Synthesis of bis-(benzocyclohexan-ketoimino) Ni(II) with different electron groups and their catalytic copolymerization of norbornene and polar norbornene†

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Four N,O-chelating type bidentate ligand nickel(II) complexes, Ni(C_{10}H_{8}(O)C[ArN]CH_{3})_{2}, two of them containing electron-donating groups (Ni1: Ar = p-PhCH_{3}, Ni2: Ar = p-PhOCH_{3}) and another two containing electron-withdrawing groups (Ni3: Ar = p-PhF, Ni4: Ar = p-PhCF_{3}), were synthesized and the molecular structures of Ni2, Ni3 and Ni4 were determined by X-ray crystallography. Copolymerization of norbornene (NB) and 5-norbornene-2-carboxylic acid methyl ester (NB-COOCH_{3}) were carried out in toluene with the above complexes as catalyst precursors and B(C_{6}F_{5})_{3} as the co-catalyst. All complexes showed high catalytic activity toward the copolymerization (up to 2.80 × 10^{5} g_{polymer} mol_{Ni}^{-1} h^{-1}) and the complexes with electron-withdrawing groups (Ni3 and Ni4) showed higher catalytic activity, and the activity was enhanced with the increased electron-withdrawing ability of the substituent (Ni4 > Ni3). The obtained poly(NB-co-NB-COOCH_{3})s were confirmed to be vinyl-addition copolymers and non-crystalline. All copolymers exhibited better solubility in common organic solvents, and showed high molecular weights (up to the grade of 10^{5} g mol^{-1}) and good thermal stability (T_{d} > 370 °C). Meanwhile, variation of the substituted electron group could slightly affect the above-mentioned copolymers’ properties.

1. Introduction

Cyclic olefin copolymers (COCs) as a good candidate for engineering plastics and optical apparatus have aroused great attention from both science and industry over the past decade. Cyclic olefin polymers are usually produced by addition polymerization and ring-opening metathesis polymerization, and the addition polymerization will not destroy the ring structure of the monomer itself. Norbornene (NB) and its derivatives are polymerizable owing to the existence of ring strain, thus norbornene has become one of the most active participants in cyclo-olefin copolymerization. Vinyl-type poly-norbornene (PNB) does not contain any double bonds and with a rotationally strongly constrained configuration, which consists of rigid alicyclic polymer backbone, it features many advantageous qualities, such as high thermal stability, high glass transition temperatures (T_{g}), high optical transparency, large refractive index, low birefringence, low dielectric constant, low moisture absorption as well as low cost. These advantages have been widely applied in many microelectronic and optical applications. However, the widespread application of PNB has been hampered by its low solubility, mechanical brittleness as well as poor processability. It has been reported that PNB obtained by nickel catalysts could be dissolved in chlorobenzene at room temperature in the 2000s, and the solubility and processability of PNB have been improved. Introducing polar groups or flexible chains into the PNB backbone has become an effective means of solving the problem. The design and synthesis of particularly efficient and stable catalysts is very important for the polymerization. It is generally known that the vinyl-type poly-norbornene can be efficiently obtained by using traditional Ziegler–Natta catalysts (TiCl_{4}, TiCl_{3}), metalloocene catalysts (Ti, Zr, Hf), and late transition metal catalysts (Ni, Pd, Fe, Co, Cu). Among these catalysts, the late transition metal catalysts have attracted more attention owing to their lower oxophilicity, higher catalytic activity, and better stability in polar solvents. The most common late transition metal catalysts are Ni(II) and Pd(II) complexes. Ni(II) complexes endow the catalysts with the ability to produce copolymers with...
a variety of polar functionalized olefins, allowing the preparation of complex functional polymer architectures.\(^{30}\) Ni(\(n\)) complexes are the most frequently used catalyst species because of the better catalytic performances and stability than that of Pd(\(n\)) complexes and illustrated reaction mechanisms. In recent years, \(\beta\)-ketoimino metal complexes have drawn wide attention from researchers owing to the remarkable simplicity of ligand syntheses and rich opportunities for fine-tuning of their steric and electronic properties. These complexes exhibit excellent activity and good tolerance to polar groups toward the functionalized vinyl-type polybutadiene in the presence of MAO, modified MAO (MMAO), or B(C\(6\)F\(5\))\(_3\).\(^{31–33}\) Our group has also synthesized and characterized a series of \(\beta\)-ketoimino nickel and palladium complexes that could effectively catalyze copolymerization of norbornene (NB) and NB derivatives.\(^{34–39}\) However, the important ligand-designing parameters, steric and electronic factors, were not completely involved in our previous reports. In this work, we aimed to further examine the impact of electronic effects on the catalytic activity. To this end, we prepared four \(\beta\)-ketoimino nickel complexes (Ni1–Ni4), of which two contain electron-donating groups (Ni1, Ni2) and another two contain electron-withdrawing groups (Ni3, Ni4), and compared their activities via the copolymerization of NB and NB-COOCH\(_3\) upon activation with B(C\(6\)F\(5\))\(_3\). All complexes appeared to be highly active catalysts, and the catalytic activities of Ni3 and Ni4 are higher than those of Ni1 and Ni2. The properties of the obtained polymers, such as molecular weight, solubility and thermal stability, were slightly affected by variation of the substituted electron group. X-ray structures of Ni2, Ni3 and Ni4 were acquired.

