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N,O-chelating bidentate Ni (II) and Pd (II) complexes for copolymerization of norbornene and norbornene ester

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ABSTRACT

A series of N,O-chelating type bidentate ligands nickel (II) and palladium (II) complexes Mt[$C_{10}H_8(O)C(ArN)CH_3]_2$ [Ar = 2,6-$C_6H_3(CH_3)_2$, Mt = Ni (II) (C1) and Mt = Pd (II) (C2); Mt = Ni (II), Ar = 2,6-$C_6H_3Cl_2$ (C3) and Ar = 2,6-C_6H_4Cl (C4)] were synthesized and characterized by single crystal X-ray diffractions. Homo-polymerization and copolymerization of norbornene (NB) and 5-norbornene-2-carboxylic acid methyl ester (NB-$COOCH_3$) proceeded in toluene with the above complexes as catalyst precursors and tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] as a unique co-catalyst. Higher activity was observed for complexes with electron-donating ortho-substituents on arylimino, which resulted in activity order C1 > C3, and higher activity was observed for bulky ortho-substituents on arylimino, which resulted in activity order C3 > C4. The C2 system presented much lower catalytic activity toward copolymerization of NB and NB-$COOCH_3$, while the C1 and C3 system showed high catalytic activity and produced the copolymers with relatively high molecular weights, as well as narrow distribution. The fraction of NB-$COOCH_3$ in copolymer can reach up to 44.6 mol% in the presence of C1 by controlling monomer feed ratio of 50%. The achieved vinyl-addition type copolymers displayed high transparency, good thermal stability and solubility in common solvents. The reactivity ratios of co-monomers were $r_{NB\text{-}COOCH3} = 0.5$ and $r_{NB} = 0.72$ under the catalytic system of C1.

1. Introduction

Norbornene (NB; bicyclo[2.2.1]hept-2-ene) is an important monomer in cyclic olefins and usually polymerized through ring-opening metathesis polymerization (ROMP) [1–6], cationic or radical polymerization [7], and vinyl-addition polymerization [8–13], respectively. The vinyl-addition type polynorbornene (PNB) displays interesting and unique chemical and physical properties, such as high optical transparency (more than 90% at 400 nm), low birefringence [14], high thermal stability, high glass transition temperature ($T_g > 370$ °C), low moisture absorption, and excellent dielectric properties, so it has been the subject of many studies. First articles about vinyl-addition polymerization of norbornene were reported by Sartori and coworkers [15,16]. Within the decades, the field of catalytic vinyl-addition polymerization of norbornene has expanded dramatically [17–30].

However, homopolymer of norbornene presents plenty of disadvantages, such as low solubility, mechanical brittleness, low adhesivity and poor processability, which importantly hamper the application of PNB. To modify these disadvantages and get functionalized PNB, polar functionalities incorporation of the polynorbornene backbone is an efficient method. A series of co-monomers, such as ethylene [9,31], propylene [32], and norbornene derivatives [33–36] have also been studied. Shiono et al. [13] prepared the copolymer of NB with propylene and 1-octene which exhibited excellent performance in promoting NB and propylene copolymerization. The propylene content could reach up to 29%, and the glass transition temperatures could arrive in 292 °C of the copolymer obtained. Sen et al. [37] got the copolymers of NB and ethene in the case of N–O-ligated Pd (II) complexes with BPh_3. The copolymers have high molecular weights ($M_n = 1.7–6.5 \times 10^4$), narrow M_w distributions ($M_w/M_n = 1.3–2.3$). Kaita et al. [38] used cyclopentadienyl nickel and palladium complexes catalyzed the copolymerization of NB with NB carboxylic acid esters. The yield reached up to 68%. The contents of the methyl ester monomer unit of these copolymers were 17.4–60.7 mol%. The copolymers have high molecular weights ($M_n = 1.1–2.3 \times 10^5$), narrow M_w distributions ($M_w/M_n = 1.78–1.89$), and high glass transition temperature (316.0–352.8 °C).

