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Synthesis of well defined C-C bridged Ni(II) complexes bearing β-ketoiminato-fluorene ligands by bifluorenyl in situ coupling and application for norbornene (co)polymerization

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ABSTRACT: Well defined 9-substituted fluorene C-C bridged constrained geometry configuration (CGC) Ni(II) complexes bearing β-ketoiminato-fluorene ligands， $\{CH_3C(O)CHC[N(\text{ fluorenyl})]\text{-}CH_3\}_2Ni$ (**Ni1**) and $\{CF_3C(O)CHC[N(\text{ fluorenyl})]\text{-}CH_3\}_2Ni$ (**Ni2**) were synthesized by coordination reaction and in situ coupling reaction in the presence of $(DME)NiBr_2$. The complexes were characterized by NMR and elemental analyses. And the quality **Ni1** and **Ni2** crystals structure was confirmed from X-ray with C-C bridged constrained geometry configuration. On activation with $B(C_6F_5)_3$, the Ni-based complexes showed high catalytic activities for norbornene homo-polymerization, activities up to 10^6 g PNB

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molNi^{-1} h^{-1}. The copolymerization of 2-heptoxymethylene norbornene(HN) with norbornene by the pre-catalysts **Ni1** and **Ni2** was also explored in the presence of B$(C_6F_5)_3$. High molecular weight polymers with unimodal molecular weight distributions were obtained, indicating that the nature of the polymerization was single site. The catalytic activity, co-monomer incorporation and the properties of the resultant polymers can be controlled over a wide range by tuning the catalyst structures and reaction parameters.

Keywords: bifluorenyl coupling, vinyl-addition polymerization, C-C bridged complexes, constrained geometry configuration, norbornene

1. Introduction

Polymerizations of cycloolefins have attracted intensive research from both academia and industry.[1-6] To date, norbornene is recognized as a versatile monomer，which easily polymerizes in the presence of vinyl addition polymerization catalysts. Since the vinyl-poly(norbornene) has many unique physical characteristics such as good mechanical strength, heat resistivity, a large refractive index, a small optical birefringence, a very high glass transition temperature (T_g), it has been extensively applied to many electronic and optical applications.[7] Many interests are focused on this kind of polymerization. Vinyl-type PNBs can be prepared by transition metal catalysts based on titanium,[8] zirconium,[9] chromium,[10] cobalt,[11] nickel,[12] palladium,[13] and copper complexes.[14] Nickel complexes are important type of catalysts for vinylic polymerization of NB and have a great potential to effectively polymerize functional

NB.[15] For example， a lot of nickel catalysts were reported to be able to copolymerize NB derivatives containing pendant silyls, carboxyls, amines, sulfonamides to improve polymer solubility and potentially other application-specific properties such as stronger adhesion to substrates and reduced dielectric constant.[16] In general, these nickel(II) complexes mainly adopt one bidentate neutral ligand or monoanionic ligand such as [NN] type (e.g., anilido-imine， benzamidinato, β-diketiminato, diimine, imino-pyrrolylato, benzimidazole, bipyridine, α-dioxime), [NO] type (e.g.,β-ketoiminato, β-diketonato, salicylaldiminato, acylhydrazone, indanimine).[17-22] Due to the significance and versatility of the ligands in the homogeneous olefin polymerization nickel(II) catalysts, the design of the pre-catalysts is mainly focused on the design and modification of the ligand itself. We have had a longstanding interest in bis(β-ketoiminato)-based catalysts of olefin polymerization,[23−26] due to the remarkable simplicity of ligand synthesis and rich opportunities for fine-tuning of its steric and electronic properties by the introduction of substituent into the phenyl rings of the β-ketoiminato ligand. Up to now, synthesis of bifluorene units as an extension of fluorenes for ligand applications of the transition metal catalyst has received little attention. Coupling of 9-substituted fluorenes has been accomplished using [Cu^I(tris(2-pyridyl-methyl)amine)CH_3CN]PF_6,[27] nickel halides,[28] $LiCrH_2$,[29] Grignard couplings,[30] (η^1-$C_{13}H_9$)Mn(CO)[31] and (η5-fluorenyl)Ti(IV) complexes.[32.] Yields in these bifluorene syntheses are not ideal or multiple steps were required to prepare fluorene precursors. Bradley *et al.* reported one pot synthesis of bifluorenes from the corresponding fluorenes via a readily available and inexpensive cobalt halide radical coupling agent. [33] Considering the steric and electronic effect in the design of catalyst, both the combination of fluorene and β-ketoiminato would to be expected lead a new catalyst for olefin homomerization and copolymerization. To the best of our knowledge, herein, we first reported the synthesis of well defined 9-substituted fluorene C-C bridged constrained geometry configuration (CGC) complexes bearing β-ketoiminato-fluorene ligands. Their catalytic behaviors in norbornene homopolymerization and copolymerization with 2-heptoxymethylene norbornene(HN) in the presence of cocatalyst tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) were also investigated.

2. Experimental section

2.1. Materials

All manipulations of air-sensitive and/or water-sensitive compounds were performed under a dry nitrogen atmosphere by means of standard Schlenk techniques. Toluene and THF were refluxed and distilled from sodium/benzophenone ketyl under dry nitrogen prior to use. The $B(C_6F_5)_3$ (95%) and norbornene (bicyclo-[2.2.1]hept-2-ene) (98%) were all purchased from Aldrich Chemical, and NB was purified by distillation over sodium and used as a solution 0.4g/mL (0.0425 mol/L) in toluene. 9-Aminofluorenehydrochloride was purchased from Aldrich (98%). All the other commercial chemicals were used as received.

2.2 Characterization

The ^1H and ^{13}C NMR spectra of the ligands, Ni(II) complexes, and copolymers were obtained on a Bruker ARX 600 NMR spectrometer at room temperature with $CDCl_3$ as solvent and tetramethylsilane (TMS, δ=0) as an internal reference. Elemental analyses were characterized by means of elemental analysis with Vario Elementar III. Fourier transform infrared (FTIR) spectra were recorded as KBr pellets on 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 (PL-GPC220), Refractive Index Detector, 1,2,4-trichlorobenzene as an eluent with a flow rate of 1.0mL/min and the detector at 150 ºC. Thermo gravimetric analysis (TGA) was performed on a TAQ600 SDT for thermogravimetry at a heating rate of 10℃/min under nitrogen. 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 .

2.3 Synthesis of 2-heptoxymethylene norbornene (HN).

The 5-norbornene-2-methanol (6.0 mL, 0.05 mol) and NaH (9.6 g, 0.24 mol) were charged into a 250mL three-necked flask containing 80 mL of THF under nitrogen protection at room temperature under vigorous stirring at room temperature. The mixture was heated and refluxed for 3 h, the 1-bromoheptane (15.7 mL, 0.1 mol) was added dropwise, and the mixture was stirred for additional 24 h at 78 °C. Then, the mixture was washed by deionized water, and the organic layer was separated and dried with magnesium sulfate for 24 h. After removing the magnesium sulfate, the solution was concentrated by evaporation. The raw product was purified by the column chromatography with petroleum ether and ethyl acetate (8/1 in v/v). After evaporation, 8.9 g of HN (yield, 60%) was finally obtained. ^{1}H NMR ($CDCl_3$, d, ppm): 6.18–5.89 (m, 2H), 3.8–3.2 (m, 4H), 3.06–0.82 (m, 13H), 0.82 (t, 3H).