## 2. Experimental

### 2.1 Materials

All operations with water and oxygen-sensitive compounds were performed under a dry nitrogen atmosphere using Schlenk lines or a glove box (M Braun), and all solvents were dehydrated before use. Toluene and tetrahydrofuran (THF) were dried over sodium and distilled under dry nitrogen. Norbornene (NB) was purchased from Alfa Aesar and purified by drying over sodium and distilling at 110 °C under nitrogen atmosphere, used as a solution (0.4 g mL\(^{-1}\)) in toluene. 5-Norbornene-2-carboxylic acid methyl ester (NB-COOCH\(_3\)) was purchased from energy chemical and purified by distillation over CaH\(_2\) at a reduced pressure under dry nitrogen atmosphere.

### 2.2 Measurements

The structures of the ligands and polymers were characterized by \(^1\)H and \(^13\)C NMR spectra, which were recorded on a Bruker ARX 400 NMR spectrometer at room temperature in CDCl\(_3\) using tetramethylsilane (TMS) as the internal standard. The FTIR spectra were recorded using 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 of the polymers were determined by gel permeation chromatography (PL-GPC220), with a refractive index detector using tetrahydrofuran as the eluent with a flow rate of 0.5 mL min\(^{-1}\) and the detector at 40 °C.

The wide-angle X-ray diffraction (WXRD) curves were obtained on a Bruker D8 Focus X-ray diffractometer, operating at 40 kV and 40 mA with a copper target (\(\lambda = 1.54 \text{ Å}\)) at a scanning rate of 2° min\(^{-1}\) from 3° to 50°. Thermal gravimetric analysis (TGA) was performed on a PerkinElmer TA-600 under nitrogen atmosphere from room temperature to 650 °C at a heating rate of 10 °C min\(^{-1}\), and 5% loss of the polymer weight was used to evaluate its thermal stability. The differential scanning calorimetry (DSC) measurements were obtained on a Shimadzu DSC-60 with a heating-cooling rate of 10 °C min\(^{-1}\) under a nitrogen atmosphere.

### 2.3 Crystal structure determination

The X-ray diffraction data of single crystals of the complexes were obtained using the \(o\)–2\(\theta\) scan mode on a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo K\(\alpha\) radiation (\(\lambda = 0.71073\)). The structures were solved by 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.

### 2.4 Syntheses of ligands (L1–L4) and nickel complexes (Ni1–Ni4)

\(\text{NiO}\)-Chelating type ligands and their bidentate nickel complexes were synthesized referring to the synthetic procedure reported by our group\(^{40}\) and shown in Scheme 1.

