

Novel Ni and Pd(benzocyclohexan-ketonaphthylimino)₂ Complexes for Copolymerization of Norbornene with Octene

Yueman Liu,¹ Meng Ouyang,¹ Xiaohui He,² Yiwang Chen,^{1,2} Kaiti Wang²

¹Department of Chemistry, Nanchang University, Nanchang 330031, China

²Institute of Polymers, Nanchang University, Nanchang 330031, China

Correspondence to: X. He (E-mail: hexiaohui@ncu.edu.cn) or Y. Chen (E-mail: ywchen@ncu.edu.cn)

ABSTRACT: Two novel late transition metals complexes with bidentate $\hat{O}N$ chelate ligand, $Mt(\text{benzocyclohexan-ketonaphthylimino})_2$ $\{Mt(\text{bchkni})_2: \text{bchkni} = \text{C}_{10}\text{H}_8(\text{O})\text{C}[\text{N}(\text{naphthyl})\text{CH}_3]; Mt = \text{Ni, Pd}\}$, were synthesized. In the presence of $\text{B}(\text{C}_6\text{F}_5)_3$, both complexes exhibited high activity toward the homo-polymerization of norbornene (NB) (as high as $2.7 \times 10^5 \text{ g}_{\text{polymer}}/\text{mol}_{\text{Ni}}\cdot\text{h}$ for $\text{Ni}(\text{bchkni})_2/\text{B}(\text{C}_6\text{F}_5)_3$ and $2.3 \times 10^5 \text{ g}_{\text{polymer}}/\text{mol}_{\text{Pd}}\cdot\text{h}$ for $\text{Pd}(\text{bchkni})_2/\text{B}(\text{C}_6\text{F}_5)_3$, respectively). Additionally, both catalytic systems showed high activity toward the copolymerization of NB with 1-octene under various polymerization conditions and produced the addition-type copolymer with relatively high molecular weights ($0.1\text{--}1.4 \times 10^5 \text{ g/mol}$) as well as narrow molecular weight distribution. The 1-octene content in the copolymers can be controlled up to 8.9–14.0% for $\text{Ni}(\text{bchkni})_2/\text{B}(\text{C}_6\text{F}_5)_3$ and 8.8–14.6% for $\text{Pd}(\text{bchkni})_2/\text{B}(\text{C}_6\text{F}_5)_3$ catalytic system by varying comonomer feed ratios from 10 to 70 mol %. The reactivity ratios of two monomers were determined to be $r_{1\text{-octene}} = 0.052$, $r_{\text{NB}} = 8.45$ for $\text{Ni}(\text{bchkni})_2/\text{B}(\text{C}_6\text{F}_5)_3$ system, and $r_{1\text{-octene}} = 0.025$, $r_{\text{NB}} = 7.17$ for $\text{Pd}(\text{bchkni})_2/\text{B}(\text{C}_6\text{F}_5)_3$ system by the Kelen-TüdÖs method. The achieved NB/1-octene copolymers were confirmed to be noncrystalline and exhibited good thermal stability ($T_d > 400^\circ\text{C}$, $T_g = 244.1\text{--}272.2^\circ\text{C}$) and showed good solubility in common organic solvents. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: catalytic polymerization; late-transition metals complexes; norbornene; 1-octene; additional polymerization

Received 18 June 2011; accepted 7 June 2012; published online

DOI: 10.1002/app.38171

INTRODUCTION

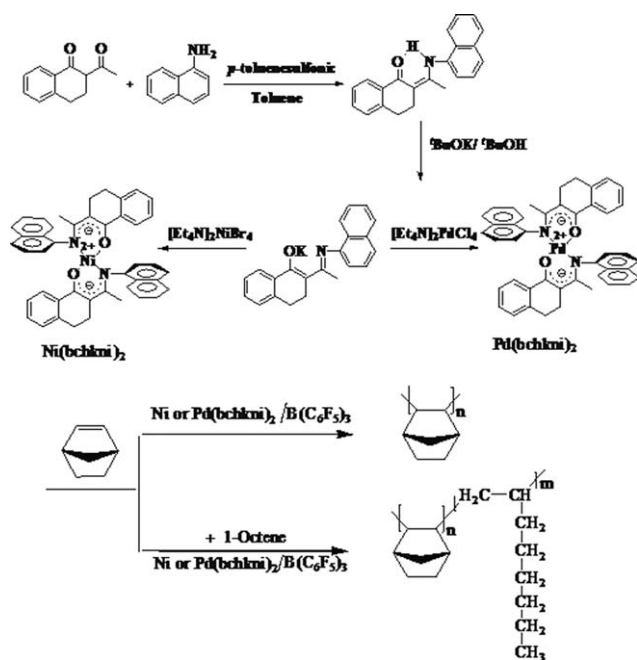
Polyolefin is a class of materials with enormous economic impact due to its good heat and chemical resistance as well as high transparency, nonhydroscopicity, and low dielectric constants.¹ Norbornene (NB) as the typical olefin, it and its derivatives can be polymerized by three different methods, that is ring-opening metathesis polymerization,^{2,3} cationic or radical polymerization,^{4–6} and vinylic polymerization.⁷ Vinyl-addition type of polynorbornene (PNB) is of considerable interest because of its unique physical properties, including good mechanical strength and heat resistivity ($T_g > 350^\circ\text{C}$), and optical transparency for applications such as deep ultraviolet photoreists, excellent dielectrics in microelectronics applications, and as cover layers for liquid-crystal displays. However, low solubility, mechanical brittleness, weak adhesive properties and poor processability currently hinder the application of PNB. Processing of homopolymers constituting cyclic olefins is difficult due to they do not exhibit sharp melt characteristics like other thermoplastic materials. So the use of such polymers is very limited. In order to obtain more elastic optical materials holding their

characteristic natures, copolymerizations of norbornene with 1-octene have been reported in the literature.^{8–13}

It is well known that the vinyl addition polymerization of norbornene can be efficiently proceeded using conventional Ziegler-Natta catalysts,¹⁴ Metallocene catalysts.^{15–17} The homogeneous Ziegler-Natta catalysts were effective for olefin oligomerization or polymerization, of which properties can be easily controlled with comonomer content and comonomer sequence. But these complexes are hard to handle and incompatible with polar monomers due to the high oxophilicity and the tendency for functionalities to coordinate to active species. Metallocene catalysts exhibited both high catalytic activities and efficient comonomer incorporations for the copolymerization of ethylene with α -olefin, styrene and NB. However, the catalysts are not suitable for general gas phase and silt polymerization as well as easily being poisoned with polar monomers containing O, S, or N atoms. Moreover, high cost of cocatalyst MAO and beyond control polymerization product morphology is the shortcomings.^{18–24}

Additional Supporting Information may be found in the online version of this article.

© 2012 Wiley Periodicals, Inc.



Scheme 1. Syntheses of Ni and Pd(bchkn)₂ complexes.

