Supporting Information

Random Copolymerization of Ethylene with 5-Norbornen-2-yl Acetate Using Palladium Anilinonaphthoquinone Catalysts

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Table of Contents

Table of Contents	2	
1. Experimental section	3	
1.1 General Procedures.	3	
1.2 General Polymerization Procedure.	3	
1.3 Standard Procedure for the Synthesis of Complexes.	3	
2. Chracterization of Compounds	4	
3. X-Ray Crystallography		
4. Characterization of Polymers	9	

1. Experimental section

1.1 General Procedures.

All operations were carried out using standard Schlenk techniques or glovebox under a nitrogen atmosphere. All solvents were purified by passage through the PS-MD-5 (Innovative Technology) solvent purification system. Research grade ethylene was purified by dehydration column of ZHD–20 and deoxidation column of ZHD–20A. Comonomers were distilled over calcium hydride. MMAO was donated by Tosoh-Finechem Co. All the other reagents were purchased and used as received. Ligands were synthesized according to the literature.⁵¹

The single crystals were mounted on a glass fiber and at low temperature, and the data collection was made on a Bruker APEX2 diffractometer with graphite monochromated with Mo K α radiation ($\lambda = 0.710$ 73 Å). Elemental analyses were performed with the Vario ELIII elemental analyzers manufactured by Elementar Analysensysteme GmbH. NMR spectra of complexes and E–NB_{AC} copolymers were carried out on Bruker-600 spectrometer at ambient temperature in chloroform-d (δ : 7.26 for ¹H NMR; 77.16 for ¹³C NMR). NMR analyses of other polymers were performed in 1,1,2,2-tetrachloroethane-d₂ (δ : 5.91 for ¹H NMR; 74.47 for ¹³C NMR) at 110 °C. GPC analyses of the molecular weights and molecular weight distributions were determined by a polymer laboratory PL GPC-220 using 1,2,4-trichlorobenzene as eluent at 150 °C and calibrated by polystyrene standards. DSC analyses were performed on a TA differential scanning calorimeter Q2000, and the DSC curves of the samples were recorded under a nitrogen atmosphere at a heating rate of 10 °C/min. WCA on the polymer films were determined by the Automatic video micro contact angle meter(*/OCA40Micro) at room temperature. At least three measurements made at different positions of the film. Stress/strain experiments was performed on an electronic universal material testing machine (Instron 5969) at 20 °C. At least three samples of each polymer were tested.

1.2 General Polymerization Procedure.

The polymerization under atmospheric pressure was performed in a 100 mL glass reactor equipped with a magnetic stirrer. High pressure polymerization was performed in a 200 mL Quick-open Micro Autoclaves/Pressure Vessels purchased from Anhui Kemi Machinery Technology Co., Ltd. The reactor was cleaned and evacuated at 110 °C for at least an hour before polymerization. Then a certain amount of toluene, comonomer, and MMAO were charged into the reactor. Stirring the mixture until the temperature was established, the catalyst solution of toluene was added, and the ethylene was purged into the reactor. The polymerization was conducted for a certain time and terminated with acidic alcohol. The polymers obtained were washed with alcohol to remove MMAO and ligand residue and then dried under vacuum at 80 °C for 6 h until a constant weight was reached.

1.3 Standard Procedure for the Synthesis of Complexes.

Synthesis of Palladium Complex 1. Ligand L1 (0.5953 g, 1.0 mmol), KH(0.044g, 1.1 mmol) and THF (50 mL) were mixed in a 250 mL flask and stirred for 4 h at room temperature to afford potassium salt of L1. The THF solution of potassium salt of L1 was then added slowly into the THF solution of (COD)PdMeCl(0.265g, 1.0 mmol). After stirred for 3 h, the pyridine (0.2415 mL, 3.0 mmol) was added in to the solution and stirred for 12 h at room temperature. The reaction solution was evaporated to dryness under vacuum and washed three times by n-hexane. The obtained solid was purified by recrystallization with a mixture of CH₂Cl₂/n-hexane to afford dark blue X-ray quality single crystals at 53% yield (0.4137 g, 0.53 mmol). ¹H NMR(CDCl₃): δ (ppm) = 8.60-8.55 (m, 2H), 7.90-7.92 (m, 2H), 7.67-7.69 (m, 1H), 7.46-7.43 (m, 3H), 6.93-7.25 (m, 21H), 6.67 (s, 2H), 5.86 (s, 2H), 4.81 (s, 1H), 2.15 (s, 3H), 0.06(s, 3H). Anal. Calcd for C₄₉H₄₀N₂PdO₂: C, 74.00; H, 5.07; N, 3.52. Found: C, 73.71; H, 5.04; N, 3.31.