**Synthesis of C\(_{10}\)H\(_8\)(O)C[HN(p-PhCH\(_2\))]CH\(_3\) (L1).** To a 250 mL round-bottomed flask equipped with a magnetic stir bar was added 2-acetyl-1-tetralone (1.88 g, 0.01 mol), \(p\)-methylphenol (1.07 g, 0.01 mol), a catalytic amount of \(\text{NiCl}_2\), and toluene (150 mL). The mixture was heated to reflux for 5 h, while water was removed as a toluene azeotrope at 125 °C using a water separator. The resulting solution was evaporated under vacuum to remove the residual toluene (concentrated to 4–5 mL), then the raw mixture was purified by column}

![Scheme 1](image-url)
chromatography with n-hexane and ethyl acetate (20/1 v/v). After concentration, yellow crystals were finally obtained.

Yield: 1.68 g (57.4%). 1H NMR (CDCl₃, δ, ppm): 14.06 (s, 1H, O--H--N); 7.27–8.07 (m, 4H, C₁₀H₈); 6.97–7.22 (m, 4H, C₆H₄); 2.56–2.96 (m, 4H, C₁₀H₈); 2.35 (m, 3H, R-CH₃); 2.10 (s, 3H, CH₃).

**Synthesis of C₁₀H₈(O)[HN(p-PhOCH₃)]CH₃ (L2).** Analogous to the synthetic route of L₁, p-methylaniline was substituted by p-methoxylaniline and yellow crystals were obtained.

Yield: 1.49 g (48.4%). 1H NMR (CDCl₃, δ, ppm): 13.99 (s, 1H, O--H--N); 7.12–8.06 (m, 4H, C₁₀H₈); 6.81–7.10 (m, 4H, C₆H₄); 2.59–2.94 (m, 4H, C₁₀H₈); 3.80 (s, 3H, OCH₃); 2.06 (s, 3H, CH₃).

**Synthesis of C₁₀H₈(O)[HN(p-PhF₃)]CH₃ (L3).** Analogous to the synthetic route of L₁, p-methylaniline was substituted by p-trifluoromethyl aniline and yellow crystals were obtained.

Yield: 1.92 g (68.4%). 1H NMR (CDCl₃, δ, ppm): 14.01 (s, 1H, O--H--N); 7.26–8.01 (m, 4H, C₁₀H₈); 6.98–7.22 (m, 4H, C₆H₄); 2.58–2.93 (m, 4H, C₁₀H₈); 2.08 (s, 3H, CH₃).

**Synthesis of C₁₀H₈(O)[HN(p-PhCF₃)]CH₃ (L₄).** Analogous to the synthetic route of L₁, p-methylaniline was substituted by p-trifluoroaniline and yellow crystals were obtained.

Yield: 2.06 g (60.3%). 1H NMR (CDCl₃, δ, ppm): 14.13 (s, 1H, O--H--N); 7.27–8.08 (m, 4H, C₁₀H₈); 6.67–7.23 (m, 4H, C₆H₄); 2.50–2.95 (m, 4H, C₁₀H₈); 2.23 (s, 3H, CH₃).

**Synthesis of Ni(C₁₀H₈(O)[N(p-PhCF₃)]CH₃)₂ (Ni1).** To a 100 mL round-bottomed flask equipped with a magnetic stir bar was added L₁ (0.554 g, 0.002 mol) and THF (20 mL) under nitrogen protection. When the ligand dissolved completely, 0.08 g of NaH (60%, 0.002 mol) was added under a dry nitrogen atmosphere. After being stirred vigorously for 8 h at room temperature, the solution changed to orange color and the excess THF was removed in vacuo. Then, (DME)NiBr₂ was introduced under an atmosphere of dry and oxygen-free nitrogen, then dichloromethane (20 mL) was injected and the reacting mixture immediately turned to green color. After being stirred vigorously for 24 h at room temperature, the precipitate was separated by filtration and concentrated, and the dark-green nickel complex (Ni1) was obtained in 70% yield.

**Synthesis of Ni(C₁₀H₈(O)[N(p-PhOCH₃)]CH₃)₂ (Ni2).** Ni2 was prepared according to a similar procedure to that for Ni1 and was obtained as a dark-green crystal in 58% yield.