In recent years, the late-transition-metal catalysts are new type of complexes due to their lower oxophilicity and resistance toward deactivation by polar functionalities, relative to early transition metal catalysts.^{25–29} The observation that the late transition metal can be stabilized by various heterodonor ligands and give mono- or dinuclear complexes with several coordination modes. Especially catalysts which have two metal centers can catalyze the polar olefins more efficiently than analogous monometallic species. Also, nickel and palladium are considered to be the most common late-transition metals, which constitute a large group of compounds for the polymerization of NB. In heteroleptic complexes of the type (AB)CD, the bidentate AB chelate ligand was usually viewed as the major ligand.³⁰ During the past few years, our groups has focused our attention on nickel and palladium complexes bearing N, O ligands because they are very effective catalysts in NB, NB derivative, and α -olefin polymerization, for example, recently some nickel and palladium based systems were found to be highly active for the polymerization of NB. We are interested in the design and synthesis of efficient transition metal catalysts for precise, controlled olefin polymerization. Previously, we reported the type of nickel and palladium catalysts bearing two β -ketoiminato (N, O) ligands and their use as the catalyst precursors for NB polymerization.^{10,31–40}

In this article, as shown in Scheme 1, two new late transition metal complexes based on the benzocyclohexan-ketonaphthylimine ligand {C₁₀H₈(O)C[HN(naphthyl)CH₃]} were synthesized and explored the potential application in NB homo- and copolymerization with 1-octene. These catalysts display effective ability to copolymerize NB with 1-octene after activated by B(C₆F₅)₃ and produce vinyl addition type cyclic olefin copolymers with high molecular weight.

EXPERIMENTAL

General Considerations

All manipulations of air-sensitive and water-sensitive compounds were performed under an inert atmosphere. Solvents were purified using standard procedures. Toluene was dried over sodium/benzophenone and distilled under nitrogen before use. Tris(pentafluorophenyl)borane (B(C₆F₅)₃, 95%) and norbornene (NB, 98%) were all purchased from Aldrich Chemical company, and was purified by drying over sodium and distilling at 106°C under N₂ atmospheres, used as a solution 0.4 g/mL (4.25 mol/L) in toluene. 1-alkene was purchased from ACROS organics and purified by washing twice with aqueous sodium hydroxide (5.0 wt %) and twice with water for removing inhibitors, followed by drying over anhydrous CaCl₂ and distillation over CaH₂ under argon atmosphere at reduced pressure. Nickel(II) bromide (Acros), palladium(II) chloride (Acros) were used without further purification.

Measurements

Elemental analyses (EA) were characterized by means of elemental analysis with Vario Elementar III. The ¹H- and ¹³C-NMR spectra of the ligand, and Mt(bchkn)₂ complexes, and copolymers were obtained on a Bruker ARX 600 NMR spectrometer at room temperature with CDCl₃ as solvent and tetramethylsilane (TMS, $\delta = 0$) as an internal reference. Mass spectra were recorded by ESI methods, HRMS (ESI) was measured on a Bruker Daltonics APEXIII 7.0 TESLA FTMS. Fourier transform infrared (FTIR) spectra were recorded as KBr pellets on a Shimadzu IRPrestige-21 FTIR spectrophotometer. The Gel permeation chromatography (GPC) was carried out on a Breeze Waters system consisting of a Rheodyne injector, a 1515 Isocratic pump, a Waters 2414 differential refractometer, and a Styragel column set, Styragel HT3 and HT4, at a flow rate of 1.0 mL/min with chloroform as an eluent. Thermogravimetric analysis (TGA) was performed on a TA Q600 SDT for thermogravimetry at a heating rate of 10°C/min under nitrogen with a sample size of 8–10 mg. The differential scanning calorimetry (DSC) measurements were obtained on a Shimadzu DSC-60 with a heating/cooling rate of 10°C/min under nitrogen atmosphere. The wide-angle X-ray diffraction (WAXD) curves of the polymer powders were obtained 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. Scanning was performed with 2 θ ranging from 3° to 60°.

Synthesis of {C₁₀H₈(O)C[HN(naphthyl)CH₃]}

According to the literature,³³ 2-acetyl-1-tetralone (4 g, 0.0213 mol), α -naphthyl-amine (3.05 g, 0.0213 mol), and a catalytic amount of *p*-toluene-sulfonic acid in toluene (23 mL) were combined and heated to reflux for 3 h, while H₂O removed as a toluene azeotrope at 125–130°C using a water separator. The resulting solution was evaporated under vacuum to remove the residual toluene and recrystallization from hexane yielded benzocyclohexan-ketonaphthylimine in yellow crystals. Yield: 4.92 g (73.9%; m.p.: 151–153°C). C₂₂H₁₉ON elemental analysis (%), found: C, 84.13; H, 6.07; N, 4.50; calcd: C, 84.24; H, 6.06; N, 4.47. ¹H-NMR (CDCl₃, δ , ppm): 14.42 (s, 1H, NH), 8.13 (d, 1H, C₁₀H₈), 7.89–8.09 (d, 2H, C₁₀H₇), 7.56–7.88 (d, 2H,

$C_{10}H_8$), 7.54–7.55 (d, 2H, $C_{10}H_7$), 7.53 (d, 1H, $C_{10}H_8$), 7.39–7.52 (d, 3H, $C_{10}H_7$), 2.73–2.93 (m, 4H, $C_{10}H_8$), 2.05 (s, 3H, CH_3). ^{13}C -NMR ($CDCl_3$, δ , ppm): 187.0 (s, 1C, C=O), 141.32 (s, 1C, N- C_6H_5), 135.67 (s, 1C, $C_{10}H_7$), 130.97–135.46 (s, 3C, $C_{10}H_8$), 129.99 (s, 1C, $C_{10}H_7$), 128.21–129.02 (s, 2C, $C_{10}H_8$), 128.15 (s, 1C, $C_{10}H_7$), 127.22 (s, 1C, $C_{10}H_8$), 125.25–126.79 (s, 4C, $C_{10}H_7$), 125.25 (s, 1C, $C_{10}H_8$), 102.8–124.06 (s, 3C, $C_{10}H_7$), 24.85–29.16 (s, 2C, $C_{10}H_8$), 16.61 (s, 1C, CH_3). MS (ESI, m/z): 313 $[M]^+$. HRMS (ESI): found 313.88; calcd for $C_{22}H_{19}ON$ $[M]^+$ 313.80.