2.4 Synthesis of β-ketoiminato-fluorene ligands **L1−L2** and Complexes **Ni1**-**Ni2**

Synthetic procedure for **L1**: The starting material 9-fluorenylamine was prepared by washing CH_2Cl_2 solution of 9-aminofluorenehydrogen chloride with sat. aq $NaHCO_3$ before used.[34] To a solution of 9-fluorenylamine (1.82 g, 10 mmol) in anhydrous ethanol (30 mL), acetylacetone (1.1 mL, 10 mmol) and 0.5 mL acetic acid were added. After refluxing with stirring for 30 h, the resulting mixture was cooled to room temperature to afford a yellow solid. The solid was further purified by silica column chromatography (10/1 v/v petroleum ether/ethyl acetate) to give pale yellow crystal L1, yield 1.58 g (65%).^{1}H NMR($CDCl_3$, δ, ppm): 12.29 (s, 1H, O¨H-N), 8.42-8.94(m, 8H, $C_{13}H_9$), 6.89(d, 1H, $C_{13}H_9$), 6.33(s, 1H, CH), 3.08(s, 3H, CH_3), 3.20(s, 3H,CH_3).^{13}C NMR ($CDCl_3$,δ,ppm):19.81, 25.63, 54.40, 127.91, 131.13, 133.62, 136.35, 143.68, 147.82, 150.73, 173.51. Analysis calculated for $C_{18}H_{16}NO$：C, 82.10; H, 6.50; N 5.32,; Found: C, 82.14; H, 6.58; N, 5.29.

Synthetic procedure for **L2**: $NaHCO_3$ saturated solution (20 mL) was added to a solution of 9-aminofluorenehydrogen chloride (3.3 g, 15 mmol, 1 mmol in 4 mL of CH_2Cl_2). The solution was stirred for 0.5 h and was then separated the organic phase .The organic phase was collected, and then the solvent was removed under low pressure. 9-Fluorenylamine was obtained as a colorless oily liquid. To a solution of 9-fluorenylamine (2.73 g, 15 mmol) in anhydrous ethanol (70 mL), 1,1,1-Trifluoro-2,4-pentanedione(1.83mL, 15mol), and 1 mL acetic acid were added. After refluxing with stirring for 48h, the resulting mixture was cooled to room temperature to afford a yellow solid. The solid was further purified by silica column chromatography (10/1 v/v petroleum ether/ethyl acetate) to give yellow solid L2. Yield: 2.14 g (45%). ^{1}H NMR($CDCl_3$, δ, ppm): 14.02(s, 1H, O$\cdots$H-N), 7.8-8.4(m, 8H, $C_{13}H_9$), 6.49(d, 1H, $C_{13}H_9$), 5.93(s, 1H,CH), 2.08(s, 3H,CH_3).^{13}C NMR($CDCl_3$, δ, ppm): 16.9, 54.3, 66.1, 128.5, 130.7, 132.4, 133.0, 144.2, 145.9, 158.3, 180.2 Analysis calculated for $C_{18}H_{13}NOF_3$： C, 68.13; H, 4.45; N, 4.41; Found: C, 68.20; H,4.42 ; N, 4.48.

The nickel complexes were synthesized by the reaction of (DME)$NiBr_2$ with 1 equiv. of the corresponding ligand in CH_2Cl_2. A typical synthetic procedure can be described for **Ni1** as follows.

Syntheis of complex **Ni1**

A 100 mL Schlenk flask was charged with ligand **L1** (1.32 g, 5 mmol), sodium hydride (0.6 g, 15 mmol) and 30 mL THF. After stirring for 4 h at room temperature, the resulting mixture was centrifuged and the upper clear solution was transferred and concentrated in vacuum to afford a pale yellow solid residue. After washing with hexane (20 mL), the sodium salt was obtained. A solution containing the sodium salt and (DME)$NiBr_2$ (1.86 g, 5 mmol) in CH_2Cl_2 (40 mL) was stirred at room temperature. The reaction mixture was stirred at room temperature for 24 h and filtered, and the filtrate was concentrated in vacuum. Dry hexane was then added via syringe, precipitating a green solid. Green single crystals suitable for X-ray analysis were recrystallized from hexane/CH_2Cl_2 at room temperature. Yield: 0.87 g (56%).^{1}H NMR($CDCl_3$, δ, ppm): 1.92 (s, 6H, CH_3),2.23 (s, 6H, CH_3)，4.59(s, 2H,CH),7.11-7.89(m, 16H, $C_{13}H_8$). ^{13}C NMR($CDCl_3$, δ, ppm): 17.21, 25.23, 64.40, 127.61, 131.23, 134.32, 140.36, 143.68, 147.82, 150.73, 169.54. Anal. Calc. for $C_{36}H_{30}O_2N_2Ni$: C, 74.38; H, 5.20; N, 4.82. Found: C, 74.40; H, 5.19; N, 4.79%.

Complex **Ni2** was prepared in 45% yield. Green single crystals suitable for X-ray analysis were recrystallized from hexane/CH_2Cl_2 at room temperature. ^{1}H NMR($CDCl_3$, δ, ppm): 1.36 (s, 6H, CH_3),5.33 (s, 2H,CH)7.09-7.16(m, 16H, $C_{13}H_8$). ^{13}C NMR($CDCl_3$, δ, ppm): 20.36, 74.40, 125.89, 127.65, 128.63, 130.41, 131.62, 135.40, 136.68, 140.82, 148.62, 159.66, 170.54. Anal. Calc. for $C_{36}H_{24}O_2F_6N_2Ni$: C, 62.73; H, 3.51; N, 4.06.Found: C, 62.75; H, 3.48; N, 4.09%.

2.5 Procedure for NB homopolymerization

In a typical experiment, 50 μmol of $B(C_6F_5)_3$ in 2 mL of toluene, 2.35mL (0.0425mol/L) toluene solution of NB and 4.65 mL toluene were placed in a Schlenk flask (100 mL) with a strong stirrer under a nitrogen atmosphere. After stirring at 60 °C for 1min, 5 μmol of the nickel complex in 1 mL toluene was added to the mixture via a syringe and the reaction was initiated. The total volume was kept constant at 10 mL. After 10 minutes, acidic ethanol (ethanol–HCl = 9/1) was added to terminate the reaction. The PNB was isolated by filtration, washed with ethanol, dried at 50 °C for 24 h under vacuum. The condition of other NB homopolymerization setup is similar to this procedure except that the amount of $B(C_6F_5)_3$ was added at the beginning of the process.

2.6 Copolymerization of NB with HN

In a typical experiment, 50 μmol of $B(C_6F_5)_3$ in 2 mL of toluene,1.64 mL (0.0425 mol/L) toluene solution of NB, 1.33 mL 2-heptoxymethylene norbornene (HN) and 4.13 mL toluene were placed in a Schlenk flask (100 mL) with a strong stirrer under a nitrogen atmosphere. After stirring at 60 °C for 1min, 5 μmol of the nickel complex in 1 mL toluene was added to the mixture via a syringe and the reaction was initiated. The total volume was kept constant at 10 mL. After 30 minutes, acidic ethanol (ethanol–HCl = 9/1) was added to terminate the reaction. The polymer was isolated by filtration, washed with ethanol, dried at 50 °C for 24 h under vacuum. The condition of other copolymerization reaction of NB with HN is similar to this procedure except that the amount of NB and HN was added at the beginning of the process.