**Synthesis of Ni(C₁₀H₈(O)[N(p-PhF₃)]CH₃)₂ (Ni₃).** Ni₃ was prepared according to a similar procedure to that for Ni1 and obtained as a green crystal in 64% yield.

**Synthesis of Ni(C₁₀H₈(O)[N(p-PhCF₃)]CH₃)₂ (Ni₄).** Ni₄ was prepared according to a similar procedure to that for Ni1 and was obtained as a dark-green crystal in 44% yield.

### 2.5 Polymerization

All experimental manipulations were performed under a dry nitrogen atmosphere. NB and NB-COOCH₃ (the total amount was kept at 0.01 mol) were added to a 100 mL two-necked round-bottom flask containing a magnetic stir bar. The nickel complex Ni₁–Ni₄ (5 × 10⁻⁴ mol) solutions were added by syringe followed by B(C₆F₅)₃ (1.0 × 10⁻⁴ mol). The solution was continuously stirred for 30 min at 60 ℃. The reaction was terminated by addition of methanol/hydrochloric acid (V_m/V_s = 9/1) and was stayed over 12 h. After filtering and washing with methanol several times, the products were collected and dried in a vacuum oven at 40 ℃ to a constant weight. The routes of copolymerization are shown in Scheme 2.

### 3. Results and discussion

#### 3.1 Structures of catalysts

Crystals of the catalysts suitable for single crystal X-ray diffraction were obtained by slow evaporation from dichloromethane solution. The ORTEP plots of Ni₂–Ni₄ are shown in Fig. 1, 3–4, respectively. The crystallographic data are summarized in Table 1. The data showed that the crystal systems of Ni₂, Ni₃ and Ni₄ were monoclinic. Selected bond lengths and angles are listed in Table 2. The structure of Ni₂ is mononuclear and a four-coordinate square planar configuration. The center metal ion (Ni²⁺) and the N,O-chelator form two stable six-member metallacyclic chelate rings (NiOCCCN). In the solid state, the coordination geometries around nickel atoms are typically square plane where the N or O atoms lie in the trans-position and are similar to some known nickel(n) complexes. The benzocyclohexan-ketoimino ligand is stable rigid structure and the catalyst structure is stable and symmetrical, which will be conducive to stable catalytic activity.

Crystal structure of Ni₂ was shown in Fig. 1. The structures of Ni₃ and Ni₄ are similar to that of Ni₂, and crystal structures are shown in Fig. 2 and 3, respectively.

The ligand electronic effect led to different charge distribution on the nickel metal atom, and the catalytic activity predominantly increased with an increase in the electrophilicity of the nickel metal center. The steric effect of the aryl ring effectively shielded the axial plane of the central metal and suppressed the side reaction of chain growth. The results indicated that the electronic effect of the para-position substituent on the arylimino groups and the steric effect of the aryl ring had a great influence on the catalytic activity.

#### 3.2 Copolymerization of NB and NB-COOCH₃

To further examine the impact of electronic effects on the catalytic activity, Ni₁–Ni₄ were applied in homo-polymerization of NB as well as copolymerization of NB and NB-COOCH₃ upon activation with B(C₆F₅)₃. The detailed data are summarized in Table 3 and were collected under similar conditions. All of the complexes are quite similar and showed high catalytic activity for the copolymerization of NB and NB-COOCH₃ (up to 2.80 × 10⁵ gpolymer mol⁻¹ h⁻¹). Comparing the activities of these catalysts, we found that the activities of Ni₃ and Ni₄ containing...
electron-withdrawing groups were higher than those of Ni1 and Ni2 containing electron-donating groups, and the activity of Ni4 containing the –CF3 substituent was higher than that for Ni3 containing the –F substituent, which illustrated that the electron-withdrawing effect was beneficial to the improvement of the catalytic performance. Therefore, the reactivity and