Synthesis of Palladium Complex 2. Complex 2 was synthesized in a similar way to that for complex 1 at 48% yield. ¹H NMR(CDCl₃): δ (ppm) = 8.81-8.80 (m, 2H), 8.09-8.08 (d, 1H), 8.04-8.03 (d, 1H), 7.94-7.91 (t, 1H), 7.75-7.73 (t, 1H), 7.51-7.47 (m, 3H), 7.20-7.15 (m, 3H), 5.21 (s, 1H), 3.35-3.30 (m, 2H), 1.27-1.26 (d, 6H), 1.15-1.14 (d, 6H), 0.54 (s, 3H). Anal. Calcd for C₂₈H₃₀N₂PdO₂: C, 63.10; H, 5.67; N, 5.26. Found: C, 62.72; H, 5.60; N, 5.03.

Synthesis of palladium complex 3. Complex 3 was synthesized in a similar way to that for complex 1 at 68% yield. ¹H NMR (DMSO): δ (ppm) = 8.58-8.57 (m, 2H), 8.10-8.09 (d, 1H), 7.90-7.88 (t, 1H), 7.85-7.84(d, 1H), 7.80-7.78 (m, 1H), 7.71-7.69 (t, 1H), 7.40-7.38 (m, 2H), 7.20-7.17 (t, 1H), 6.75-6.73 (2, 2H), 4.83 (s, 1H), 3.73 (s, 6H), 0.50 (s, 3H). Anal. Calcd for C₂₄H₂₂N₂PdO₄: C, 56.65; H, 4.36; N, 5.51. Found: C, 55.08; H, 4.48; N, 5.54.