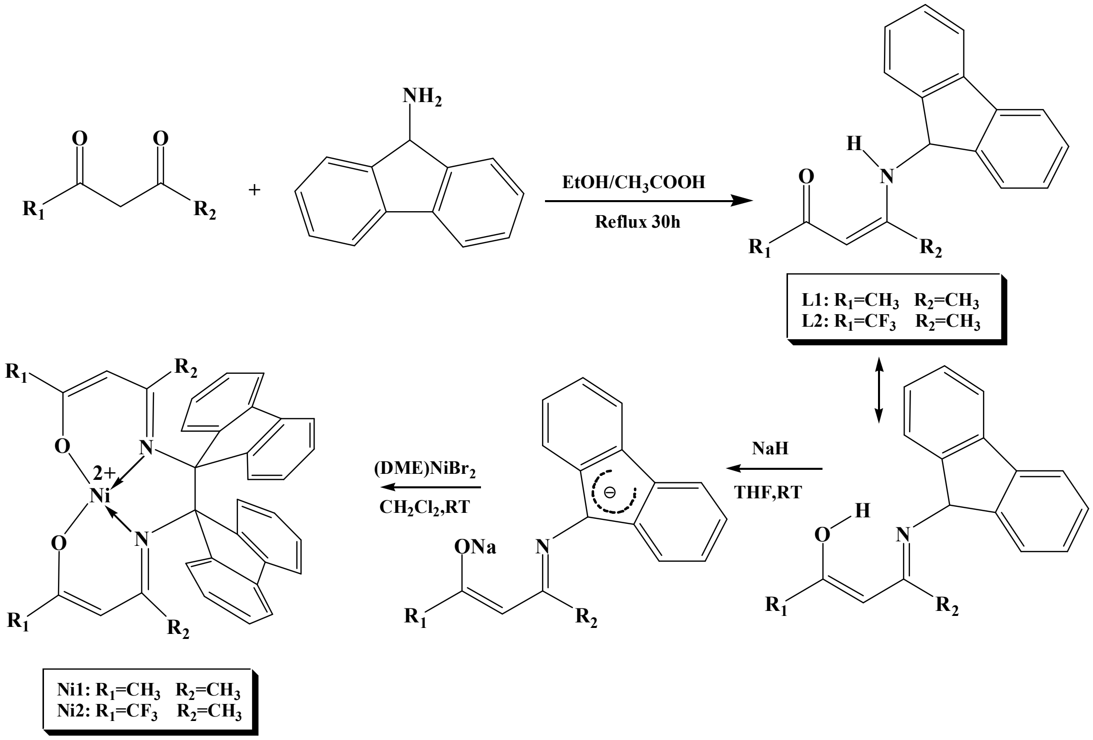
2.7 X-ray crystallography

Crystals suitable for X-ray analysis were manipulated in a glove box. The intensity data were collected with the ω scan mode (296(2)K) on a Bruker Smart APEX diffractometer with a CCD detector using Mo Kα radiation ($\lambda = 0.71073$ Å). Absorption corrections were performed using the SADABS program. The crystal structures were solved using the SHELXTL program and refined using full matrix least-squares techniques. The positions of hydrogen atoms were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbons.

3 Results and discussion

Synthesis and characterization of the complex

A general synthetic route for the C-C bridged constrained geometry configuration (CGC) Ni(II) complexes bearing β-ketoiminato-fluorene ligands is shown in **Scheme 1**.



Scheme 1. Synthesis of C-C bridged Ni(II) complexes bearing β-ketoiminato-fluorene ligands

Single crystals of **Ni1** and **Ni2** suitable for X-ray diffraction analysis were grown from a concentrated hexane–CH_2Cl_2 solution. The crystallographic data, together with the collection and refinement parameters, are summarized in **Table 1**. Selected bond distances and angles for complexes **Ni1**-**Ni2** are listed in **Table 2**.

Table 1. Crystallographic data for the Complexes **Ni1**–**Ni2**

Complex	**Ni1**	**Ni2**
Empirical formula	$C_{36}H_{30}N_2 NiO_2.CH_2Cl_2$	$C_{36}H_{24} F_6 N_2 NiO_2.CH_2Cl_2$
Formula weight	666.26	774.21
Crystal color	Green	Green
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Monoclinic, P2(1)/n	Monoclinic, P2(1)/n
a (Å)	9.0438(8)	9.1247(18)
b (Å)	19.4513(18)	22.750(5)
c (Å)	18.1240(17)	16.595(3)
α (deg)	90	90
β (deg)	96.817(10)	103.533(2)
γ (deg)	90	90
Volume ($Å^3$)	3165.7(5)	3349.3(11)
Z, Calculated density(Mg m^{-3})	4, 1.398	4, 1.535

Absorption coefficient (mm $^{-1}$)	0.818	0.810
F(000)	1384	1576
Crystal size (mm)	0.22 x 0.20 x 0.15	0.25 x 0.22 x 0.15
θ range for data collection (deg)	2.26 to25.50	2.19 to 25.50
Limiting indices	-10<=h<=10, -22<=k<=23, -21<=l<=21	-11<=h<=11, -26<=k<=27, -20<=l<=20
Max. and min. transmission	0.8871and0.8405	0.8882 and 0.8232
Refinement method.	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5882 / 0 / 386	6224 / 0 / 453
Goodness-of-fit on S $(F^2)^a$	0.962	1.047
Final R indices [I>2ó(I)]	R1 = 0.0638, wR2 = 0.1735	R1 = 0.0516, wR2 = 0.1379

R indices (all data)	R1 = 0.1007, wR2 = 0.2031	R1 = 0.0585, wR2 = 0.1455
Largest diff peak and hole (e/Å^3)	0.888 and -0.866	1.343 and -0.980

Table 2 Selected bond distances (Å) and angles (deg) for complexes **Ni1**–**Ni2**

Ni1		**Ni2**	
bond	length	bond	length
Ni(1)- O(1)	1.837(3)	Ni(1)- O(1)	1.849(2)
Ni(1)- O(2)	1.844(3)	Ni(1)- O(2)	1.844(2)
N(1)- Ni(1)	1.876(4)	Ni(1)- N(1)	1.884(3)
N(2)- Ni(1)	1.874(3)	Ni(1)- N(2)	1.888(2)
C(31)- C(30)	1.538(6)	C(31)- C(30)	1.580(4)
bond	angle	bond	angle
C(13)- N(1)- Ni(1)	124.2(3)	C(13)- N(1)- Ni(1)	125.2(2)
C(30)- N(1)- Ni(1)	110.0(3)	C(30)- N(1)- Ni(1)	110.79(18)
C(33)- N(2)- Ni(1)	123.7(3)	C(33)- N(2)- Ni(1)	125.1(2)
C(31)- N(2)- Ni(1)	111.9(3)	C(31)- N(2)- Ni(1)	111.42(17)
O(1)- Ni(1)- O(2)	81.01(16)	O(1)- Ni(1)- O(2)	81.08(10)
O(1)- Ni(1)- N(1)	95.72(16)	O(1)- Ni(1)- N(1)	95.85(11)
O(2)- Ni(1)- N(1)	170.72(16)	O(2)- Ni(1)- N(1)	172.62(11)

O(1)- Ni(1)- N(2)	172.29(17)	O(1)- Ni(1)- N(2)	172.76(10)
O(2)- Ni(1)- N(2)	95.89(15)	O(2)- Ni(1)- N(2)	95.52(10)
N(1)- Ni(1)- N(2)	88.39(15)	N(1)- Ni(1)- N(2)	88.26(10)
C(16)- O(1)- Ni(1)	126.6(4)	C(16)- O(1)- Ni(1)	124.1(2)
C(35)- O(2)- Ni(1)	126.1(3)	C(35)- O(2)- Ni(1)	124.4(2)

As depicted in **Fig. 1–2**, the crystal structures of the complexes **Ni1** and **Ni2** shared the four coordination binding mode around nickel(II) center, similar with our previously reported bis(β-ketoamino) ligand complexes.[23−26] The Ni−O and Ni−N distances and the bond angles about nickel are all typical for a square planar nickel(II) derivatives. X-ray quality crystals of **Ni1** and **Ni2** confirm C–C bridged bond has generated. The C–C bridged bond C(31)-C(30) 1.538(6)(**Ni1**),C(31)-C(30) 1.580(4) (**Ni2**) was structurally characterized bifluorenyl and formed during the reaction with similar length to analogous C–C single bonds.[33]

