

# Preparation and characterization of acylhydrazone nickel(II) complexes and their catalytic behavior in vinyl polymerization of norbornene and oligomerization of ethylene

Junxian Hou<sup>a</sup>, Wen-Hua Sun<sup>a,\*</sup>, Dongheng Zhang<sup>a</sup>, Liyi Chen<sup>a</sup>, Wei Li<sup>b</sup>,  
Dongfeng Zhao<sup>b</sup>, Haibin Song<sup>c</sup>

<sup>a</sup> Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

<sup>b</sup> R&D Center, Xiangyang Chemical Corporation, Yingkou, Liaoning 115005, China

<sup>c</sup> State Key Laboratory of Functional Polymer, Nankai University, Tianjin 300071, China

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## Abstract

The derivatives of 4,5-diazafluorene-9-one-benzoylhydrazone (**1–4**) and 2-pyridine-carboxaldehyde-benzoylhydrazone (**5–9**) were prepared. The compounds **1–4** reacted with  $\text{Ni}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$  to form diaquabis[4,5-diazafluorene-9-one-benzoylhydrazone]nickel(II) (**10–13**), while the compounds **5–9** reacted with  $(\text{DME})\text{NiBr}_2$  to form bis[*N*-(pyridine-2-carboxaldehyde-benzoylhydrazone)]nickel(II) dibromide (**14–18**), respectively. All ligands and complexes were characterized by elemental analysis and spectroscopic analysis, along with the X-ray single crystal diffraction techniques for **10**, **13** and **14**. The nickel(II) centers are six-coordinated with two corresponding ligands and two coordinated solvents for **10–13**, while the geometry around the nickel atom of **14–18** is distorted octahedron with two ligands and two bromides. Activated with methylaluminumoxane, all nickel complexes show good activities for vinyl polymerization of norbornene and considerable activities for ethylene oligomerization at ambient pressure. By using **10**, the influence of reaction conditions was carefully examined on the catalytic behavior of vinyl polymerization of norbornene. The catalytic conditions were varied to investigate their effects on activity of ethylene oligomerization. The resulting poly(norbornene)s were characterized by IR, <sup>1</sup>H NMR, TGA, DSC and the viscosity measurement.

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## 1. Introduction

The polynorbornenes have been recognized as the advanced materials with interesting and unique properties [1]. Though vinyl polymerization of norbornene was found with  $\text{TiCl}_4$ -based Ziegler catalyst [2], nickel-based complexes have been of more interest because of their good activity and property of resulting polynorbornene (PNB) [3–8]. The ethylene oligomerization presents one of the major industrial processes for the production of linear  $\alpha$ -olefins, and the commercially practiced shell high olefin process

(SHOP) based on nickel complex bearing P–O bidentate ligands produces olefins at 1 million tons every year [9]. Recently, various late transition metal complexes have been explored for ethylene activations [10]. In our laboratory, we have engaged in ethylene activation with various nickel complexes having chelating ligands of diimine [*N,N*] [11], salicylaldimine [*N,O*] [12] and 8-(diphenylphosphino)quinoline [*P,N*] [13]. Subsequently, the nickel complexes containing 8-(diphenylphosphino)quinoline [14] and salicylideneimide [15] were found to show high catalytic activity in vinyl polymerization of norbornene, and the resulting PNBs have good solubility in halogenated aromatic hydrocarbons. This has triggered a renewed interest in the development of a family of nickel complexes which are useful for both vinyl

\* Corresponding author. Tel.: +86 1062557955; fax: +86 1062618239.  
E-mail address: [whsun@iccas.ac.cn](mailto:whsun@iccas.ac.cn) (W.-H. Sun).

polymerization of norbornene and ethylene oligomerization. The nickel complexes containing 4,5-diazafluorene-9-one-benzoylhydrazone derivatives showed reasonable activities for ethylene oligomerization [16]. The acylhydrazone can be of two types of ketone and enolate in their nickel complexes under different condition of the complexation. The variations of these complexes are investigated here. All nickel complexes were characterized by elemental analysis and spectra measurements as well as X-ray diffraction for the molecular structures of representative complexes. In the presence of cocatalyst methylaluminoxane (MAO), all nickel complexes show reasonable catalytic activity for ethylene oligomerization and good catalytic activity for vinyl polymerization of norbornene. The influence of reaction conditions on the catalytic behavior was examined. The resulting PNBs were characterized by IR,  $^1\text{H}$  NMR, TGA, DSC and the viscosity measurement.

## 2. Experimental

### 2.1. General procedures

All manipulations of air- or moisture-sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Toluene was refluxed over sodium-benzophenone until purple color appeared and distilled under nitrogen atmosphere prior to use.  $\text{CH}_2\text{Cl}_2$  was dried over calcium hydride and distilled under nitrogen. Methylaluminoxane (MAO) was purchased from Albemarle as 1.4 M toluene solution. Norbornene (from Acros) was purified by distillation over potassium and used as a solution in dichloromethane or toluene. All other chemical reagents were commercially obtained unless otherwise stated.

IR spectra were recorded on a Perkin Elmer system 2000 FT-IR spectrometer. The chemical shifts of NMR spectra were measured with a Bruker BMX-300 MHz instrument and expressed in ppm using TMS as internal standard. Elemental analyses were performed by using an HP-MOD 1106 microanalyzer. Viscosity measurements were carried out in chlorobenzene at 25 °C using an Ubbelohde viscometer. Distribution of oligomers obtained was measured on a Varian Vista 6000 GC spectrometer and an HP 5971A GC-MS detector.

