., 1988, 355, 525–532.
- (10) A. M. Kawamoto, M. Wills, J. Chem. Soc., Perkin Trans. 1, 2001, 1916–1928.





Figure S1. ¹H NMR spectrum of **2a** (500 MHz, CD_2Cl_2).



Figure S2. ¹³C NMR spectrum of 2a (101 MHz, CD₂Cl₂).

NMR Spectra of Ni complex 2b:



Figure S3. ¹H NMR spectrum of 2b (500 MHz, CD₂Cl₂).



Figure S4. ¹³C NMR spectrum of 2b (101 MHz, CD₂Cl₂).

NMR Spectra of Ni complex 2c:



Figure S5. ¹H NMR spectrum of 2c (500 MHz, CD₂Cl₂).



Figure S6. ¹³C NMR spectrum of 2c (126 MHz, CDCl₃).

Polyethylene Obtained in Entry 1 in Table 1:



Figure S7. SEC trace of polyethylene obtained in entry 1 in Table 1. M_n (PS) = 1,270 was corrected to M_n (PE) = 570 by universal calibration.



Figure S8. ¹H NMR spectrum of polyethylene obtained in entry 1 in Table 1 (400 MHz, Cl₂CDCDCl₂, 120 °C).



Figure S9. ¹³C NMR spectrum of polyethylene obtained in entry 1 in Table 1 under quantitative conditions (101 MHz, Cl₂CHCHCl₂, 120 °C).

Ethylene/Allyl Acetate (3a) Cooligomer Obtained in Entry 3 in Table 1:



GPC-8020 REPORT

Page 1 / 1

Figure S10. SEC trace of ethylene/**3a** cooligomer obtained in entry 3 in Table 1. M_n (PS) = 1,970 was corrected to M_n (PE) = 880 by universal calibration.



Figure S11. ¹H NMR spectrum of ethylene/**3a** cooligomer obtained in entry 3 in Table 1 (400 MHz, Cl₂CDCDCl₂, 120 °C).



Figure S12. ¹³C NMR spectrum of ethylene/**3a** cooligomer obtained in entry 3 in Table 1 under quantitative conditions (101 MHz, Cl₂CHCHCl₂, 120 °C).

Ethylene/Allyl Acetate (3a) Cooligomer Obtained in Entry 4 in Table 1:



GPC-8020 REPORT

Page 1 / 1

Figure S13. SEC trace of ethylene/**3a** cooligomer obtained in entry 4 in Table 1. M_n (PS) = 2,250 was corrected to M_n (PE) = 1,000 by universal calibration.



Figure S14. ¹H NMR spectrum of ethylene/**3a** cooligomer obtained in entry 4 in Table 1 (400 MHz, Cl₂CDCDCl₂, 120 °C).

Ethylene/Allyl Trimethylsilyl Ether (3b) Cooligomer Obtained in Entry 8 in Table 1:



Figure S15. SEC trace of ethylene/**3b** cooligomer obtained in entry 8 in Table 1. M_n (PS) = 1,880 was corrected to M_n (PE) = 830 by universal calibration.



Figure S16. ¹H NMR spectrum of ethylene/**3b** cooligomer obtained in entry 8 in Table 1 (400 MHz, Cl₂CDCDCl₂, 120 °C).

Ethylene/Allyltrimethlsilane (3e) Cooligomer Obtained in Entry 11 in Table 1:



Figure S17. SEC trace of ethylene/**3e** cooligomer obtained in entry 11 in Table 1. M_n (PS) = 1,710 was corrected to M_n (PE) = 760 by universal calibration.



Figure S18. ¹H NMR spectrum of ethylene/**3e** cooligomer obtained in entry 11 in Table 1 (400 MHz, Cl₂CDCDCl₂, 120 °C).



Figure S19. ¹³C NMR spectrum of ethylene/**3e** cooligomer obtained in entry 11 in Table 1 under quantitative conditions (101 MHz, Cl₂CHCHCl₂, 120 °C).