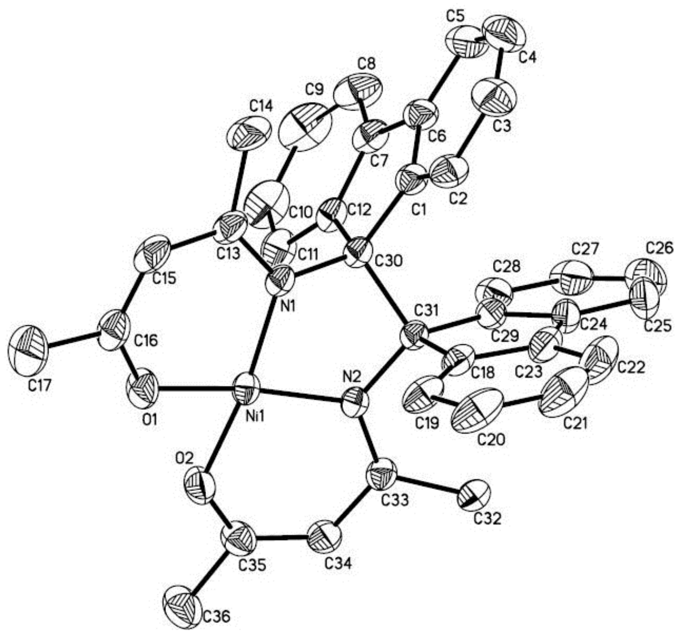


Fig. 1 View of the molecular structure of complex **Ni1** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and one dichloromethane solvent molecule are omitted for clarity.

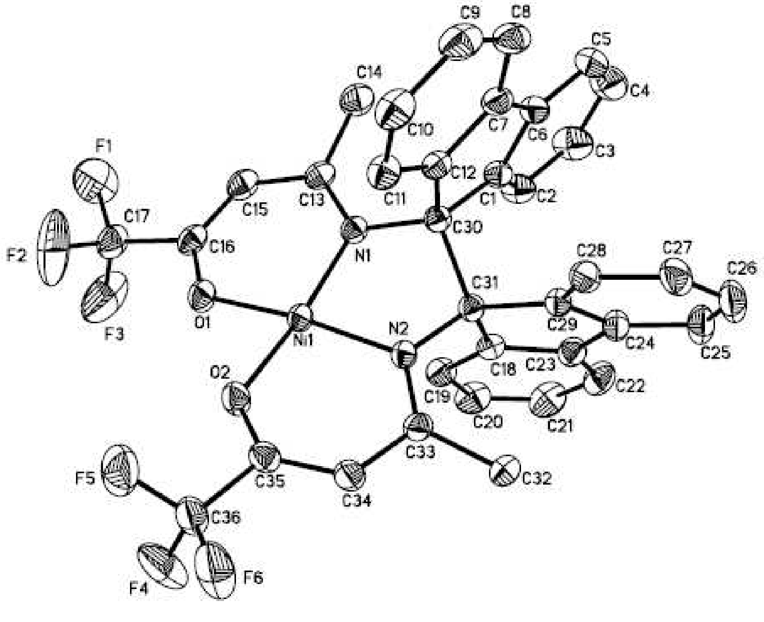
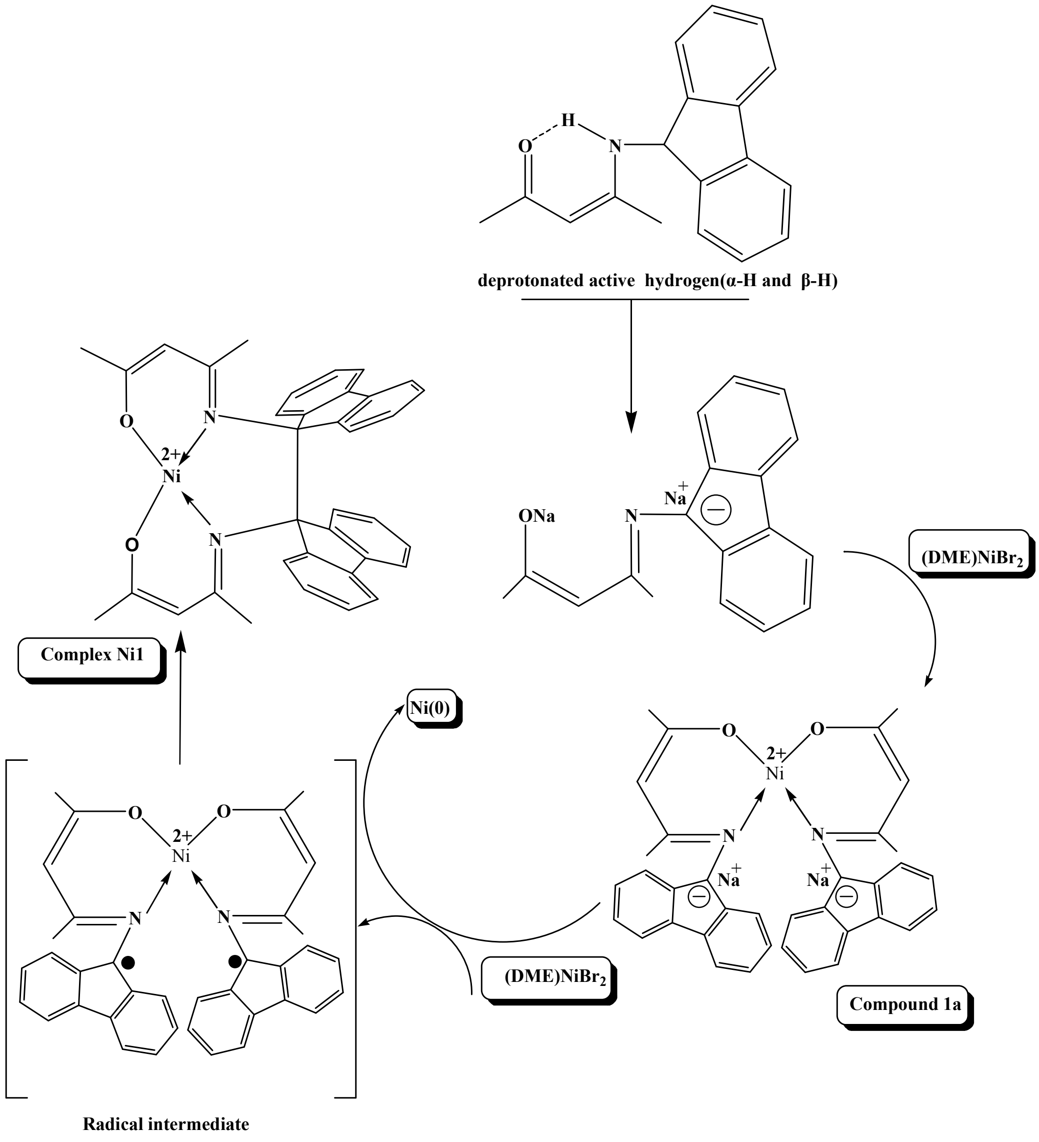


Fig. 2 View of the molecular structure of complex **Ni2** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and one dichloromethane solvent molecule are omitted for clarity.

