



Highly thermo-stable and electronically controlled palladium precatalysts for vinyl homo/co-polymerization of norbornene-ethylene

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ABSTRACT

In this contribution, the influence of substitutions ranging from electron donating to the electron withdrawing, on the bis(arylimino)acenaphthenes-palladium catalysts is investigated. A series of symmetrical bis(arylimino)acenaphthene-palladium complexes, [1,2-bis[2,6-(CHPh₂)₂-4-R-C₆H₂N]C₂C₁₀H₆]PdMeCl (R = Me **L1**, Et **L2**, ^tPr **L3**, ^tBu **L4**, Cl **L5**, F **L6**) has been prepared and investigated toward the polymerization of norbornene as well as its copolymerization with ethylene comonomer. These palladium complexes displayed moderate to high activities for norbornene polymerization in the presence of MAO and (C₆F₅)₄B-C₆H₅NH(CH₃)₂ co-catalysts. Specifically, complex **Pd4** (R = ^tBu) displayed a highest activity up to 6.1×10^6 g_{PNBE} mol_{Pd}⁻¹ h⁻¹ with 54.2% conversion of monomer at 60 °C and showed exceptionally high thermal stability (act: 4.81×10^5 g_{PNBE} mol_{Pd}⁻¹ h⁻¹ with 51.2% conversion at 100 °C), and generating insoluble polynorbornene. Toward the copolymerization of norbornene-ethylene, **Pd4** exhibited good activities with high incorporation of ethylene (up to 49.1%) and the resultant copolymer showed high molecular weights as high as 100.3 kg/mol⁻¹ with narrow molecular weights distributions (PDI = 2.15).

1. Introduction

Copolymer of norbornene-ethylene (NBE-E) is an important class of cyclic polyolefins owing to their superior properties, particularly high chemical resistance, high biocompatibility and processability [1–3]. Their high refractive index, low dielectric constant and high transparency make them suitable in widespread application especially in optical industries including lenses, medical equipment and blister packings [4,5]. In 1991, Kaminsky et al. reported zirconocene catalysts for copolymerization of ethylene-norbornene [6]. Subsequently various companies commercialized this material: a German company Hoechst AG produces norbornene-ethylene copolymer using metallocene catalysts, Mitsui commercialized these material using vanadium catalysts [3,5] and Ticona provided commercial TOPAS products of COC type polymeric materials.

To achieve the functionalization of ethylene with norbornene or vice versa, early transition metal catalysts are extensively investigated [7,8]. For example bis(pyrrrolide-imine) titanium [9,10], bis(imino-indolide)titanium [11], bis(enaminoketonato) titanium [12], bis

(diketiminato) titanium [13], [2-(2,6-dialkylphenylamino)-1-phenylethoxy TiCl₂] [14], and titanium complexes bearing tridentate ligands [15,16], are efficiently employed for norbornene-ethylene homo/co-polymerization. However, these and commercially used early transition catalysts are prone to poisoning from polar impurities and polar functionalities, therefore suffer from poor stability. On the other hand, late transition metal catalysts exhibit good stabilities to tolerate the polar functionalities because of their low oxophilicity.

In 1995, Brookhart reported α-diimino-Ni(II) and Pd(II) complexes that are highly active catalysts for the ethylene polymerization [17,18]. These catalysts can also efficiently mediate the copolymerization of ethylene with norbornene as well as polar functionalized norbornene comonomers [19–23]. Kaminsky et al. first studied the copolymerization of ethylene-norbornene using α-diimine-palladium catalysts [24,25]. Goodall et al. investigated a variety of late transition metal catalysts, especially bulky aryl substituted α-diimine-Pd(II) precatalyst for ethylene/cycloolefin copolymerization [26,27]. Recently, an emerging class of phosphine-sulfonate palladium and nickel catalysts has also been effectively employed for copolymerization of ethylene with

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NBE as well as polar functionalized NBE comonomers. In this contribution, we have reported a family of unsymmetrical 1,2-bis(arylimino)acenaphthene–nickel (A, Chart 1) [28–32] and –palladium precatalysts (B, Chart 1) [33] for polymerization of ethylene, and copolymerization of norbornene with ethylene comonomer respectively. High incorporation of ethylene (up to 59.2–77.4%) was achieved and the resultant copolymer showed high molecular weights (up to 150.5 kg mol⁻¹). Generally, it is observed that sterically crowded α -diimino-Ni(II) or Pd(II) precatalysts are more effective for the high activities and high molecular weight (Mw) polymeric materials [28–32]. In view of these results, it would be an effective approach to design more sterically crowded α -diimino-Pd(II) precatalysts for the purposes to achieve high productivities with extended lifetimes on the elevated reaction temperatures.