Synthesis of $\{C_{10}H_8(O)C[N(\text{naphthyl})CH_3]\}_2Ni$

A 0.273 g (0.007 mol) sample of potassium was added to 25 mL dried t BuOH. After the potassium had dissolved completely, the solution was heated to 50°C and 2.194 g (0.007 mol) of benzocyclohexan-ke-tonaphthylimine added. The solution changed to yellow–orange as ligand completely reacted with t BuOK and was kept stirring for 30 min. The solution was cooled slowly to room temperature, and 2.236 g (0.0035 mol) of $[Et_4N]_2NiBr_4$ was introduced in; the reacting mixture immediately formed a gray green precipitate. After it was stirred vigorously at room temperature for several hours, the residual t BuOH was removed by evaporating in vacuum. The residue slurry was then extracted successively with enough hot n -heptane/toluene, the filtrate was collected by fast hot filtering and the resulting hot filtrate was induced to crystallize by cooling slowly overnight. Then the product was isolated by filtration and drying under reduced pressure. One or two further recrystallizations from n -heptane/toluene mixture solution resulted in dark green block crystals. Yield: 1.13 g (47.1%; m.p.: 223–225°C). $C_{44}H_{36}N_2O_2Ni$ elemental analysis (%), found: C, 77.19; H, 5.36; N, 4.19. calcd. C, 77.25; H, 5.27; N, 4.10. 1H -NMR ($CDCl_3$, δ , ppm): 7.9 (d, 2H, $C_{10}H_8$), 7.78–7.85 (d, 4H, $C_{10}H_7$), 7.36–7.41 (d, 4H, $C_{10}H_8$), 7.12–7.18 (d, 4H, $C_{10}H_7$), 7.12 (d, 2H, $C_{10}H_8$), 6.59–6.90 (d, 6H, $C_{10}H_7$), 2.06–2.94 (m, 8H, $C_{10}H_8$), 1.56 (s, 6H, CH_3). ^{13}C -NMR ($CDCl_3$, δ , ppm): 184.99 (s, 2C, C=O), 139.5 (s, 2C, N- C_6H_5), 138.49 (s, 2C, $C_{10}H_7$), 130.99–134.02 (s, 6C, $C_{10}H_8$), 130.64 (s, 2C, $C_{10}H_7$), 128.23–129.32 (s, 4C, $C_{10}H_8$), 128.15 (s, 2C, $C_{10}H_7$), 127.8 (s, 2C, $C_{10}H_8$), 123.27–126.73 (s, 12C, $C_{10}H_7$), 123.09 (s, 2C, $C_{10}H_8$), 105.92 (s, 2C, $C_{10}H_7$), 25.22–29.12 (s, 4C, $C_{10}H_8$), 23.79 (s, 2C, CH_3). MS (ESI, m/z): 683 $[M]^+$. HRMS (ESI): found 683.22; calcd for $C_{22}H_{19}ON$ $[M]^+$ 683.26 (see more spectra in Supporting Information).

Synthesis of $\{C_{10}H_8(O)C[N(\text{naphthyl})CH_3]\}_2Pd$

In a similar manner with $Ni(bchkni)_2$, $Pd(bchkni)_2$ complex was prepared as a red/brown solid (yield: 51%; m.p.: 240–242°C). $C_{44}H_{36}N_2O_2Pd$ elemental analysis (%), found: C, 72.26; H, 4.87; N, 3.85. calcd. C, 72.21; H, 4.92; N, 3.83. 1H -NMR ($CDCl_3$, δ , ppm): 7.96 (d, 2H, $C_{10}H_8$), 7.66–7.87 (d, 4H, $C_{10}H_7$), 7.62–7.65 (d, 4H, $C_{10}H_8$), 7.58 (d, 2H, $C_{10}H_7$), 7.56 (d, 2H, $C_{10}H_8$), 6.77–7.54 (d, 8H, $C_{10}H_7$), 2.01–2.85 (m, 8H, $C_{10}H_8$), 1.73 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, δ , ppm): 185.01 (s, 2C, C=O), 135.69 (s, 2C, N- C_6H_5), 135.69 (s, 2C, $C_{10}H_7$), 130.99–135.5 (s, 6C, $C_{10}H_8$), 130.04 (s, 2C, $C_{10}H_7$), 128.16–129.03 (s, 4C, $C_{10}H_8$), 127.23 (s, 2C, $C_{10}H_7$), 126.81 (s, 2C, $C_{10}H_8$), 123.27–126.65 (s, 12C, $C_{10}H_7$), 123.13 (s, 2C, $C_{10}H_8$), 102.8 (s, 2C, $C_{10}H_7$), 24.88–29.19 (s, 4C, $C_{10}H_8$), 16.65 (s, 2C,

CH_3). MS (ESI, m/z): 731 $[M]^+$. HRMS (ESI): found 731.34; calcd for $C_{22}H_{19}ON$ $[M]^+$ 731.29.

Norbornene Homo- and Copolymerization with 1-Octene

Solution polymerizations of norbornene were carried out in a 100-mL two-necked round-bottomed flask containing a magnetic stir bar and connected with a vacuum system. A typical copolymerization procedure is as follows; a $B(C_6F_5)_3$ solid was introduced into a two necked round-bottom flask containing a magnetic stirrer, the toluene solvent was then introduced followed by $B(C_6F_5)_3$. Then an NB toluene solution (0.0425 mol/L), and 1-octene were added sequentially to the flask. Finally, the designated amount of Ni or $Pd(bchkni)_2$ complex toluene solution was added to initiate the polymerization. The reaction solution was kept well stirred at a constant polymerization temperature for 30 min and under inert gas atmosphere. The total volume was kept constant at 10 mL. The reaction was terminated by addition of 40.0 mL of acidic ethanol ($V_{\text{ethanol}}/V_{\text{HCl}} = 10:1$). The resulting precipitated polymers were collected by filtration and washed with ethanol several times, and were dried under vacuum for 24 h until the weight of the polymers did not decrease. The yield was determined by gravimetry. Polymerization runs were carried out at least three times to ensure the reproducibility.

RESULTS AND DISCUSSION

Ligand and Complexes Syntheses

The benzocyclohexan-ke-tonaphthylimine ($bchkni$) was efficiently prepared via the condensation of 2-acetyl-1-tetralone and α -naphthyl-amine according to the literature method. Further treatment of the $bchkni$ with $[Et_4N]_2NiBr_4$ or $[Et_4N]_2PdCl_4$ afforded the desired Ni or $Pd(bchkni)_2$ complex in 47.1–51% yields. Although these complexes had good thermal stability ($T_d > 200^\circ C$), they were so insensitive to moisture and oxygen that they must be stored in the glove box. And the ligand and complexes showed good solubility in common organic solvents (such as $CHCl_3$, CH_2Cl_2 , toluene, and cyclohexane) as well as o -dichlorobenzene.

All synthesized compounds were characterized by elemental analysis and 1H - and ^{13}C -NMR spectrometry. The signals of the naphthyl-imine protons for the $bchkni$ disappeared completely in the 1H -NMR spectra of both Ni and $Pd(bchkni)_2$ complexes. And the chemical shifts of the N-substituent slightly shifted downfield in comparison with that in benzocyclohexan-ke-tonaphthylimine owing to the coordination of the NHOs to the metal center (as shown in Figure 1). The chemical shift of the complexes in ^{13}C -NMR was moved to the downfield compared to the ligand, which further determine the successful of coordination. The structure of the Ni and $Pd(bchkni)_2$ catalysts were very similar to the catalysts which had been reported recently.⁴⁰ According to the X-ray crystallographic structure analysis, the coordination geometry of complexes were mononuclear and nearly ideally a four-coordinate, square-planar configuration. The nickel or palladium ion was arranged in a nearly perfect square-planar coordination environment where β -ketoamino acts as a monoanionic bidentate N, O-chelator, and lies in the trans-configuration to create two stable six-membered metallacyclic chelate rings.