Mechanism of C-C bridged Ni(II) complexes

The preparation of C-C bridged complexes Ni(II) bearing β-ketoiminato-fluorene ligands mainly include deprotonating reaction, coordination reaction and C-C coupling reaction. (DME)NiBr$_2$ is ligand exchange agent as well as coupling agent. Here, we take the process of complex **Ni1** synthesis as an example to explain the potential reaction mechanism. In the deprotonating reaction, the **L1** reacted with excess NaH to generate the sodium salt (**L1** anion). When the sodium salt with one part of (DME)NiBr$_2$ via ligand exchange, the intermediate Compound **1a** was formed. Another part of (DME)NiBr$_2$ as coupling agent react with Compound **1a** generating fluorenyl radical. In the meantime, Ni(II) is reduced to Ni(0). The complex **Ni1** was prepared after radical coupling. The radical coupling mechanism is similar to Bradley reported.[33] Reaction mechanism of the complex **Ni1** synthesis was proposed as the **Scheme 2**.



Scheme 2. Proposed reaction mechanism of the complex **Ni1** synthesis

NaH play a important role in deprotonating reaction to generate the sodium salt. To explore the generality of the reaction, the effect of the amount of the NaH investigated (**Fig. 3**). Seen from structure of **L1**, there have two kinds active hydrogen (β-H and α-H). From the ^{1}H NMR spectroscopy (THF) in deprotonating reaction, we can see that the β-H (a) is deprotonated firstly under base condition, the α-H (b) is deprotonated completely when a molar ratio of NaH/ligand is more than 1. These results clearly indicated that the activity of β-H is higher than that of α-H. There is no radical generated when the molar ratio (NaH/β-ketoiminato-fluorene ligand) is less than 1 on the following reaction. At the same time, no C-C bridged nickel(II) complex was synthesized.

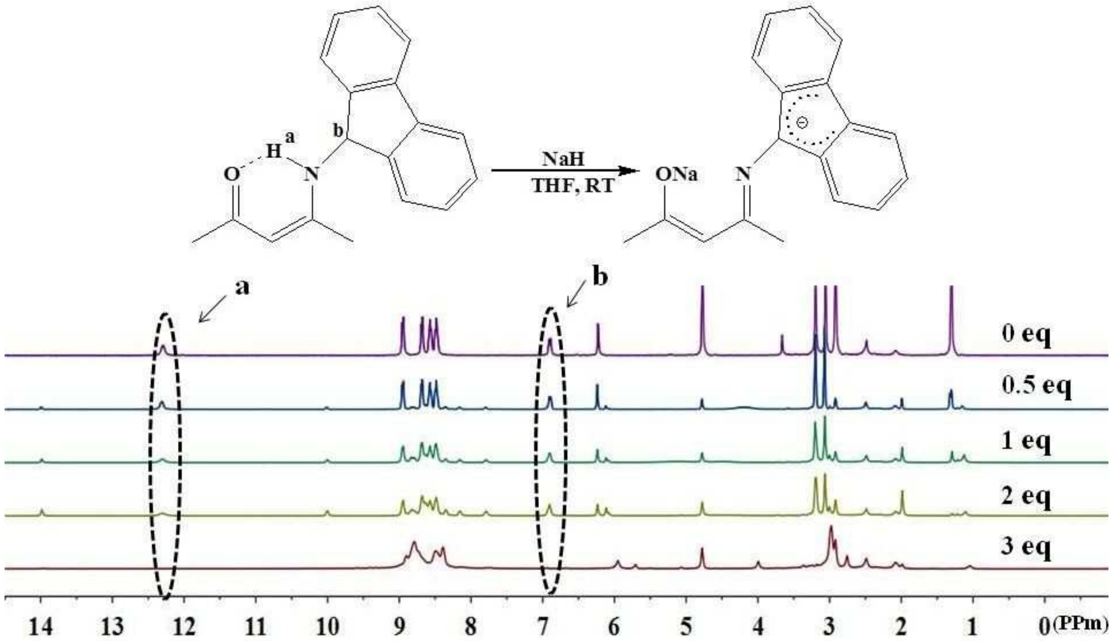


Fig. 3 ^{1}H NMR(THF) of different equiv.of NaH in deprotonated reaction of **L1**, reaction time=4h

Furthermore, details of C–C bond coupling reaction mechanism were studied by the density functional theory calculation using the B3LYP/6-31G(d, p) method in the synthesis of **Ni1**. All theoretical calculations were performed using the GAUSSIAN09 suite of programs. Vibrational frequency calculations were then performed at the optimized geometry of each reactant, product, transition structure, and intermediate. We confirmed that all reactants and intermediates have no imaginary frequencies, and each transition structure has one, and only one, imaginary frequency. The intrinsic reaction coordinate (IRC) calculations, at the same level of theory, were performed to ensure that the transition structures leding to the expected reactants and products. In pathway, Compound **1a** was set to zero in the free energy profile (**Fig. 4**), and pathway was computed. The **Ni1** via a transition-state TS with a small energy barrier of 7.41 kcal/mol^{-1}. During following process, it is strongly exothermic by 28.1 kcal/mol^{-1}.The result indicate that the formation of **Ni1** is thermodynamically favorable at room temperature. These results are consistent with our experiments.

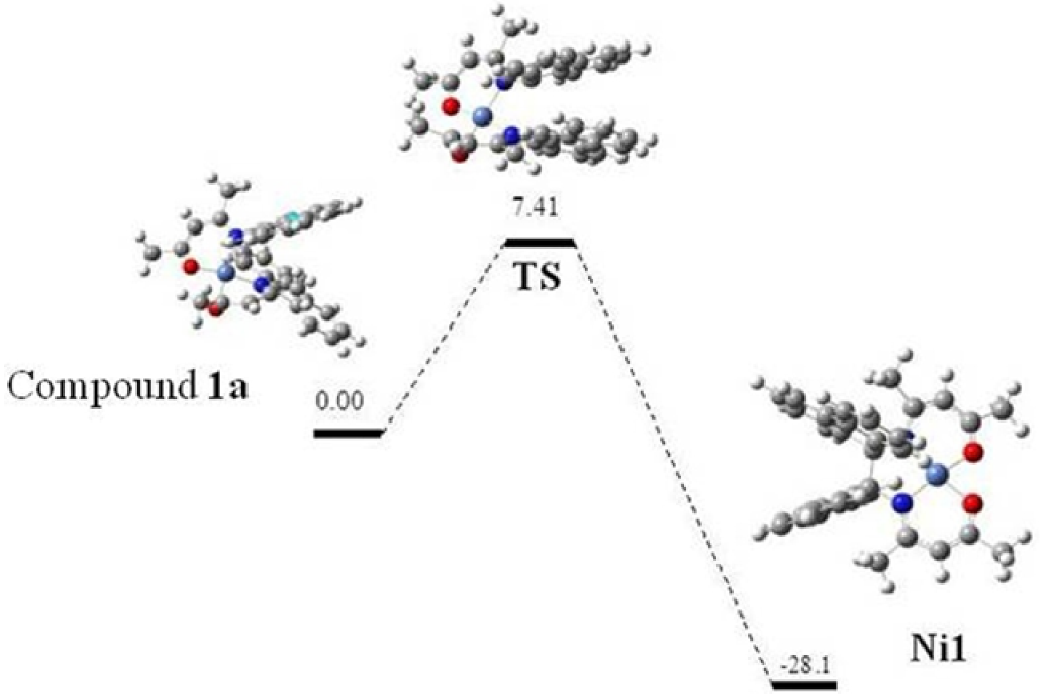


Fig. 4 Energy profile for the reaction pathway of the C–C bond coupling reaction for **Ni1** (Kcal mol^{-1}).