## 3. Synthesis of Schiff-base ligands and complexes

### 3.1. Synthesis of ligands 1–9

4,5-Diazafluorene-9-one (dafo) was prepared according to the literature method [16,17]. The condensation reaction of dafo with benzoylhydrazine in ethanol gave the ligands 1–4 in approximately 80–95% yield. Ligands 5–9 were synthesized as described in the literature [18] (Scheme 1).

#### 3.1.1. 4,5-Diazafluorene-9-one-benzoylhydrazone (1)

The synthesis of 4,5-diazafluorene-9-one-benzoylhydrazone (**1**) was reported in our previous paper [16]; mp: 162–164 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{SOCD}_3$ ),  $\delta$  (ppm): 7.50–7.69 (m, 5H), 8.03 (d,  $J=6$  Hz, 2H), 8.245 (d,  $J=9$  Hz, 1H), 8.545 (d,  $J=9$  Hz, 1H), 8.74–8.77 (t, 2H), 12.07 (NH).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_3\text{SOCD}_3$ ),  $\delta$  (ppm): 124.3, 124.9, 125.3, 128.7, 129.1, 130.0, 132.5, 132.7, 133.3, 135.7, 152.1, 157.7, 159.0. IR (KBr,  $\text{cm}^{-1}$ ): 3386 (br), 3150 (br), 3061 (w), 2927 (w), 1741 (w), 1692 (s), 1593 (m), 1564 (s), 1515 (s), 1486 (m), 1402 (s), 1341 (w), 1265 (s), 1182 (m), 1164 (m), 1132 (s), 1094 (m), 1073 (m), 1028 (w), 1001 (w). Anal. Calcd. (%) for  $\text{C}_{18}\text{H}_{12}\text{N}_4\text{O}\cdot\text{CH}_3\text{CH}_2\text{OH}$ : C, 69.35; H, 5.24; N 16.17. Found (%): C, 69.24; H, 5.16; N, 16.49.

#### 3.1.2. 4,5-Diazafluorene-9-one-2-methylbenzoylhydrazone (2)

4,5-Diazafluorene-9-one (360 mg, 2 mmol) was added to a solution of 2-methylbenzoylhydrazine (280 mg, 2 mmol) in absolute ethanol (30 ml). After the addition of *p*-toluene sulfonic acid (catalytic amount), the solution was refluxed for 6 h. The ethanol was partly removed in vacuum and the remainder was kept cool over night. Yellow crystalline product, **2**, was obtained, which was then washed with ethanol and dried in a vacuum oven overnight. Yield 540 mg (80%); mp: 221–223 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{SOCD}_3$ ),  $\delta$  (ppm): 2.55 (s, 3H), 7.29–7.37 (m, 4H), 7.42–7.50 (m, 1H), 7.55–7.58 (d,  $J=7$  Hz, 1H), 8.20 (s, 2H), 8.74 (d,  $J=3$  Hz, 1H), 8.81 (d,  $J=5$  Hz, 1H), 9.90 (NH) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_3\text{SOCD}_3$ ),  $\delta$  (ppm): 39.8, 123.9, 124.7, 124.9, 126.0, 128.1, 129.6, 130.6, 131.0, 132.6, 134.9, 135.2, 136.5, 151.9, 157.4, 158.9. IR (KBr,  $\text{cm}^{-1}$ ): 3339 (w), 3272 (w), 3092 (w), 3060 (w), 2962 (w), 2928 (w), 2856 (w), 1674 (s), 1607 (m), 1589 (m), 1562 (m), 1488 (m), 1456 (m), 1402 (s), 1343 (s), 1284 (m), 1205 (w), 1179 (w), 1165 (w), 1142 (m), 1112 (w), 1085 (m), 1045 (w). Anal. Calcd. (%) for  $\text{C}_{19}\text{H}_{14}\text{N}_4\text{O}\cdot(1/2)\text{EtOH}$ : C, 71.20; H, 5.08; N, 16.61. Found (%): C, 71.64; H, 5.06; N, 16.51.

#### 3.1.3. 4,5-Diazafluorene-9-one-3-methylbenzoylhydrazone (3)

Compound **3** was synthesized by a procedure similar to that for **2** except that 3-methylbenzoylhydrazine was used, and was obtained as yellow powder. Yield 590 mg (87%); mp: 160–162 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{SOCD}_3$ ),  $\delta$  (ppm): 2.48 (s, 3H), 7.27–7.46 (m, 4H), 7.75 (s, 1H), 7.82 (s, 1H), 8.20 (t,  $J=9$  Hz, 2H), 8.75 (d,  $J=5$  Hz, 1H), 8.81 (d,  $J=5$  Hz, 1H), 10.03 (NH).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_3\text{SOCD}_3$ ),  $\delta$  (ppm): 39.9, 124.4, 124.9, 125.4, 125.8, 129.0, 129.1, 130.0, 132.6, 133.2, 133.3, 135.7, 138.5, 152.1, 157.7, 159.0. IR (KBr,  $\text{cm}^{-1}$ ): 3203 (br), 3062 (w), 3012 (w), 2965 (w), 2922 (w), 1734 (w), 1696 (s), 1672 (s), 1588 (m), 1564 (m), 1512 (s), 1401 (s), 1340 (w), 1274 (s), 1196 (s), 1128 (m), 1096 (m), 1050 (w), 1001 (w). Anal. Calcd. (%) for  $\text{C}_{19}\text{H}_{14}\text{N}_4\text{O}\cdot(1/2)\text{EtOH}$ : C, 71.20; H, 5.08; N, 16.61. Found (%): C, 70.88; H, 5.00; N, 16.47.

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