Quinolinyl Imidazolidin-2-imine Nickel Catalyzed Efficient Copolymerization of Norbornene with para-Chlorostyrene

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Abstract A series of novel quinolinyl imidazolidin-2-imine nickel complexes with different substituents on the imidazolidin-2-imine ligand were synthesized and characterized. The complexes in the presence of methylaluminoxane (MAO) as a cocatalyst catalyzed the copolymerization of norbornene (N) and styrene (S) or para-chlorostyrene (CS) with high activity (up to 1070 kg·mol\textsuperscript{-1}·h\textsuperscript{-1}). The installation of sterically bulky substituents on the imidazolidine-2-imine ligand was effective for the increase of the molecular weight and the comonomer content, affording high molecular weight copolymers with tunable CS content (0.57 mol%–11.7 mol%), in which the existence of Cl group can provide reaction site for the further functionalization of copolymers as well as the synthesis of graft or cross-linked polymers. The linear relationship between the comonomer content and the glass transition temperature of the copolymers and the monomer reactivity ratios in the copolymerization indicated the formation of the expected functionalized cyclic olefin copolymers (COC).

Keywords Imidazolidin-2-imine ligand; Nickel complex; Norbornene; para-Chlorostyrene; Copolymerization

INTRODUCTION

Norbornene (N) based cyclic olefin copolymers (COCs) obtained by vinyl-addition type polymerization have attracted great attention due to their unique properties such as optical transparency, great heat and chemical resistance, and low dielectric constant, etc.\textsuperscript{[1–30]} However, relatively poor adhesion and high birefringence of COCs prohibit their further application in the field of optical products. Compared with olefin comonomers, the incorporation of aromatic structure into the COC backbone would compensate their birefringence. Shiono et al.\textsuperscript{[31]} synthesized N-styrene (S) copolymer and N-S-ethylene terpolymer using titanium catalyst and demonstrated that the random incorporation of even small amount of S unit effectively reduces the birefringence.\textsuperscript{[4,5]} With interest in late-transition metal catalysts, the copolymerization of N with S was obtained using nickel,\textsuperscript{[6–13]} palladium,\textsuperscript{[14]} and copper\textsuperscript{[15,16]} catalysts. However, the synthesis of high molecular weight of copolymers with controlled S content is still very limited.

Most importantly, the incorporation of polar functional group would improve the properties of polyolefins such as adhesion, compatibility, and toughness.\textsuperscript{[17]} Recent developments of late transition metal catalysts allowed us to synthesize polar functionalized polyethylene and polypropylene via direct olefin copolymerization with polar monomers.\textsuperscript{[18–23]} In contrast, the synthesis of polar functionalized COCs is very limited. Therefore, it is still necessary to develop late transition metal catalysts for preparing the functionalized N-S copolymers.

In the light of recent progress related to nickel complexes that contain N\textsubscript{meso}\textsuperscript{[31]}-donor ligand, which can be classified as azidine-type (Chart 1, I), pyridinylimine-type (Chart 1, II), and 5,6,7-trihydroquinoline-type (Chart 1, III) nickel complexes, numerous diimine ligands have been developed with unique properties of olefin (co)polymerization, which strongly depended on the structure modifications of pre-catalysts.\textsuperscript{[30]} However, the (co)polymerization of N was not investigated with these nickel catalysts, probably due to the sterically hindrance of N monomer.

Inspired by this fact, we designed a novel nickel complex by replacing a phenyl-imine group with an imidazolidin-2-imine group combined with quinoline framework (Chart 1, NiI–NiIV), which can provide coordination space for the sterically bulkier N and S monomers. Another advantage of this complex can be attributed to the electron effect of imidazolidin-2-imine group, which acts as strong π-electron N-donor by the mesomeric structures (Chart 2) to reduce the...
on a Bruker APEX2 diffractometer using graphite monochromated with Mo Kα radiation (λ = 0.71073 Å). Elemental analyses were performed with the Vario ELIII elemental analyzers manufactured by Elementar Analysensysteme GmbH. The transparency of the copolymer film in the range of visible wavelengths (350–800 nm) was measured by a UV/Vis spectrometer (Lambda 950).