Vinyl-addition type PNB can be obtained through Ziegler–Natta catalyst ($TiCl_4$, $TiCl_3$) [39,40], Metallocene catalyst (Ti, Zr, Hf) [31,41–44], Late transition metal catalyst (Ni, Pd, Fe, Co) [45–51]

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and Rare earth metal catalyst (Sc, Ce, La) [52–54]. Late transition metals catalysts are low oxy-sensitive, display high catalytic activity, produce high molecular weight polymers and show excellent performance toward heteroatom-functionalized monomers. Particularly, nickel and palladium complexes exhibit high catalytic activities and produce high molecular weight polymers toward copolymerization NB derivatives with polar groups.

In recent years, some β-ketoamino ligand metal complexes have been synthesized and reported [55–62]. These complexes can efficiently polymerize NB and NB derivatives with co-catalyst (such as MAO, modified MAO (MMAO), or $B(C_6F_5)_3$), exhibited high activities and good immune ability to ester functional and other polar groups. In our group, a series of β-ketoamino complexes of nickel and palladium have been synthesized and characterized, which can effectively catalyze vinyl-addition copolymerization of NB and NB derivatives and the catalytic activity could reach up to 10^5 $g_{polymer}/mol_{Ni}$ h. However, the important ligand-designing parameters, steric and electronic factors, were not completely involved in our previous reports [57–61]. In this article, we aim to present a further investigation of both the steric and electronic effects (CH_3 or Cl) of the β-ketoamino ligand on Ni (II) and Pd (II) polymerization catalysts. These complexes were applied in homo-polymerization of NB and copolymerization of NB and NB-$COOCH_3$ activated by $B(C_6F_5)_3$. Variation of the substituted Ar group could slightly affect the catalytic properties, including activity, molecular weight, solubility, thermostability and mechanical properties of the polymers obtained.

2. Experiment

2.1. Materials

All manipulations with air- and moisture-sensitive compounds were performed under a dry argon atmosphere by using standard vacuum-line and Schlenk techniques or under a standard glove box unless otherwise noted. Toluene and tetrahydrofuran (THF) were purified from an MBraun SPS system and distilled from sodium-benzophenone ketyl under dry nitrogen. All solvents were deoxygenated before using. Norbornene (NB) was purchased from Aldrich Chemical Company and purified by distillation at 110 °C over sodium and dry nitrogen, used as a solution (4.25 mol/L) in toluene. 5-Norbornene-2-carboxylic acid methyl ester (NB-$COOCH_3$) was purchased from Puyang Huicheng Chemical, dried over anhydrous $CaCl_2$ and CaH_2 under nitrogen atmosphere and distilled at reduced pressure condition. Other chemicals and reagents were used as received without further purification.

2.2. Characterization

The ^1H NMR and ^{13}C NMR spectra of ligands $C_{10}H_8(O)C(ArNH)CH_3$ and their complexes $Mt[C_{10}H_8(O)C(ArN)CH_3]_2$, and copolymers were performed on a Bruker ARX 600 NMR spectrometer at ambient temperature with $CDCl_3$ ($\delta = 7.26$ for ^1H and $\delta = 77.0$ for ^{13}C) as solvent and tetramethylsilane (TMS, $\delta = 0$) as an internal reference. Elemental analyses (EA) were recorded on elementar-vario EL cube elemental analyzer. IR spectra were obtained by a Shimadzu IR Prestige-21 FTIR spectrophotometer and average data were obtained from the standard wave number range from 500 to 4000 cm^{-1}. The molecular weight and molecular weight distribution (MWD) of the polymers were carried out by Gel permeation chromatography (GPC) with a Breeze Waters system consisting of a Rheodyne injector, a Waters 1515 Isocratic HPLC Pump, a Waters 2414 Refractive Index Detector, a Waters column Heater module, and a Styragel columnset, Styragel HT3 and HT4, tetrahydrofuran as an eluent with a flow rate of 1.0 mL/min and the detector at 40 °C. Thermal gravimetric analysis (TGA) data were carried out on Perkin–Elmer instrument TGA 7 under nitrogen atmosphere from room temperature to 650 °C at a heating rate of 10 °C/min. The wide-angle X-ray diffraction (XRD) curves of the polymer powders were characterized by using a Bruker D8 Focus X-ray diffractometer, with monochromatic radiation at a wavelength of 1.54 Å at a scanning rate of 2°/min and with 2θ scanning ranging from 3° to 60°. The UV–vis absorption measurements of the polymer films were collected on a Hitachi UV-2300 spectrometer. The mechanical properties were performed on a CMT8502 Machine model GD203A (ShenZhen Sans Testing Machine, China) at a rate of 5 mm/min.