2. Chracterization of Compounds











Figure S8. ¹H NMR spectrum of Complex 1 in the presence of MMAO

3. X-Ray crystallography

1 dole D1	. Crystal data and sil detaie i	ennement for complexes 1	
	1	2	3
Empirical formula	$C_{49}H_{40}N_2O_2Pd$	$C_{28}H_{30}N_2O_2Pd$	$C_{24}H_{22}N_2O_4Pd$
Formula weight	795.23	532.94	508.83
Temperature	300.11K	303.02K	130K
Wavelength	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	triclinic
Space group	P-1	C2/c	P-1
Unit cell dimensions	a = 10.4912(4)Å	a = 15.0290(8) Å	a = 8.3132(7) Å
	b= 13.4734(6)Å	b=21.2571(8) Å	b= 10.8410(9) Å
	c = 14.7253(6) Å	c = 15.4985(7) Å	c = 12.8010(11)Å
	$\alpha = 94.369(2)^{\circ}$	$\alpha = 90^{\circ}$	$\alpha = 110.224(2)^{\circ}$
	$\beta = 109.580(2)^{\circ}$	$\beta = 94.786(2)^{\circ}$	$\beta = 92.769(2)^{\circ}$
	$\gamma = 90.382(2)^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 105.358(2)^{\circ}$
Volume	1954.24(14) Å	4934.1(4) Å	1031.34(15) Å
Z	2	8	2
Density (calculated)	1.351 g/cm ³	1.435 g/cm ³	1.639 g/cm ³
Absorption coefficient	0.517 mm ⁻¹	0.779 mm ⁻¹	0.934 mm ⁻¹
F(000)	820.0	2192.0	516.0
Crystal size	$0.22 \times 0.2 \times 0.15 \text{ mm}^3$	$0.12 \times 0.1 \times 0.08 \text{ mm}^3$	$0.3 \times 0.05 \times 0.01 \text{ mm}^3$
Theta range for data collection	5.228 to 50.998°	5.44 to 60.104°	3.432 to 61.1°
Index ranges	$-12 \leq h \leq 12$	$-11 \le h \le 21$	$-11 \leq h \leq 11$
	$-16 \leq k \leq 16$	$-29 \le k \le 28$	$-14 \leq k \leq 15$
	$-17 \leq l \leq 17$	$-21 \le l \le 21$	$-18 \leq l \leq 18$
Reflections collected	22183	15181	10506
Independent reflections	7103[Rint=0.0429]	7093 [R _{int} = 0.0386]	6259 [Rint = 0.0277]
Completeness to theta = 26.000°	98.2%	97.6%	99%
Absorption correction	Semi-empirical from	Semi-empirical from	Semi-empirical from
	equivalents	equivalents	equivalents
Max. and min. transmission	0.613 and 0.746	0.630 and 0.746	0.625 and 0.746
Refinement method	Full-matrix least-squares on	Full-matrix least-squares on	Full-matrix least-squares on
	F2	F2	F2
Data / restraints / parameters	7103/38/489	7093/0/303	6259/0/283
Goodness-of-fit on F ²	1.142	1.053	1.034
Final R indices [I>2sigma(I)]	R1=0.0563,wR2=0.1181	$R_1 = 0.0470, wR_2 = 0.0872$	R1=0.0352,wR2=0.0746
R indices (all data)	R1=0.0657,wR2=0.1233	$R_1 = 0.0930, wR_2 = 0.1075$	R1=0.0442,wR2=0.0787
Extinction coefficient	n/a	n/a	n/a
Largest diff. peak and hole	1.50and-0.57 e.Å ⁻³	0.55and-0.56 e.Å ⁻³	0.64 and -0.73 e.Å ⁻³

Table S1. Crystal data and structure refinement for complexes 1,2 and 3



6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 f1 (ppm) Figure S10. ¹H NMR spectrum of PE obtained by 1 (table 1, entry 3). (C₂D₂Cl₄ at 110 °C) $BD=1000 \times (2 \times 0.57)/(3 \times (31.36+0.57))=11.9/1000C$

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<u>ب</u>

0.57



 $BD=1000 \times (2 \times 0.54)/(3 \times (32.68+0.54))=10.8/1000C$





Figure S15. ¹H NMR spectrum of E-NB_{AC} copolymer obtained by2 (table 3, entry 8). (CDCl₃ at room temperature)



temperature)



Figure S17. ¹³C NMR spectrum of E-NB copolymer obtained by **1** (table 3, entry 9). ($C_2D_2Cl_4$ at 110 °C)



Fugure S18. DSC of PE obtained by 1 (table1, entry 2)



Fugure S19. DSC of E-NB_{AC} copolymer obtained by 1 (table3, entry 1)



Fugure S20. DSC of E-NB_{AC} copolymer obtained by **1** (table3, entry 2)



Fugure S21. DSC of E-NB_{AC} copolymer obtained by 1 (table3, entry 3)



Fugure S22. DSC of E-NB_{AC} copolymer obtained by **1** (table3, entry 4)



Fugure S23. DSC of E-NB_{AC} copolymer obtained by 1 (table3, entry 5)



Fugure S24. DSC of E-NB_{AC} copolymer obtained by MMAO (table3, entry 6)



Fugure S25. DSC of E-NB_{AC} copolymer obtained by 1 (table3, entry 7)



Fugure S26. DSC of E-NB_{AC} copolymer obtained by **2** (table3, entry 8)



Fugure S27. DSC of E-NB copolymer obtained by 1 (table3, entry 9)



Fugure S28. DSC of E-NB copolymer obtained by 1 (table3, entry 10)



Fugure S29. DSC of E-NB copolymer obtained by 1 (table3, entry 11)



Fugure S30. DSC of E-NB copolymer obtained by 2 (table3, entry 12)