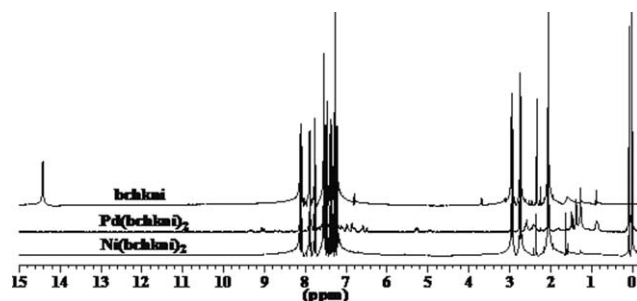


Figure 1. $^1\text{H-NMR}$ spectra of bchkni, Ni and $\text{Pd}(\text{bchkni})_2$ complexes.

Homo-Polymerization of NB

Preliminary blank experiments were conducted to check the polymerization activity with Ni or $\text{Pd}(\text{bchkni})_2$ complexes, no polymer was obtained in the absence of $\text{B}(\text{C}_6\text{F}_5)_3$. However, the vinyl polymerization of NB with Ni or $\text{Pd}(\text{bchkni})_2/\text{B}(\text{C}_6\text{F}_5)_3$ catalytic systems has been successfully carried out under various conditions. Therefore, all the polymerizations were carried out in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$. The obtained PNBs were completely soluble in chlorobenzene and dichlorobenzene at room temperature and partly dissolved in chloroform, which implying that the homopolymer of PNBs were much more stereo regularity.⁴¹ Both complexes exhibited high activity toward the homo-polymerization of NB (as high as 2.7×10^5 $g_{\text{polymer}}/\text{mol}_{\text{Ni}}\cdot\text{h}$, for $\text{Ni}(\text{bchkni})_2/\text{B}(\text{C}_6\text{F}_5)_3$ and 2.3×10^5 $g_{\text{polymer}}/\text{mol}_{\text{Pd}}\cdot\text{h}$ for $\text{Pd}(\text{bchkni})_2/\text{B}(\text{C}_6\text{F}_5)_3$, respectively.). TGA analysis results showed that the homopolymers exhibited good thermal stability than copolymers and the glass transition temperature of the homopolymers were 286.2°C obtained by $\text{Ni}(\text{bchkni})_2$ and 275.2°C obtained by $\text{Pd}(\text{bchkni})_2$, respectively (as seen in Table I).

To investigate the influence of the catalysts framework on the polymerization activity, a series of experiments in the presence of complex Ni or $\text{Pd}(\text{bchkni})_2/\text{B}(\text{C}_6\text{F}_5)_3$ system at different condition such as the reaction temperature have been done. The

catalytic activities of two complexes gradually increase first and then decrease with reaction temperature increasing. Increasing temperature is helpful to enhance the yield and activity, but the activity decreases with temperature further increase probably because of thermal instability, the highest yield and activity value can be achieved when reaction temperature is up to the range from 50 to 70°C.

Copolymerization of NB with 1-Octene

A series of experiments in the presence of complex Ni or $\text{Pd}(\text{bchkni})_2/\text{B}(\text{C}_6\text{F}_5)_3$ system in toluene at constant temperature were performed with different comonomers and monomer feed ratios. The results of copolymerization of norbornene and higher 1-alkene (1-hexene, 1-octene, 1-decene) with various Ni or $\text{Pd}(\text{bchkni})_2/\text{B}(\text{C}_6\text{F}_5)_3$ catalytic systems and the yield and activity were summarized in Table II. We can see that the order of activity is 1-hexene > 1-octene > 1-decene as the literature reported.¹² The activities detected in copolymerization of NB with 1-alkene by $\text{Ni}(\text{bchkni})_2/\text{B}(\text{C}_6\text{F}_5)_3$ systems ($0.2\text{--}2.3 \times 10^5$ $g_{\text{polymer}}/\text{mol}_{\text{Ni}}\cdot\text{h}$) were somewhat higher in comparison with the activities observed by $\text{Pd}(\text{bchkni})_2/\text{B}(\text{C}_6\text{F}_5)_3$ systems ($0.2\text{--}1.7 \times 10^5$ $g_{\text{polymer}}/\text{mol}_{\text{Pd}}\cdot\text{h}$).

To study the influence of the monomer feed ratios on the polymerization activity as well as on the incorporation rates. As shown in Table I, the 1-octene contents in the copolymers were 8.9–14.0% for $\text{Ni}(\text{bchkni})_2/\text{B}(\text{C}_6\text{F}_5)_3$ and 8.8–14.6% for $\text{Pd}(\text{bchkni})_2/\text{B}(\text{C}_6\text{F}_5)_3$ by varying the comonomer feed ratios from 10 to 70% (see Table I). For both catalytic systems, the presence of 1-octene dramatically decreased the polymer productivity and molecular weights. Although the yields detected in copolymerization of norbornene and 1-octene using $\text{Ni}(\text{bchkni})_2/\text{B}(\text{C}_6\text{F}_5)_3$ systems (5.3–58.6%) were somewhat higher than that observed by using $\text{Pd}(\text{bchkni})_2/\text{B}(\text{C}_6\text{F}_5)_3$ systems (6.8–44%), the mol % of 1-octene in copolymer was lower. The copolymer composition showed that 1-octene incorporation rate into the copolymer chains is much slower than that of

Table I. NB Homo- and Copolymerization with 1-Octene Catalyzed by $\text{M}(\text{bchkni})_2/\text{B}(\text{C}_6\text{F}_5)_3$ Systems

[Mt]	NB/1-octene (mol/mol)	$M_w \times 10^5$	M_w/M_n	1-octene (mol %) ^a	T_g (°C)	T_d (°C)
Ni	100/0	1.9	2.2	0	282.6	424.6
Ni	90/10	1.4	2.1	8.9	261.1	420.7
Ni	70/30	0.3	2.4	9.1	252	411.4
Ni	50/50	0.2	2	11.6	246.3	403.9
Ni	30/70	0.1	2.3	14.0	244.1	389.0
Ni	10/90	- ^b	- ^b	- ^b	- ^b	- ^b
Pd	100/0	- ^b	- ^b	0	275.2	420.0
Pd	90/10	0.3	2.6	8.8	272.2	408.6
Pd	70/30	0.3	2.3	10.4	268.2	406.5
Pd	50/50	0.2	2.1	12.5	265.4	402.9
Pd	30/70	0.2	2.3	14.6	262.4	396.6
Pd	10/90	- ^b	- ^b	- ^b	- ^b	- ^b

^aDetermined from $^1\text{H-NMR}$ spectra. Higher 1-octene (mol %) = $I_{\text{CH}_3}/(I_{\text{CH}_3} + 1.5I_{\text{C}_2/\text{C}_3})$ (where I_{CH_3} represents the area of the methyl in the higher 1-octene region and $I_{\text{C}_2/\text{C}_3}$ represents the area of the position C_2 and C_3 methine in the norbornene, see Figures 4 and 5), ^bNot determined.