**Table 1**  Crystal data and structure refinement details for Ni2, Ni3 and Ni4

|          | Ni2          | Ni3          | Ni4          |
|----------|--------------|--------------|--------------|
| Empirical formula | C$_{38}$H$_{36}$N$_{2}$NiO$_{4}$ | C$_{36}$H$_{30}$F$_{2}$N$_{2}$NiO$_{2}$ | C$_{38}$H$_{30}$F$_{6}$N$_{2}$NiO$_{2}$ |
| Formula weight | 643.40 | 619.31 | 719.35 |
| Crystal color | Green | Green | Green |
| Temperature (K) | 293(2) | 296(2) | 100 |
| Wavelength (Å) | 0.71076 | 0.71073 | 0.71076 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | P2$_{1}$/c | P2$_{1}$/n | P2$_{1}$/n |
| a (Å) | 14.6652(13) | 8.916(3) | 7.148(3) |
| b (Å) | 14.8520(13) | 7.111(3) | 7.351(3) |
| c (Å) | 7.0027(6) | 21.905(8) | 24.392(10) |
| a (deg) | 90 | 94.988(2) | 94.484(10) |
| b (deg) | 90 | 93.538(9) | 94.484(10) |
| γ (deg) | 90 | 90 | 90 |
| Volume (Å$^3$) | 1519.5(2) | 1386.2(9) | 1558.6(10) |
| Z | 2 | 2 | 2 |
| Dcal (g m$^{-3}$) | 1.406 | 1.484 | 1.533 |
| Abs coeff. (mm$^{-1}$) | 0.684 | 0.752 | 0.698 |
| f(000) | 676.0 | 644.0 | 740.0 |
| Crystal size (mm) | 0.22 × 0.16 × 0.15 | 0.24 × 0.16 × 0.14 | 0.20 × 0.16 × 0.12 |
| θ Range (deg) | 3.108 to 25.500 | 3.42 to 26.00 | 3.239 to 24.795 |
| Limiting indices | –17 ≤ h ≤ 17, –17 ≤ k ≤ 13, –8 ≤ l ≤ 8 | –10 ≤ h ≤ 10, –7 ≤ k ≤ 8, –27 ≤ l ≤ 22 | –10 ≤ h ≤ 10, –8 ≤ k ≤ 8, –24 ≤ l ≤ 28 |
| Refinement method | Full-matrix least-squares on F$^2$ | Full-matrix least-squares on F$^2$ | Full-matrix least-squares on F$^2$ |
| Data/restraints/parameters | 2810/0/207 | 2632/0/197 | 2618/6/225 |
| Goodness-of-fit on S(F$^2$) | 1.061 | 0.950 | 1.116 |
| Final R indices [I > 2σ(I)] | $R_1 = 0.0304$, $WR_2 = 0.0729$ | $R_1 = 0.0478$, $WR_2 = 0.092$ | $R_1 = 0.0958$, $WR_2 = 0.2224$ |
| $R_1 = 0.0404$, $WR_2 = 0.0759$ | $R_1 = 0.0585$, $WR_2 = 0.1003$ | $R_1 = 0.1224$, $WR_2 = 0.2299$ |
| Largest diff peak and hole (eÅ$^{-3}$) | 0.182 and –0.872 | 0.571 and –0.424 | 1.162 to –0.543 |

$R = \sum||F_o|| - |F_c||\sum|F_o|$, $R_w = \frac{\sum (F_o^2 - F_c^2)^2}{\sum (F_o^2)^2}^{1/2}$. 

Fig. 1  ORTEP plots of Ni2 showing the crystal structure. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.
paper yield increased with the increasing electron-withdrawing ability of the substituents on the arylimino groups. Beyond that, the activities and polymer yields decreased with the content of NB-COOCH₃ increasing in co-monomers. The phenomenon could be explained by oxygen atoms competing with the double-bond for coordination, and a high concentration of oxygen atoms impedes the coordination of the double-bond.

The poly[NB-co-NB-COOCH₃]s were soluble in common organic solvents (such as CHCl₃, CH₂Cl₂, cyclohexane, and THF) as well as o-dichlorobenzene at room temperature, which exhibited better solubility compared with the PNB.