Homopolymerization of NB and Copolymerization of NB with HN

In the presence of $B(C_6F_5)_3$, complexes **Ni1** and **Ni2** were investigated for NB polymerization in toluene under mild conditions (**Table 3**). In contrast to previous reports,[23-26] these catalysts showed higher activity at lower B/Ni molar ratio (B/Ni =

10). To the best of our knowledge, we speculate the potential cause that $B(C_6F_5)_3$ active the center metal by oriented way due to the C-C bridged Ni(II) complexes have constrained geometry configuration and bulky fluorenyl, in which $C_6F_5^-$ group transfer from $B(C_6F_5)_3$ to nickel easily. Compared to the electron-rich complex **Ni1** (90.64% conversion), the electron-withdrawing analogue **Ni2** showed a slightly high monomer conversion (96.68%) and catalytic activity (1.1×10^6 g PNB $molNi^{-1}$ h^{-1}) in 10 min trials. The produced homopolymers are soluble at room temperature in common organic solvents such as chloroform and 1,2,4-trichlorobenzene, indicating a low stereo regularity. Similarly to NB homopolymerization，Li group reported series of nickel(II) complexes bearing two nonsymmetric bidentate β-ketoiminato chelate ligands used modified methylaluminoxane (MMAO) as a cocatalyst, the activity up to 1.16×10^7g PNB $molNi^{-1}h^{-1}$.[35] Wu group applied Neutral palladium complexes bearing β-ketoiminato ligand $Pd[CH_3C(O)CHC(NAr)CH_3](PPh_3)(Me)$ (Ar = fluorenyl) also showed high activities (8.0×10^7 g PNB $molPd^{-1}$ h^{-1}) when activated by MAO,[36] but the PNB insoluble in common solvents such as cyclohexane, chlorobenzene, and 1,2-dichlorobenzene, 1,2,4-trichlorobenzene.

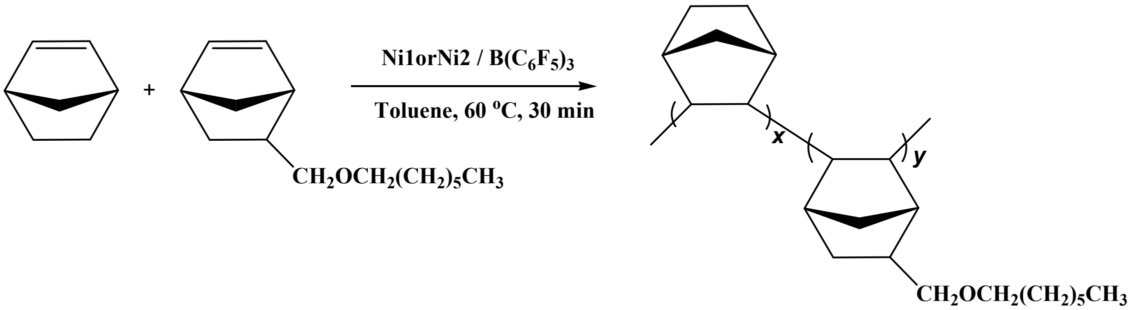
Table 3 Nobornene polymerization with **Ni1**-**Ni2**/ $B(C_6F_5)_3$[a]

No.	Ni complex	NB/Ni (mol/mol)	B/Ni (mol/mol)	T,°C	Reaction time, min	PNB Yield, %	Activity[b]
1	**Ni1**	2000	20	60	10	75.13	0.85
2	**Ni1**	2000	10	60	10	90.64	1.02
3	**Ni1**	2000	5	60	10	28.6	0.32
4	**Ni2**	2000	20	60	10	82.03	0.93
5	**Ni2**	2000	10	60	10	97.68	1.2
6	**Ni2**	2000	5	60	10	30.5	0.34

[a] Reaction conditions: Ni[Cat.]= 5 μmol; n[NB] = 0.01 mol; Solvent: toluene; Vp= 10 mL

[b] In units of 10^6 g PNB molNi^{-1} h^{-1}.

The norbornene derivative 2-heptoxymethylene norbornene (HN) was used as comonomer for the copolymerization catalyzed by complexes **Ni1** and **Ni2**. The M_W of the copolymers obtained by complexes **Ni1**-**Ni2**/$B(C_6F_5)_3$ systems are over 50kg mol^{-1} and decreased with increasing the content of HN in the copolymer (**Table 4**). Moreover, the PDIs of the obtained polymers are all relatively narrow (1.53 to 3.10) and appear as a single modal in the GPC spectra, which indicated that the copolymerization occurs at single active sites and the products are true copolymers rather than blends of the homopolymers. Polymerization activity has different due to the various steric and electronic interactions of ligand. The activities detected in copolymerization of norbornene and HN using **Ni1**/B(C_6F_5)$_3$ system were somewhat lower in comparison with the activities observed by using **Ni2**/B(C_6F_5)$_3$. Similar result was reported in the literature[37-38] and indicated that the CF_3 group with a strong electron-withdrawing effect is beneficial to the catalytic activity toward the copolymerization. The obtained poly(NB-co-HN) copolymer is soluble in THF when incorporation of HN in the copolymer is above 7 mol%, which suggests that the introduction of HN segments in the copolymer obviously can improve its solubility and processability relative to polynorbornene. The copolymerization procedure is shown in **Scheme 3**.



Scheme 3. Copolymerization of norbornene and 2-heptoxymethylene norbornene(HN) catalyzed by C-C bridged Ni(II) complexes combined with B(C_6F_5)$_3$

Table 4 Results of NB/HN copolymerization using nickel complexes **Ni1**-**Ni2**[a]

Complex	NB (mol%)	Yield (%)	Activity	M_w (Kg/mol)[b]	M_w/M_n[b]	Incorp.(%)
Ni1	90	82	7.8×10^5	210	1.53	93
Ni1	70	75	2.1×10^5	68	2.01	82
Ni1	50	48	8.6×10^4	57	2.18	77
Ni2	90	90	8.6×10^5	298	1.68	94
Ni2	70	81	4.6×10^5	170	1.99	78
Ni2	50	56	1.2×10^5	96	3.10	65

[a] Reaction conditions: Ni[Cat.]= 5 μmol; n[NB] +[HN]= 0.01 mol; Solvent: toluene; Vp= 10 mL, Reaction time = 30 min, $B(C_6F_5)_3$=50μmol

[b] Determined by GPC, solvent: 1,2,4-Trichlorobenzene; temperature: 150ºC; calibration with polystyrene standards.

A clear absorption signal of the ester group (C-O-C) at 1105 cm^{-1} in the FTIR spectrum signified the incorporation of HN comonomers (**Fig. 5**) and the characteristic absorption peak signals at about 941cm^{-1} could be attributed to the ring of bicyclo[2.2.1] heptane as Kennedy and Makowski[39] noted were quite clear, the absorption strength of the ester group (C-O-C) group increased with an decrease of the NB content in the co-monomer feed. The fact that no absorptions were observed in the vibration bands of carbon–carbon double bonds (1620–1680 cm^{-1} and at 960 cm^{-1}) indicated a vinyl-type NB/HN copolymerization.