Table II. NB Homo- and Copolymerization with 1-Alkene Catalyzed by $Mt(bchkn)_2/B(C_6F_5)_3$ Systems

[Mt]	NB/alkene (mol/mol)	NB-cohexene Yield (%) ^a	NB-cohexene activity $\times 10^5$ ($g_{polymer}/mol_{Mt}\cdot h$)	NB-cooctene yield (%) ^a	NB-cooctene activity $\times 10^5$ ($g_{polymer}/mol_{Mt}\cdot h$)	NB-codcene yield (%) ^a	NB-codcene activity $\times 10^5$ ($g_{polymer}/mol_{Mt}\cdot h$)
Ni	100/0	71.9	2.7	71.9	2.7	71.9	2.7
Ni	90/10	59.2	2.2	58.6	2.3	57.6	2.3
Ni	70/30	41.3	1.5	37.7	1.5	34.5	1.5
Ni	50/50	21.6	0.8	19.3	0.8	19.7	1
Ni	30/70	5.7	0.2	5.3	0.2	4.2	0.2
Ni	10/90	trace	- ^b	trace	- ^b	trace	- ^b
Pd	100/0	60.3	2.3	60.3	2.3	60.3	2.3
Pd	90/10	44.9	1.7	44	1.7	42.7	1.7
Pd	70/30	28.8	1.1	27.8	1.1	25.2	1.1
Pd	50/50	18.9	0.7	19	0.8	18.1	0.8
Pd	30/70	6.9	0.2	6.8	0.3	5.8	0.3
Pd	10/90	trace	- ^b	trace	- ^b	trace	- ^b

^aConditions: $c[Cat.] = 5.0 \times 10^{-4}$ mol/L; $n[NB]+n[1-alkene] = 0.01$ mol; $n[B]/n[Mt] = 20/1$; $t_p = 0.5$ h; $T_p = 60^\circ C$; Solvent: toluene; $V_p = 10$ mL, ^bNot determined.

norbornene (see Table III). Indeed, the reactivity ratios of the two monomers were determined to be $r_{1-octene} = 0.052$, $r_{NB} = 8.45$ for $Ni(bchkn)_2/B(C_6F_5)_3$ system, and $r_{1-octene} = 0.025$, $r_{NB} = 7.17$ for $Pd(bchkn)_2/B(C_6F_5)_3$ system (Figure 2) by the Kelen-TüdÖs method, illustrated the much higher reactivity of NB. This monomer reactivity order is rather unusual and is not in agreement with a free radical or cationic type polymerization but supports a coordination type mechanism.⁴²

The obtained copolymers were characterized by GPC (Figure 3) at room temperature. Their M_{wS} were in the range from 0.1 to

1.4×10^5 g/mol, and their MWDs appear as a single modal in the GPC curves, which indicated copolymerizations occur at the single active site and the products are the true copolymers instead of blends of the homopolymers.⁴³ In addition, the copolymers showed good solubility in cyclohexane and dichloromethane while pure PNB was insoluble in these solvents. These results given an impression of the high influence of 1-octene on copolymerization product and proved that the products are the true NB/1-octene copolymers instead of blends of homopolymers.

Table III. Copolymerization Results of NB and 1-Octene Catalyzed by $Mt(bchkn)_2/B(C_6F_5)_3$ Systems

[Mt]	1-Octene in the feed (mol %) ^a	1-Octene incorporated	Yield (%) ^c	Polymerization time (min)
Ni	10	- ^b	30.6	1
Ni	20	2.6	9.8	2
Ni	30	4.9	7.6	2
Ni	40	7.2	6.3	10
Ni	50	9.5	4.9	15
Ni	70	11.9	2.3	20
Pd	20	2.7	7.4	5
Pd	30	5.5	5.6	5
Pd	40	7.9	5.2	10
Pd	50	10.2	4.8	15
Pd	70	12.1	2.9	20

^aDetermined from ¹H-NMR spectra. Higher (mol %) = $I_{CH_3}/(I_{CH_3} + 1.5I_{C_2/C_3})$ (where I_{CH_3} represents the area of the methyl in the higher 1-octene region and I_{C_2/C_3} represents the area of the position C₂ and C₃ methine in the norbornene, ^bNot determined, ^cConditions: $c[Cat.] = 5.0 \times 10^{-4}$ mol/L; $n[NB]+n[1-octene] = 0.01$ mol; $n[B]/n[Ni] = 20/1$; $T_p = 60^\circ C$; Solvent: toluene; $V_p = 10$ mL.

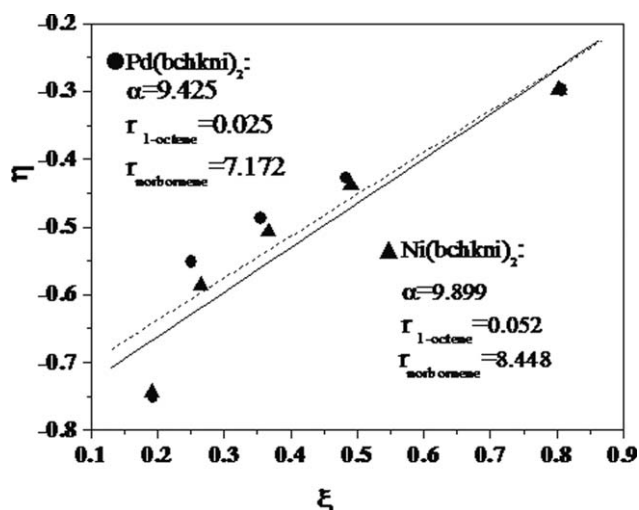


Figure 2. Linear fitting of the NB/1-octene copolymers catalyzed by Ni or $Pd(bchkn)_2/B(C_6F_5)_3$ systems according to Kelen-TüdÖs method: $\eta = (r_1 + \frac{F_2}{\alpha})\xi - \frac{F_2}{\alpha}$, $\eta = \frac{G}{\alpha + F}$, $\xi = \frac{F}{\alpha + F}$, $G = \frac{x(y-1)}{y}$, $F = \frac{x^2}{y}$, $\alpha = \sqrt{F_{min} * F_{max}}$, $F_{min} = \text{minimum}(F)$, $F_{max} = \text{maximum}(F)$, $x = \frac{[1-octene]}{[NB]}$, $y = \frac{d[1-octene]}{d[NB]}$.