With target to assess the high thermal stability and catalytic activities for the polymerization of norbornene as well as its copolymerization with ethylene, herein we reported sterically crowded symmetrical bis(arylimino)acenaphthene–palladium catalysts (C, Chart 1) and tailored the catalysts with different substituents ranging from electron donating to the electron withdrawing to find the best couple of steric and electronic influences for the high productivities. To ascertain the effects of different reaction parameters such as co-catalyst effect, reaction temperature, run time and NBE feed ratio on catalytic activities, a detailed norbornene polymerization and norbornene–ethylene copolymerization was performed. In addition a detail microstructural analysis of resultant copolymer was determined by FT IR and ¹³C NMR spectroscopies.

2. Experimental

2.1. General consideration

All air and/or moisture sensitive compounds were handled under a nitrogen atmosphere using standard Schlenk techniques. The solvents (toluene and dichloromethane) and NBE monomer were heated to reflux and distilled prior to use under a nitrogen atmosphere. Methylaluminoxane (MAO, 1.46 M in toluene) was purchased from Akzo Nobel Corp. Other reagents were purchased from Aldrich, Acros or local suppliers. ¹H and ¹³C NMR spectra were recorded on a Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard; δ values were given in ppm and J values in Hz. FT-IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analyses were carried out using a Flash EA 1112 microanalyzer. Molecular weights (M_w) and molecular weight distributions (MWD) of the copolymer were determined using a PL-GPC220 at 150 °C with 1,2,4-trichlorobenzene as the solvent. ¹³C NMR spectra of the polyethylene were recorded on a Bruker DMX 500 MHz instrument at 135 °C in deuterated 1,1,2,2-tetra-chloroethane with TMS as an internal standard.

2.2. Synthesis and characterization of ligands (L1 – L6)

2.2.1. 1,2-bis(2,6-dibenzhydryl-4-methylphenylimino)acenaphthene (L1)

All the ligand were prepared using a procedure reported elsewhere [34]. To a solution of 2,6-dibenzhydryl-4-methylaniline (0.86 g, 1.8 mmol) in toluene, trimethylaluminum, Me₃Al (0.6 mL, 3.2 M in toluene) was added dropwise under a nitrogen atmosphere. The reaction mixture was heated up to 80 °C for 3 h and then cool to room temperature. Acenaphthenequinone (0.17 g, 0.9 mmol) was added and again heated to the refluxing temperature. After 9 h reflux, the reaction mixture allowed to cool at room temperature and, then added 1 M solution of NaOH (10 mL) and washed with ethyl acetate (3 × 10 mL). The combined organic layers were dried over MgSO₄ and filtered. The solvent was removed under reduced pressure and purified by alumina column chromatography using petroleum ether/ethyl acetate (v/v = 500/8) as eluent yielding L1 as a light green powder (0.10 g, 10.2%

yield). ¹H NMR (CD₂Cl₂, 400 MHz): δ 7.49 (d, J = 8.3 Hz, 2H), 7.12 (m, 12H), 7.07 (m, 8H), 6.91 (s, 4H), 6.85 (m, 10H), 6.64 (m, 12H), 6.11 (d, J = 7.0 Hz, 2H), 5.69 (s, 4H), 2.29 (s, 6H). ¹³C NMR (CD₂Cl₂, 100 MHz): δ 163.8, 160.8, 146.89, 144.1, 142.8, 132.8, 131.7, 129.9, 129.7, 128.7, 128.2, 127.9, 126.7, 126.1, 125.8, 124.5, 51.6, 21.7. FT-IR (cm⁻¹): 3023, 2950, 2165, 2022, 2002, 1965, 1667($\nu_{C=N}$), 1646($\nu_{C=N}$), 1595, 1492, 1443, 1262, 1131, 1075, 1030, 921, 891, 861, 828, 780, 763, 696. Anal. Calcd for C₇₈H₆₀N₂ (1025.35): C, 91.37; H, 5.96; N, 2.73; Found: C, 91.36; H, 5.94; N, 2.70.

2.2.2. 1,2-bis(2,6-dibenzhydryl-4-ethylphenylimino)acenaphthene (L2)

Using a similar procedure as described for the synthesis of L1, L2 was prepared as a light green powder (21% yield). ¹H NMR (CD₂Cl₂, 400 MHz): δ 7.49 (d, J = 8.3 Hz, 2H), 7.12 (m, 12H), 7.07 (m, 8H), 6.91 (s, 4H), 6.85 (m, 10H), 6.64 (m, 12H), 6.11 (d, J = 7.0 Hz, 2H), 5.69 (s, 4H), 2.59–2.51 (m, 4H) 1.35 (t, J = 10 Hz, 6H). ¹³C NMR (CD₂Cl₂, 100 MHz): δ 163.8, 160.8, 146.8, 144.1, 142.8, 132.8, 131.7, 129.9, 129.7, 128.7, 128.2, 127.9, 126.7, 126.1, 125.8, 124.5, 51.6, 24.4, 14.1. FT-IR (cm⁻¹): 3022, 2958, 2165, 2020, 2002, 1965, 1667($\nu_{C=N}$), 1647($\nu_{C=N}$), 1597, 1492, 1443, 1260, 1131, 1075, 1030, 920, 891, 861, 828, 779, 763, 735, 696. Anal. Calcd for C₈₀H₆₄N₂ (1053.41): C, 91.22; H, 6.12; N, 2.66; Found: C, 91.26; H, 6.16; N, 2.61.