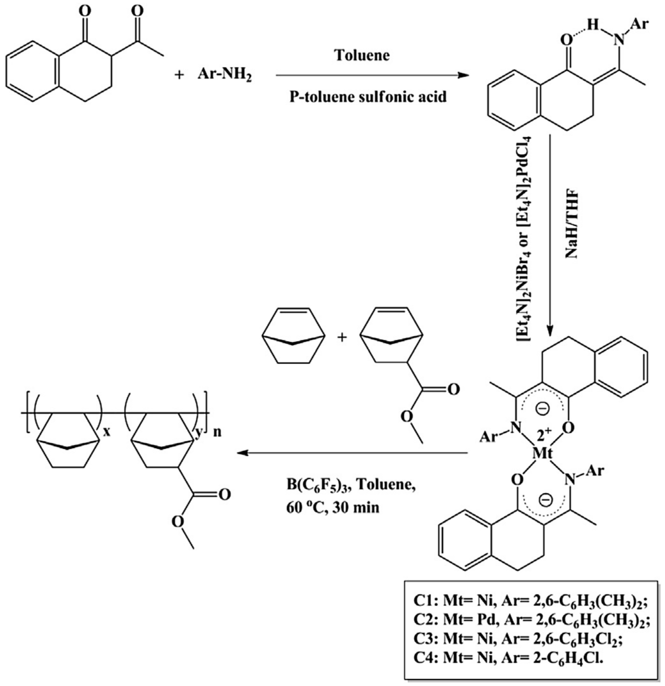
2.3. Crystal structure determination

The X-ray diffraction data of single crystals of complexes were obtained with the ω-2θ scan mode on a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$). The structures were solved using direct methods, and further refinements with full-matrix least-squares on F^2 were obtained with the SHELXTL program package. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

2.4. Ligands and complexes syntheses

According to the method that reported in our previous work [58], N,O-chelating type ligand, β-benzocyclohexan-ketoarylimine, $C_{10}H_8(O)C(ArNH)CH_3$, and their bidentate complexes, $Mt[C_{10}H_8(O)C(ArN)CH_3]_2$ [Ar = 2,6-$C_6H_3(CH_3)_2$, Mt = Ni (II) (C1) and Mt = Pd (II) (C2); Mt = Ni (II), Ar = 2,6-$C_6H_3Cl_2$ (C3) and Ar = 2,6-C_6H_4Cl (C4)], were synthesized according to the synthetic procedure that shown in Scheme 1.

$C_{10}H_8(O)C[2,6\text{-}C_6H_3(CH_3)_2NH]CH_3$: 2-Acetyl-1-tetralone (5.64 g, 0.03 mol) and 2,6-dimethyl aniline (3.63 g, 0.03 mol), a catalytic amount of *p*-toluene sulfonic acid and toluene (200 mL) were mixed



Scheme 1. The synthetic route of the complexes and copolymerization of NB and NB-$COOCH_3$ catalyzed by C1, C2, C3 or C4 systems.