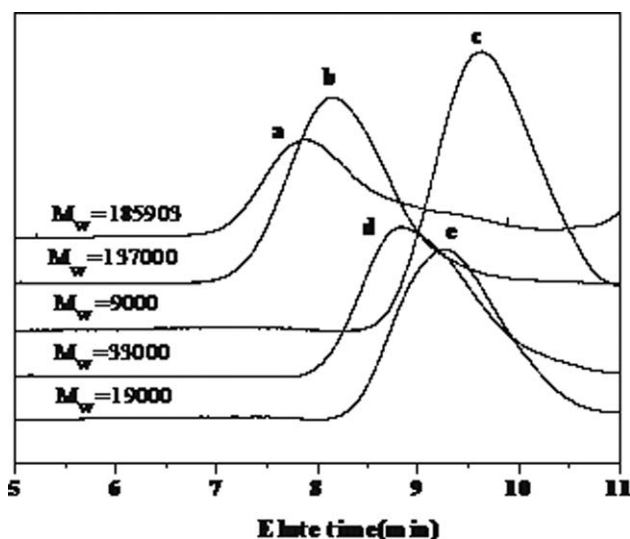


Figure 3. GPC curves of poly(NB-*co*-1-octene) with (a) PNB (b) 8.9%, (c) 14.0% of 1-octene molar ratios obtained by Ni(bchkn)₂/B(C₆F₅)₃ systems; (d) 8.8%, (e) 14.6% obtained by Pd(bchkn)₂.

¹H- and ¹³C-NMR Spectra of the Copolymers^{8,44}

¹H-NMR analysis is further performed to illustrate the structure of the copolymers obtained by Ni or Pd(bchkn)₂/B(C₆F₅)₃ catalytic system (as shown in Figures 4 and 5). Four groups of resonance peaks that appear between 0.8 and 2.3 ppm in the ¹H-NMR spectra of poly(NB-*co*-1-octene). The peak at 0.8–0.9 ppm could be attributed to the methyl hydrogen corresponding to H^{8'}, and peak at 0.9–1.5 ppm could be attributed to methylene hydrogen corresponding to H⁷/H⁵/H⁶/H¹/H³/H⁴/H⁵/H⁶/H⁷, at 1.5–2.1 ppm could be attributed to the methine hydrogen corresponding to H¹/H⁴, at 2.1–2.3 ppm could be attributed to the methine hydrogen corresponding to H²/H³/H^{2'}, respectively. The content of 1-octene in copolymers (see Table I) was calculated by the following literature way (8.9–14.0% for Ni(bchkn)₂/B(C₆F₅)₃ and 8.8–14.6% for Pd(bchkn)₂/B(C₆F₅)₃ catalytic system).⁴⁵ Although the detailed assignments of the resonances are not clear at present, the shapes of the spectra are slightly different from each other; this implies that the microstructure of the copolymers is dependent on the complex used.

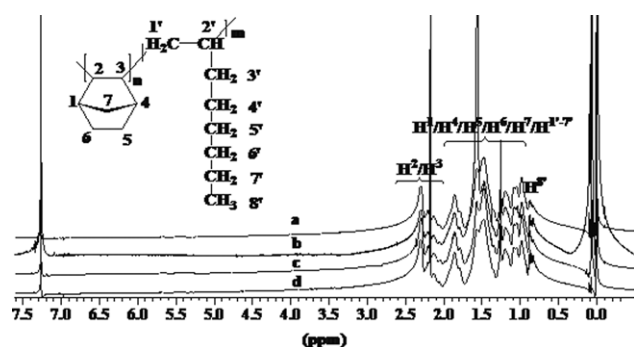


Figure 4. ¹H-NMR spectra of poly(NB-*co*-1-octene) with (a) 8.9%, (b) 9.1%, (c) 11.6%, and (d) 14.0% of 1-octene molar ratios obtained by Ni(bchkn)₂/B(C₆F₅)₃ systems at [B]/[Ni] = 20/1 and 60°C (in CDCl₃).

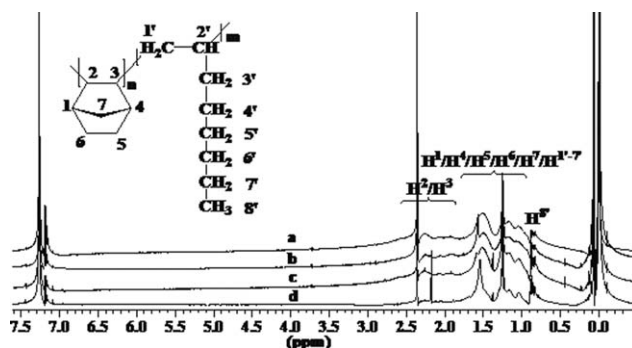


Figure 5. ¹H-NMR spectra of poly(NB-*co*-1-octene) with (a) 8.8%, (b) 10.4%, (c) 12.5%, and (d) 14.6% of 1-octene molar ratios obtained by Pd(bchkn)₂/B(C₆F₅)₃ systems at [B]/[Ni] = 20/1 and 60°C (in CDCl₃).

The ¹³C-NMR spectra of poly(NB-*co*-1-octene) containing 8.9 mol %–14.0 mol % of 1-octene molar ratio obtained with Ni(bchkn)₂/B(C₆F₅)₃ systems are shown in Figure 6. The resonances of methyl (C^{8'}) and methylene (C^{7'}) carbons of hexyl branch and methine carbon (C¹/C⁴) and C²/C³ carbons of 2,3-inserted NB unit are observed at 14, 23, 46–48, and 48–55 ppm together with those of the other carbons around 26.0–46.0 ppm, indicating the production of poly(norbornene-*co*-1-octene) with all the catalytic systems.

FTIR Spectra of the Polymers

FTIR spectra of poly(NB-*co*-1-octene) obtained by the Ni and Pd(bchkn)₂/B(C₆F₅)₃ catalytic system are shown in Figure 7. The absence of absorption at 1620–1680 cm⁻¹, especially at about 960 cm⁻¹ in the spectra which would be assigned to the characteristic transform of stretching of the C=C bond of the ROMP structure of PNB, confirmed to undergo vinyl-type addition polymerization mechanism rather than ROMP mechanism.⁴⁶ The characteristic absorption peak signals at about 941 cm⁻¹ could be attributed to the ring of bicycle [2.2.1]heptane as Kennedy and Makowski noted.⁴ Moreover, There are no absorptions at about 3050 cm⁻¹ and 2100 cm⁻¹ to the characteristic trans form of stretching of the C=C and C–H bonds of

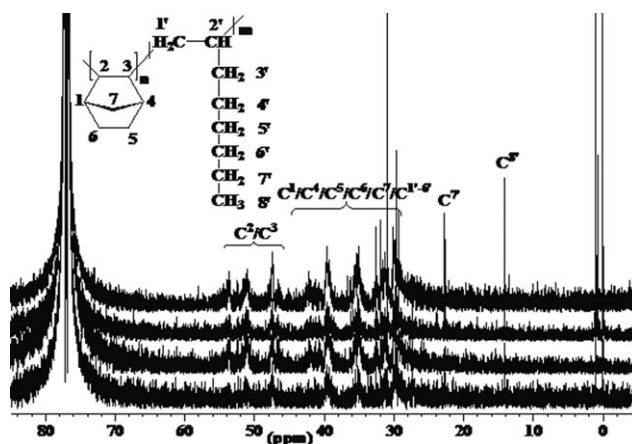


Figure 6. ¹³C-NMR spectra of poly(NB-*co*-1-octene) with (a) 8.9%, (b) 9.1%, (c) 11.6%, and (d) 14.0% of 1-octene molar ratios obtained by Ni(bchkn)₂/B(C₆F₅)₃ systems at [B]/[Ni] = 20/1 and 60°C (in CDCl₃).

the 1-octene, this indicated that the octene has been inserted into the chains of the copolymers and to be true copolymer rather than blend polymer.