### 3.3 GPC curves of copolymers

GPC curves of the poly[NB-co-NB-COOCH₃]s with different NB-COOCH₃ incorporation ratios achieved using the Ni₁–Ni₄/ B(C₆F₅)₃ systems are shown in Fig. 4. The molecular weights (M₆) of the copolymers were all up to the grade of 10⁵ and decreased with increasing NB-COOCH₃ content. The poly-dispersity of these copolymers was in the range of 1.66–3.47. The copolymers obtained by Ni₄ with wider molecular weight distribution indicated that the higher activity results in different chain growth and termination of polymerization. Moreover, all copolymers were single modal in the GPC chromatograms, which indicated that copolymerization occurred at single active sites and the products were true copolymers rather than blends of homopolymers.

### 3.4 ¹H and ¹³C NMR spectra of copolymers

The structures of the poly[NB-co-NB-COOCH₃]s were characterized by ¹H NMR spectra and are shown in Fig. 5, which demonstrated that the polymerization was carried out via vinyl-addition type mechanism by the absence of the resonance of the proton hydrogen connecting to the double bond at about 5.3–6.0 ppm. The peaks at 3.5–3.8 ppm could be assigned to the hydrogens of –COOCH₃ (H₈) and it could be seen that the intensity of the peaks increased with increasing polar comonomer feed ratios. The characteristic peaks at 2.5–2.8 ppm could be attributed to the methine hydrogen corresponding to H₅, which indicated that the NB-COOCH₃ had accessed to the backbone of norbornene successfully. The peaks at 2.0–2.5 ppm were assigned to the methine hydrogen corresponding to H₂/H³/H₂’/H³’ and those at 1.6–2.0 ppm were assigned to the methine hydrogen corresponding to H₁/H₄/H₁’/H₄’. The peaks at 0.7–1.6 ppm could be attributed to the methene hydrogen corresponding to H₅/H₆/H₇/H₆’/H₇’. The molar fractions of NB-COOCH₃ were calculated by ¹H NMR analyses and to be 24.9, 22.4, 19.3 and 11.3 mol%, respectively.

The ¹³C NMR spectra of the poly[NB-co-NB-COOCH₃]s are shown in Fig. 6. Four groups of resonance peaks appeared...
between 28 and 56 ppm: 28.3–32.5, 33.9–37.8, 38.6–44.7 and 45.1–55.6 ppm, which could be attributed to the methyl, methene or methine carbons corresponding to (C5/C6/C5′/C6′), (C7/C4/C1′/C4′) and (C2/C3/C2′/C3′/C9), respectively. Further, the peaks at 174.2–177.8 ppm were assigned to the CO carbon corresponding to C8. The absence of C–C double bond characteristic peaks at 120 ppm owing to the ROMP-type polymer structures further implied that the copolymerization of NB and NB-COOCH3 catalyzed by Ni1–Ni4/B(C6F5)3 was carried out via vinyl addition mechanism.

3.5 FTIR spectra of copolymers

The obtained copolymers were also investigated by FTIR spectroscopy (Fig. 7). The characteristic absorption peak signals at about 941 cm−1 could be assigned to the ring of vinyl-type polynorbornene (PNB), as Kennedy and Makowski noted. There were no absorptions at about 1620–1680 cm−1 and 960 cm−1, which could be attributed to the characteristic trans form of stretching of the C–C bond of the structure of ROMP-type PNB.

3.6 TGA and DSC analyses of copolymers

TGA thermograms of poly(NB-co-NB-COOCH3) obtained by the Ni1–Ni4/B(C6F5)3 systems are shown in Fig. 8. All copolymers