2.2.3. 1,2-bis(2,6-dibenzhydryl-4-*i*-propylphenylimino)acenaphthene (L3)

Using a similar procedure as described for the synthesis of L1, L3 was prepared as a light green powder (24% yield). ¹H NMR (CD₂Cl₂, 400 MHz): δ 7.49 (d, J = 8.3 Hz, 2H), 7.12 (m, 12H), 7.07 (m, 8H), 6.91 (s, 4H), 6.85 (m, 10H), 6.64 (m, 12H), 6.11 (d, J = 7.0 Hz, 2H), 5.69 (s, 4H), 2.82–2.71 (m, 2H) 1.09 (d, J = 12, 12H). ¹³C NMR (CD₂Cl₂, 100 MHz): δ 163.8, 160.8, 146.9, 144.1, 142.8, 132.8, 131.7, 129.9, 129.7, 128.8, 128.2, 127.9, 126.8, 126.2, 125.9, 124.5, 51.6, 28.4, 24.1, 23.7. FT-IR (cm⁻¹): 3024, 2957, 2166, 2002, 1659($\nu_{C=N}$), 1631($\nu_{C=N}$), 1596, 1492, 1442, 1359, 1257, 1163, 1129, 1076, 1030, 925, 892, 865, 829, 780, 763, 733, 696. Anal. Calcd for C₈₂H₆₈N₂ (1081.46): C, 91.07; H, 6.34; N, 2.59; Found: C, 91.02; H, 6.31; N, 2.57.

2.2.4. 1,2-bis(2,6-dibenzhydryl-4-*t*-butylphenylimino)acenaphthene (L4)

Using a similar procedure as described for the synthesis of L1, L4 was prepared as a light green powder (26% yield). ¹H NMR (CD₂Cl₂, 400 MHz): δ 7.49 (d, J = 8.3 Hz, 2H), 7.12 (m, 12H), 7.07 (m, 8H), 6.91 (s, 4H), 6.85 (m, 10H), 6.64 (m, 12H), 6.11 (d, J = 7.0 Hz, 2H), 5.69 (s, 4H), 2.20 (s, 18H). ¹³C NMR (CD₂Cl₂, 100 MHz): δ 163.8, 160.8, 146.9, 144.1, 142.8, 132.8, 131.7, 129.9, 129.7, 128.8, 128.2, 127.9, 126.8, 126.2, 125.9, 124.5, 51.6, 34.4, 31.5. FT-IR (cm⁻¹): 3020, 2958, 2165, 2021, 2002, 1965, 1668($\nu_{C=N}$), 1646($\nu_{C=N}$), 1596, 1492, 1443, 1260, 1132, 1075, 1030, 920, 893, 861, 828, 779, 763, 736, 696. Anal. Calcd for C₈₄H₇₂N₂ (1109.51): C, 90.93; H, 6.54; N, 2.52; Found: C, 90.90; H, 6.51; N, 2.51.

2.2.5. 1,2-bis(2,6-dibenzhydryl-4-chlorophenylimino)acenaphthene (L5)

Using a similar procedure as described for the synthesis of L1, L5 was prepared as a light green powder (9.2% yield). ¹H NMR (CD₂Cl₂, 400 MHz): δ 7.49 (d, J = 8.3 Hz, 2H), 7.12 (m, 12H), 7.07 (m, 8H), 6.91 (s, 4H), 6.85 (m, 10H), 6.64 (m, 12H), 6.11 (d, J = 7.0 Hz, 2H), 5.69 (s, 4H). ¹³C NMR (CD₂Cl₂, 100 MHz): δ 163.8, 160.8, 146.9, 144.1, 142.8, 132.8, 131.74, 129.9, 129.7, 128.7, 128.2, 127.9, 126.8, 126.2, 125.9, 124.5, 51.6. FT-IR (cm⁻¹): 2957, 2165, 2020, 2002, 1965, 1666($\nu_{C=N}$), 1644($\nu_{C=N}$), 1595, 1492, 1442, 1260, 1131, 1075, 1030, 920, 891, 828, 779, 764, 735, 696. Anal. Calcd for C₇₆H₅₄Cl₂N₂ (1066.18): C, 85.62; H, 5.11; N, 2.63; Found: C, 85.58; H, 5.16; N, 2.68.

2.2.6. 1,2-bis(2,6-dibenzhydryl-4-fluorophenylimino)acenaphthene (L6)

Using a similar procedure as described for the synthesis of L1, L6 was prepared as a light green powder (9.6% yield). ¹H NMR (CD₂Cl₂, 400 MHz): δ 7.49 (d, J = 8.3 Hz, 2H), 7.12 (m, 12H), 7.07 (m, 8H), 6.91 (s, 4H), 6.85 (m, 10H), 6.64 (m, 12H), 6.11 (d, J = 7.0 Hz, 2H), 5.69 (s,

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