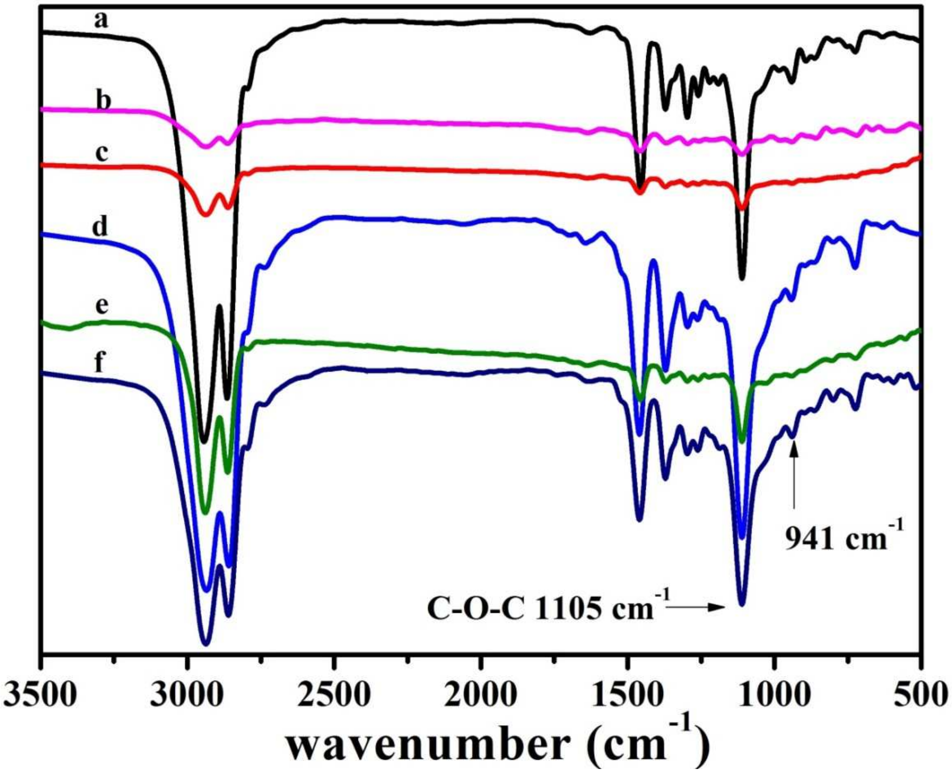


Fig. 5 FTIR spectra of poly(NB-co-HN) with (a) 93, (b) 77, (c) 65, (d) 82, (e) 78 (f) 94 mol% NB incorporation ratios obtained by Ni(II)/B(C_6F_5)$_3$ systems. (a), (b), (d) obtained by **Ni1**/B(C_6F_5)$_3$ system, (c), (e), (f) obtained by **Ni2**/B(C_6F_5)$_3$ system.

The ^{1}H NMR data of the copolymers containing different contents of NB were collected in deuterated chloroform ($CDCl_3$) at room temperature (**Fig. 6**). The absence of any trace amount of multiple signals in 5.0–6.0 ppm also confirmed a vinyl type copolymerization, which was consistent with the fact that absorption at 941cm^{-1} in the FTIR spectrum was observed. The incorporation of HN into the copolymer was calculated through the signal intensity of –CH_2OCH_2– protons at 3.39~3.68 ppm. The ^{13}C NMR spectrum (**Fig. 7**) also further confirms that the obtained polymers are vinyl-type poly(NB-co-HN). The characteristic peak from C=C double bond (120 ppm) due to ROMP was absent from the spectra, which implied that the copolymerization of norbornene and HN catalyzed by Ni(II)/B(C_6F_5)$_3$ catalyst system took place without ring opening and via an addition polymerization. Regions from 25 to 55 ppm of ^{13}C NMR spectrum, five intensive signals are safely assigned to long polynorbornene sequences. The resonances of methenes appear at 71.2–72.0 ppm for –CH_2OCH_2– carbons.

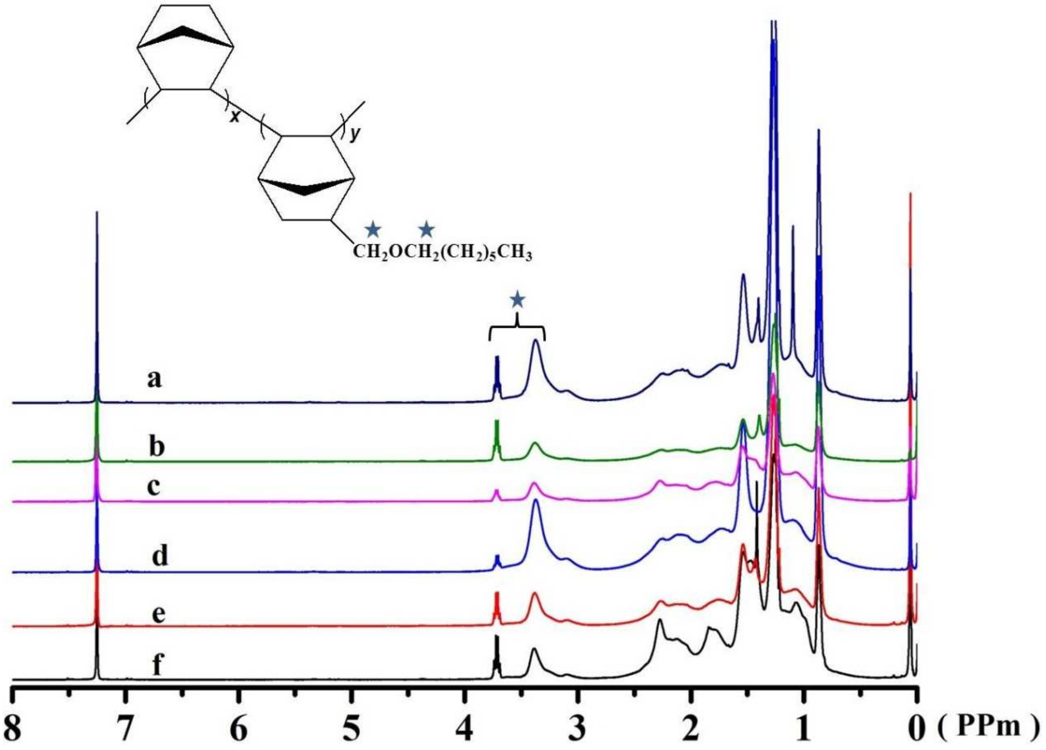


Fig.6 ^{1}H NMR spectra of poly(NB-co-HN) with (a) 77, (b) 93 , (c) 94 ,(d) 65, (e)78, (f) 82 mol% NB incorporation ratios obtained by Ni(II)/B(C_6F_5)$_3$ systems. (a), (b), (f) obtained by **Ni1**/B(C_6F_5)$_3$ system, (c), (d),(e) obtained by **Ni2**/B(C_6F_5)$_3$ system.

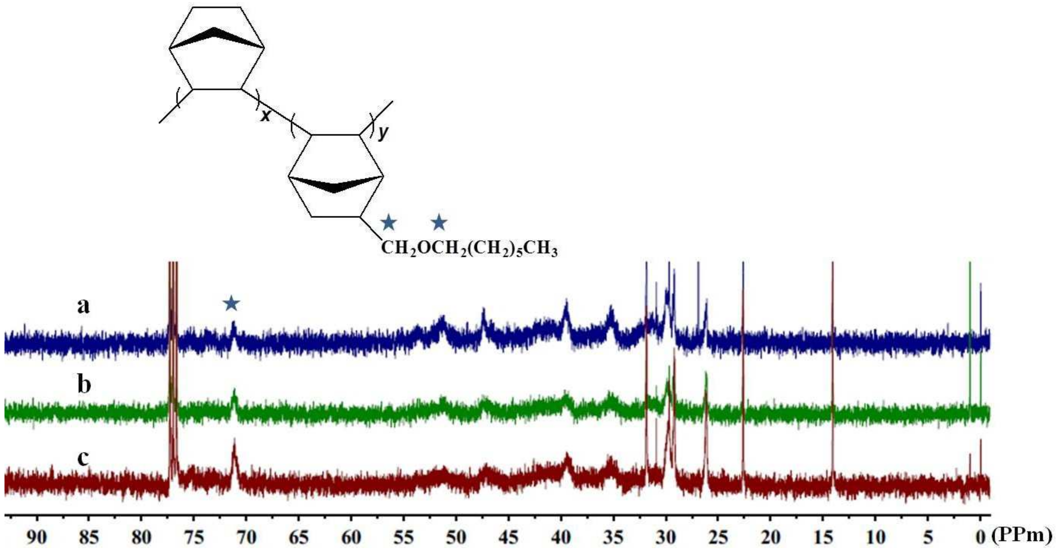


Fig.7 ^{13}C NMR spectra of poly(NB-co-HN) with (a) 93, (b) 82, (c) 65 mol% NB incorporation ratios obtained by Ni(II)/B(C_6F_5)$_3$ systems. (a), (b) obtained by **Ni1**/B(C_6F_5)$_3$ system, (c) obtained by **Ni2**/B(C_6F_5)$_3$ system.