Toluene and tetrahydrofuran were dried over sodium/benzophenone and distilled under nitrogen. Hexane and dichloromethane were subjected to the PS-MD-5 solvent purification system (Innovative Technology). Norbornene (N) was purified by distillation over CaH₂ and used as a solution (6.70 mol·L⁻¹) in toluene. Styrene (S) and para-chlorostyrene (CS) were dried over CaH₂ and distilled in vacuum before use. MAO was provided by Wuhan Methyl Technology Co., Ltd. All the other reagents were purchased and used without purification.

**General Polymerization Procedure**

All copolymerizations were performed in 100 mL glass reactor with a magnetic stirrer. Certain amount of MAO, toluene and monomers were added into the reactor. After the pre-set temperature was reached, copolymerization was started by adding the catalyst solution of toluene into the well-stirred reaction system. The total reaction volume was kept 20 mL. After certain time, the copolymerization was terminated by acidic alcohol (V_HCl/V_MCe 90/10) and the reaction system was stirred overnight. The polymers were washed with ethanol and acetonitrile alternatively, and dried in vacuum at 80 °C until a constant weight was reached.

**Preparation of Poly(N-S) and Poly(N-CS) Films**

The mixture of each copolymer (5 wt%) and 1,2,4-trichlorobenzene as a solvent was heated at 150 °C until it was completely dissolved. The mixture was then filtered off, and the copolymer film was prepared by drop-casting on a smooth glass surface at room temperature, followed by drying at 80 °C under the vacuum.

**Synthesis of Ligands and Complexes**

**Synthesis of N-(1,3-dimethylimidazolidin-2-yliden) quinoline-8-amine ligand (L1)**

2-Chloro-1,3-dimethylimidazolium chloride (6.76 g, 40 mmol) was dissolved with dry MeCN (50 mL) in a 250 mL flask, and the MeCN solution (30 mL) of 8-aminquinoline (5.77 g, 40 mmol) and triethylamine (5.57 mL, 40 mmol) was added into the flask at 0 °C. After refluxing for 3 h, the mixture solution was treated with NaOH solution (1.60 g, 40 mmol) and KOH (50%, 20 mL) to remove the acid and 2-chloro-1,3-diphenyylimidazolium chloride, respectively. The product was extracted with MeCN (5 × 40 mL), and the combined organic layers were dried over anhydrous sodium sulfate and evaporated. The crude product was purified by silica gel column chromatography (eluents: EtOAc/hexane = 1/1, V/V) to give N-(1,3-dimethylimidazolin-2-yliden) quinoline-8-amine (L1).

**EXPERIMENTAL**

**General Procedures**

All manipulations were carried out adopting standard Schlenk techniques or drybox under a high purity nitrogen atmosphere. ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker avance III 600 MHz NMR instrument at ambient temperature unless otherwise stated. ¹H-NMR spectra of polymers were recorded at 95 °C in 1,1,2,2-tetrachloroethane (CDCl₃). ¹³C-NMR spectra of polymers were recorded at room temperature in CDCl₃. The resonance signal of tetramethylsilane (TMS, δ = 0) was used as the internal reference. The glass transition temperature (Tg) of polymer was tested by TA differential scanning calorimeter Q2000 (DSC) with heating and cooling rates of 10 °C/min under nitrogen atmosphere. Molecular weight and molecular weight distribution of the polymers were determined by a polymer laboratory PL GPC-220 device with one guard column (PL# 1110-1120), two 30 cm columns (PLgel 10 µm MIXED-B 7.5 × 300 mm) and a refractive index (RI) detector. Polymer characterization was performed at 145 °C in 1,2,4-trichlorobenzene solvent and calibrated by polystyrene standards. The single crystals were mounted under a nitrogen atmosphere at low temperature, and data collection was made

https://doi.org/10.1007/s10118-020-2400-3
Li, Y. Q. et al. / Chinese J. Polym. Sci. 3

Synthesis of N-(1,3-di-tert-butylimidazolidin-2-yliden) quinoline-8-amine ligand (L2)