| Catalysts | NB/NB-COOCH3 (mol mol−1) | Yield (%) | Activityb | Mw (g mol−1) | Mw/Mn | NB-COOCH3 incorp. (mol%) |
|-----------|---------------------------|-----------|-----------|-------------|-------|-------------------------|
| Ni1       | 100/0                     | 79.2      | 2.98 × 105 | Insoluble    | —     | 0                       |
| Ni1       | 90/10                     | 52.9      | 2.11 × 105 | 1.34 × 105   | 1.92  | 7.30                    |
| Ni1       | 70/30                     | 27.3      | 1.21 × 105 | 1.19 × 105   | 1.69  | 24.9                    |
| Ni1       | 50/50                     | 7.90      | 3.90 × 104 | 1.07 × 105   | 1.83  | 35.2                    |
| Ni2       | 100/0                     | 84.6      | 3.08 × 105 | Insoluble    | —     | 0                       |
| Ni2       | 90/10                     | 58.8      | 2.33 × 105 | 1.59 × 105   | 1.79  | 8.70                    |
| Ni2       | 70/30                     | 38.1      | 1.69 × 105 | 1.24 × 105   | 1.66  | 22.4                    |
| Ni2       | 50/50                     | 18.3      | 9.00 × 104 | 1.18 × 105   | 1.74  | 38.7                    |
| Ni3       | 100/0                     | 89.5      | 3.33 × 105 | Insoluble    | —     | 0                       |
| Ni3       | 90/10                     | 62.8      | 2.51 × 105 | 1.63 × 105   | 1.83  | 8.20                    |
| Ni3       | 70/30                     | 45.1      | 2.01 × 105 | 1.45 × 105   | 2.41  | 19.3                    |
| Ni3       | 50/50                     | 22.8      | 1.12 × 105 | 1.21 × 105   | 1.94  | 42.1                    |
| Ni4       | 100/0                     | 91.2      | 3.52 × 106 | Insoluble    | —     | 0                       |
| Ni4       | 90/10                     | 70.0      | 2.80 × 105 | 1.96 × 105   | 2.83  | 7.90                    |
| Ni4       | 70/30                     | 51.3      | 2.29 × 106 | 1.84 × 104   | 3.47  | 11.3                    |
| Ni4       | 50/50                     | 26.3      | 1.30 × 106 | 1.67 × 103   | 2.58  | 34.1                    |

a Reaction conditions: [Ni] = 5 mmol L−1; n[NB] + n[NB-COOCH3] = 0.01 mol; solvent: toluene; reaction time: 30 min; temperature: 60 °C; n[B]/n [Ni] = 20/1. b In units of gpolymer mol−1Ni h−1. c Determined by GPC vs. polystyrene standards in THF. d Determined by 1HNMR spectroscopy in CDCl3.
showed similar thermal stability with a decomposition temperature ($T_d$) with 5% weight loss of about 370 °C that decreased with increasing NB-COOCH$_3$ content in the copolymers. Glass transition temperatures ($T_g$) of poly(NB-co-NB-COOCH$_3$)s achieved by different catalytic systems were analyzed by DSC and are shown in Fig. 9. The $T_g$ values of the copolymers were about 290 °C and the trend was similar to that observed for $T_d$. TGA and DSC analyses indicated that copolymers with different NB-COOCH$_3$ contents obtained using the Ni1–Ni4/B(C$_6$F$_5$)$_3$ systems exhibited good thermal stability under nitrogen.

3.7 WXRD analyses of the copolymers

Wide-angle X-ray diffraction analysis of the copolymers catalyzed by the different catalytic systems are shown in Fig. 10. No traces of Bragg reflection in the characteristic crystalline regions were revealed, and therefore the copolymers were non-crystalline. The two halos at 2$\theta$ values of 9.58–10.14 and 18.54–18.83 were characteristic peaks for polynorbornene, and the corresponding distances were obtained according to the equation:
and the activity was improved with increasing electron-attractive ability of the substituent. The analyses of the copolymer structures and properties indicated that the polymerization was carried out via vinyl addition mechanism rather than ROMP mechanism. The poly(NB-co-NB-COOCH₃)s exhibited better solubility than that of the PNB and showed high molecular weights (up to a grade of 10⁵) and thermal stability (Tₘ > 370 °C). The poly(NB-co-NB-COOCH₃)s were confirmed to be non-crystalline. Meanwhile, variation of the substituted electron group could slightly affect the properties of the above-mentioned copolymers.

Conflicts of interest

There are no conflicts to declare.

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