The thermogravimetry analysis (TGA) curve of the resulting polymers with different NB contents is shown in **Fig. 8**. The decomposition temperature at 90% weight remaining in nitrogen was from 383 to 410 °C. The introduction of HN segments in the copolymer slightly decreases its thermo stability relative to polynorbornene. TGA analysis indicated that the copolymers obtained by the C–C bridged Ni(II) complexes and B(C_6F_5)$_3$ catalytic systems exhibited good thermo stability under nitrogen.

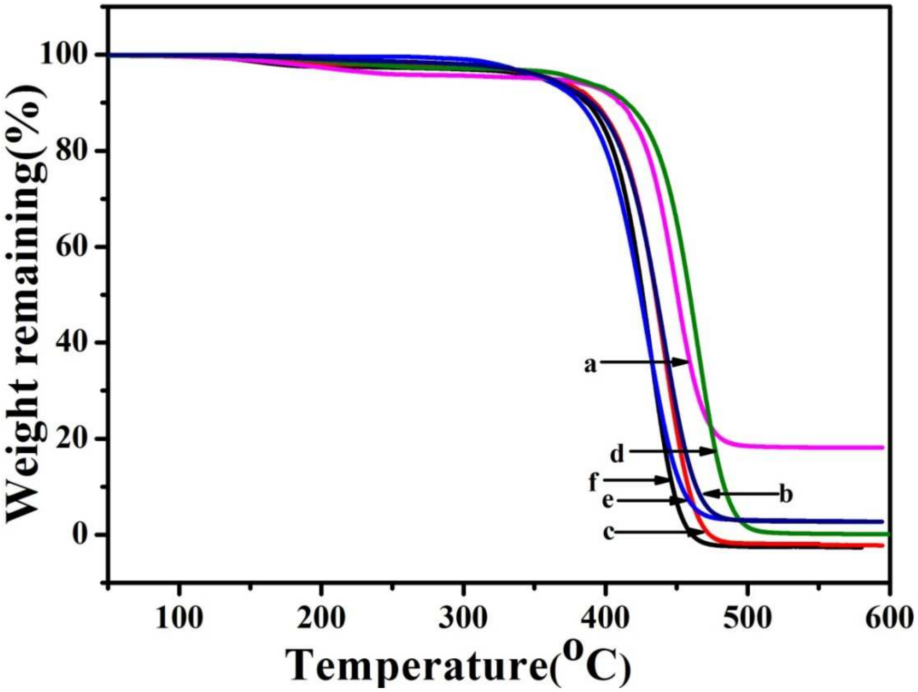


Fig. 8 The TGA thermograms of spectra of poly(NB-co-HN) with (a) 77, (b) 93 , (c) 94, (d) 65, (e) 78, (f) 82 mol% NB incorporation ratios obtained by Ni(II)/B(C_6F_5)$_3$ systems. (a), (b), (f) obtained by **Ni1**/B(C_6F_5)$_3$ system, (c), (d), (e) obtained by **Ni2**/B(C_6F_5)$_3$ system.

Wide-angle X-ray diffraction analysis (**Fig. 9**) shows that polymers are non-crystalline. No traces of Bragg reflections were revealed in the characteristic crystalline regions and the obtained poly(NB-co-HN) is also amorphous and has low stereo regularity because of presence of two broad halos (2θ=9–11, 17-19º). This result shows that HN have insert into the polymer chain and further proved the obtained polymers are copolymer. The slight difference between homopolymer and copolymer is change of the intensity of two halos.

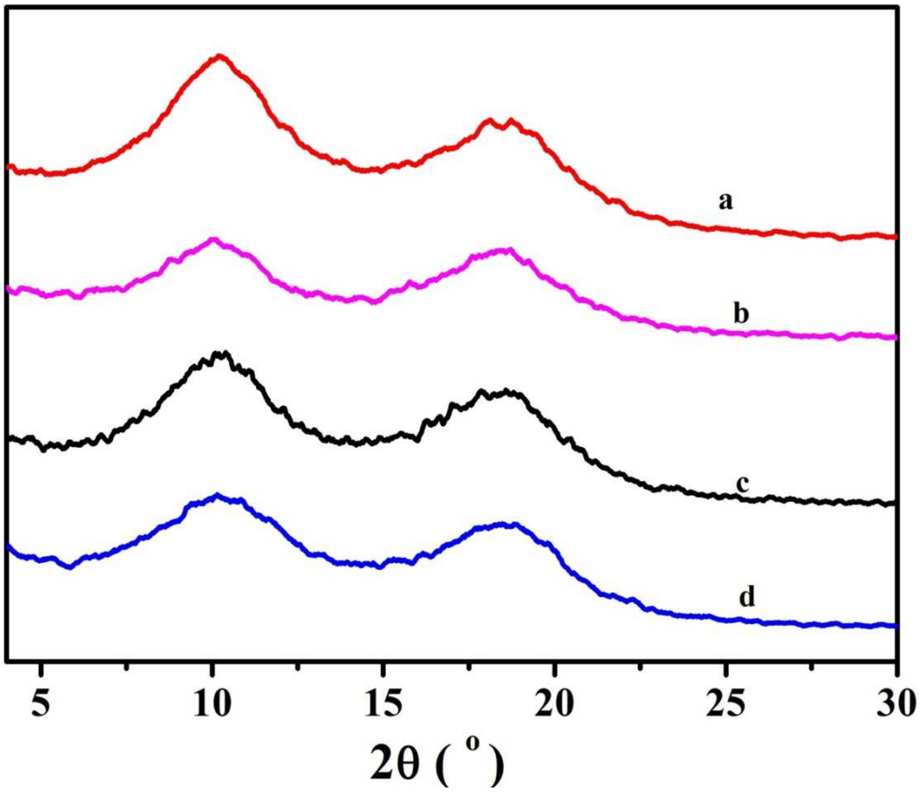


Fig. 9 XRD curves of the obtained poly(NB-co-HN) with (a) 100, (b) 77, (c) 94 ,(d) 65, NB incorporation ratios obtained by Ni(II)/B(C_6F_5)$_3$ systems. (a), (b) obtained by **Ni1**/B(C_6F_5)$_3$ system, (c), (d) obtained by **Ni2**/B(C_6F_5)$_3$ system.

Conclusions

In summary, novel C-C bridged nickel complexes have been successfully synthesized by in situ coupling reaction and characterized by single crystal X-ray technique. The complexes were used for the copolymerization of NB and HN together with B(C_6F_5)$_3$. The catalytic activities of two complexes on homopolymerization of NB are as high as 10^6 g PNB molNi^{-1} h^{-1}. Toward the copolymerization of NB and HN, **Ni2**/B(C_6F_5)$_3$ shows higher activity than **Ni1**/B(C_6F_5)$_3$ system and the catalytic activities decreased with increasing of HN in feed content. The strategy we herein presenting, may open a way for synthesis of similar transition metal catalysts for olefin polymerization.

Acknowledgement

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Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 974799, 974800 for **Ni1** and **Ni2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; email: deposit@ccdc.cam.ac.ukor.http://www.ccdc.cam.ac.uk).

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