TGA and DSC Analyses of Polymers

As shown in Table I, the thermal stabilities of all copolymers are similar and decompositions occur at high temperatures from 350 to 450°C. The decomposition temperature decreased with the increasing 1-octene content in copolymers and the T_d of the polymers obtained by Ni(II)/B(C₆F₅)₃ are higher than that of the polymers obtained by Pd(II)/B(C₆F₅)₃.

The glass transition temperatures (T_g) of the copolymers were investigated by DSC analyses which were shown in Table I. The T_g values of copolymers decreased as the 1-octene molar ratio increased in copolymers and the T_g of the polymers obtained by Ni(bchkni)₂/B(C₆F₅)₃ systems ($T_g = 244.1$ – 261.1 °C) were lower than that of the polymers obtained by Pd(bchkni)₂/B(C₆F₅)₃ systems ($T_g = 262.4$ – 272.2 °C), indicating the formation of the uniform random copolymers regardless of the metal complex used. The results also testified the microstructures of the copolymers which were depended on the used metal complex. Tritto et al.⁴⁷ reported that the stereoregularity of the NB sequence affected the T_g value of poly(NB-*co*-ethylene) with high NB contents. TGA and DSC analyses indicate that the copolymers obtained by both Ni and Pd(bchkni)₂/B(C₆F₅)₃ catalytic systems exhibit good thermo stability under nitrogen.

WAXD of the Polymers

The powder WAXD patterns of poly(NB-*co*-1-octene) prepared by Ni or Pd(bchkni)₂/B(C₆F₅)₃ catalytic systems are shown in Figure 8. Two broad halos at 2θ values of 10.42 and 18.64 were observed. The occurrence of two halos was characteristic for PNB, and the corresponding distances amount to 8.50 and 4.77 Å.⁴⁸ No traces of Bragg reflections are revealed in the characteristic of crystalline regions, and the polymers are therefore non-

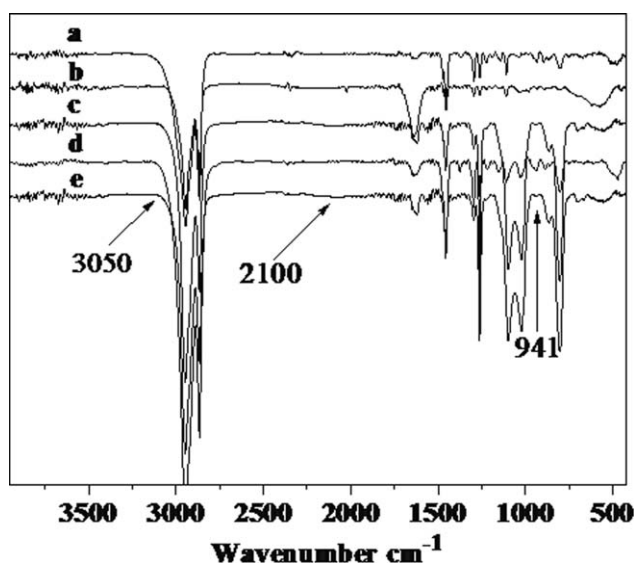


Figure 7. FTIR spectra of poly(NB-*co*-1-octene) with (a) PNB, (b) 8.9%, (c) 14.0% of 1-octene molar ratios obtained by Ni(bchkni)₂/B(C₆F₅)₃ systems; (d) 8.8%, (e) 14.6% obtained by Pd(bchkni)₂.

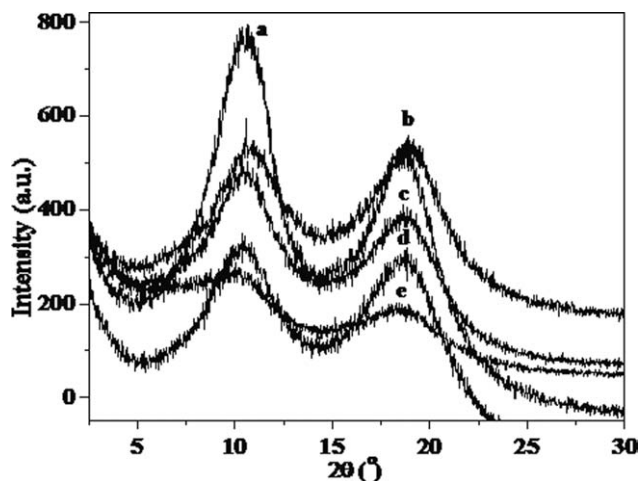


Figure 8. WAXD curves of poly(NB-*co*-1-octene) with (a) PNB, (b) 8.9%, (c) 11.6% of 1-octene molar ratios obtained by Ni(bchkni)₂/B(C₆F₅)₃ systems; (d) 8.8%, (e) 12.5% obtained by Pd(bchkni)₂.

crystalline.³⁶ The packing of the copolymers changes little when the incorporated 1-octene contents is low (8.8% for Ni(bchkni)₂/B(C₆F₅)₃ system, and 8.9% for Pd(bchkni)₂/B(C₆F₅)₃ system), but the intensity of both halos become weaker with the increase of 1-octene content (up to 14.0% for Ni(bchkni)₂/B(C₆F₅)₃ system and 14.6% for Pd(bchkni)₂/B(C₆F₅)₃ system, respectively). This also shows that the 1-octene monomers have incorporated to the polymer backbone and the packing density decreased relative to PNB through the copolymerization of NB and 1-octene, and the packing density of the copolymers obtained by Ni(bchkni)₂/B(C₆F₅)₃ system are bigger than these obtained by Pd(bchkni)₂/B(C₆F₅)₃ system.

CONCLUSIONS

The results presented in this article proved that the utility of synthesizing novel late transition metals complexes Ni and Pd(benzocyclohexan-ketonaphthylimino)₂ with heterocyclic ligand as appropriate candidates for olefin polymerization. Both Ni(II) and Pd(II) complexes bearing benzocyclohexan-ketonaphthylimine ligand can catalyze the vinyl polymerization of norbornene with high activity in the presence of B(C₆F₅)₃, and Ni(bchkni)₂ exhibited a higher activity than Pd(bchkni)₂. The molecular weight of the soluble PNB was high with narrow molecular weight distributions. Furthermore, the copolymerization of NB with 1-octene was effectively completed by both Ni or Pd(bchkni)₂/B(C₆F₅)₃ catalytic systems, and the latter show slight lower activity. The content of 1-octene incorporated into copolymer ranged from 8.8 to 14.6 mol % by varying the comonomer feed ratios. The solubility of the copolymers improved relative to PNBs.

ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (21164006).

REFERENCES

- Li, X. F.; Hou, Z. M. *Coord. Chem. Rev.* **2008**, *252*, 1842.
- Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733.
- Goodall, B. L.; McIntosh, L. H., III; Rhodes, L. F. *Macromol. Symp.* **1995**, *89*, 421.
- Kennedy, J. P.; Makowski, H. S. *J. Macromol. Sci. Chem.* **1967**, *1*, 345.
- Gaylord, N. G.; Mandal, B. M.; Martan, M. J. *Polym. Sci. Polym. Lett. Ed.* **1976**, *14*, 555.
- Gaylord, N. G.; Deshpande, A. B. *J. Polym. Sci. Polym. Lett. Ed.* **1976**, *14*, 613.
- Haselwander, T. F. A.; Heitz, W.; Krügel, S. A.; Wendorff, J. H. *Macromol. Chem. Phys.* **1996**, *197*, 3435.
- Jung, H. Y.; Hong, S. D.; Jung, M. W.; Lee, H.; Park, Y. W. *Polyhedron* **2005**, *24*, 1269.
- Cai, Z. G.; Harada, R.; Nakayama, Y.; Shiono, T. *Macromolecules* **2010**, *43*, 4527.
- Xing, Y. P.; He, X. H.; Chen, Y. W.; Nie, H. R.; Wu, Q. *Polym. Bull.* **2010**, *65*, 13.
- Roberto, M.; Laura, B.; Andrea, R.; Francesco, D. C.; Incoronata, T.; Udo, M. S. *Macromolecules* **2011**, *44*, 795.
- Shiono, T.; Sugimoto, M.; Hasan, T.; Cai, Z. G.; Ikeda, T. *Macromolecules* **2008**, *41*, 8292.
- Zhong, L.; Cui, K.; Xie, P.; Chen, J. Z.; Ma, Z. J. *Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 1617.
- Steinhausler, T.; Koros, W. J. *J. Polym. Sci. Part B: Polym. Phys.* **1997**, *35*, 91.
- Kaminsky, W.; Bark, A.; Steiger, R. J. *Mol. Catal.* **1992**, *74*, 109.
- Kaminsky, W. *Macromol. Chem. Phys.* **1996**, *197*, 3907.
- Wu, Q.; Lu, Y. J. *Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 1421.
- Nomura, K.; Naga, N.; Miki, M.; Yanagi, K.; Imai, A. *Organometallics* **1998**, *17*, 2152.
- Nomura, K.; Naga, N.; Miki, M.; Yanagi, K. *Macromolecules* **1998**, *31*, 7588.
- Nomura, K.; Fujii, K. *Organometallics* **2002**, *21*, 3042.
- Nomura, K.; Fujii, K. *Macromolecules* **2003**, *36*, 2633.
- Wang, W.; Tanaka, T.; Tsubota, M.; Fujiki, M.; Yamanaka, S.; Nomura, K. *Adv. Synth. Catal.* **2005**, *347*, 433.
- Wang, W.; Fujiki, M.; Nomura, K. *J. Am. Chem. Soc.* **2005**, *127*, 4582.
- Zhang, H.; Nomura, K. *J. Am. Chem. Soc.* **2005**, *127*, 9364.
- Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267.
- Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888.
- Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Freidrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460.
- Connor, E. F.; Younkin, T. R.; Henderson, J. I.; Hwang, S.; Grubbs, R. H.; Roberts, W. P.; Litzau, J. J. *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 2842.
- Benedikt, G. M.; Elce, E.; Goodall, B. L.; Kalamarides, H. A.; McIntosh, L. H., III; Rhodes, L. F.; Selvy, K. T.; Andes, C.; Oylar, K.; Sen, A. *Macromolecules* **2002**, *35*, 8978.
- Blank, F.; Janiak, C. *Coord. Chem. Rev.* **2009**, *253*, 827.
- Bao, F.; Lü, X. Q.; Chen, Y. *Polym. Bull.* **2007**, *58*, 495.
- Zhang, D.; Jin, G. X.; Weng, L. H.; Wang, F. *Organometallics* **2004**, *23*, 3270.
- He, X. H.; Yao, Y. Z.; Luo, X.; Zhang, J. K.; Liu, Y. H.; Zhang, L.; Wu, Q. *Organometallics* **2003**, *22*, 4952.
- He, X. H.; Chen, Y. W.; Liu, Y. M.; Yu, S. X.; Hong, S. G.; Wu, Q. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 4733.
- He, X. H.; Chen, Y. W.; Liu, Y. M.; Chen, M. Q.; Yu, S. X.; Hong, S. G.; Wu, Q. *e-Polymers* **2008**; no. 083.
- He, F. P.; Chen, Y. W.; He, X. H.; Chen, M. Q.; Zhou, W. H.; Wu, Q. *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 3990.
- Yu, S. X.; He, X. H.; Chen, Y. W.; Liu, Y. M.; Hong, S. G.; Wu, Q. *J. Appl. Polym. Sci.* **2007**, *105*, 500.
- Zhou, W. H.; He, X. H.; Chen, Y. W.; Chen, M. Q.; Shi, L.; Wu, Q. *J. Appl. Polym. Sci.* **2011**, *120*, 2008.
- Wang, L. Y.; Li, Y. F.; Zhu, F. M.; Wu, Q. *Eur. Polym. J.* **2006**, *42*, 322.
- Wang, K. T.; Chen, Y. W.; He, X. H.; Liu, Y. M.; Zhou, W. H. *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 3304.
- Mast, C.; Krieger, M.; Dehnicke, K.; Greiner, A. *Macromol. Rapid. Commun.* **1999**, *20*, 232.
- Peruch, F.; Cramail, H.; Deffieux, A. *Macromol. Chem. Phys.* **1998**, *199*, 2221.
- Gao, H. Y.; Chen, Y.; Zhu, F. M.; Wu, Q. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 5237.
- Liu, S. R.; Li, B. X.; Liu, J. Y.; Li, Y. S. *Polymer* **2010**, *51*, 1921.
- Peruch, F.; Cramail, H.; Deffieux, A. *Macromol. Chem. Phys.* **1998**, *199*, 2221.
- Tsujino, T.; Saegusa, T.; Furukawa, J. *Makromol. Chem.* **1965**, *85*, 71.
- Forsyth, J.; Perena, J. M.; Benavente, R.; Perez, E.; Tritto, I.; Boggioni, L.; Brintzinger, H. H. *Macromol. Chem. Phys.* **2001**, *202*, 614.
- Wilks, B. R.; Chung, W. J.; Ludovice, P. J.; Rezac, M. R.; Meakin, P.; Hill, A. J. *J. Polym. Sci. Part B: Polym. Phys.* **2003**, *41*, 2185.