The ligand L2 was synthesized in a similar way to treat for L1. The crude product was purified by silica gel column chromatography (eluent: EtOAc/hexane = 4/1, V/V) to give a yellow oil (L2, 1.51 g, 4.65 mmol, 46.5%). 1H-NMR (CDCl3, δ ppm): 8.65 (d, 1H, =CH), 7.82 (q, 1H, =CH), 7.20 (m, 4H, =CH), 7.08 (m, H, =CH), 6.85 (t, 1H, =CH), 6.49 (t, 1H, =CH), 3.18 (d, 4H, =CH2), 1.12 (d, 18H, – CH3). 13C-NMR (CDCl3, δ ppm): 158.09 (~N=C), 150.32 (~N=C), 146.85 (~N=C), 141.96 (~C), 135.33 (~CH), 130.08 (~CH), 127.47 (~N=C), 120.37 (~N=C), 114.21 (~CH), 113.26 (~CH), 55.13 (~C × 2), 42.52 (~CH2 × 2), 28.39 (~CH3 × 6).

Synthesis of N-(1,3-diphenylimidazolidin-2-yliden) quinoline-8-amine ligand (L3)

The ligand L3 was synthesized in a similar way to treat for L1. The crude product was purified by silica gel column chromatography (eluent: EtOAc/hexane = 1/4, V/V) to give a faint yellow oil (L3, 1.12 g, 2.94 mmol, 63.8%). 1H-NMR (CDCl3, δ ppm): 8.82 (d, 1H, =CH), 7.83 (d, 1H, =CH), 7.30 (d, 4H, =CH), 7.23 (m, 1H, =CH), 7.15 (t, 1H, =CH), 7.13 (t, 1H, =CH), 7.05 (d, 1H, =CH), 7.01 (t, 4H, =CH), 6.84 (t, 2H, =CH), 4.07 (s, 4H, =CH2), 25.68 (~CH × 4), 23.42 (~CH × 4), 119.37 (~CH=C), 10.32. Found: C, 44.22; H, 3.52; N, 9.69.

Synthesis of nickel complex Ni1

Ni(dme)Br2 (0.31 g, 1.0 mmol) and L1 (0.24 g, 1.0 mmol) were added into a 250 mL flask, and the reaction was started by adding CH2Cl2 (60 mL). After continuously reacting at ambient temperature for 24 h, the solvent was evaporated under vacuum to give a crude production. The solid was washed by n-hexene (3 × 30 mL) and dried under vacuum. It was then dissolved in CH2Cl2 and filtered off, and the reddish-brown acicular crystals suitable for X-ray measurements were obtained from CH2Cl2/n-hexene (0.35 g, 0.76 mmol, 76%). Elemental analysis: Calcd. for C38H36Br2Ni (548.81): C, 46.24; H, 3.24; N, 12.21. Found: C, 46.20; H, 3.47; N, 12.07.

Synthesis of nickel complex Ni2

Ni(dme)Br2 was synthesized in a similar way to treat for Ni1. The green petal-like crystals suitable for X-ray measurements were obtained (Ni2, 0.40 g, 0.73 mmol, 73%). Elemental analysis: Calcd. for C38H36Br2Ni (542.96): C, 44.24; H, 5.20; N, 10.32. Found: C, 44.22; H, 5.27; N, 10.29.

Synthesis of nickel complex Ni3

Ni(dme)Br2 (0.35 g, 0.76 mmol, 76%). Elemental analysis: Calcd. for C38H36Br2Ni (582.94): C, 49.45; H, 3.46; N, 9.61. Found: C, 49.40; H, 3.42; N, 9.69.

Synthesis of nickel complex Ni4

Ni(dme)Br2 was synthesized in a similar way to treat for Ni1. The red acicular crystals suitable for X-ray measurements were obtained (Ni4, 0.65 g, 0.87 mmol, 87%). Elemental analysis: Calcd. for C38H36Br2Ni (751.29): C, 57.55; H, 5.90; N, 7.46. Found: C, 57.65; H, 5.96; N, 7.38.

RESULTS AND DISCUSSION

Synthesis and Molecular Structure of Nickel Complexes

The synthesis routes to the ligands and corresponding complexes are shown in Scheme 1. The quinolinyl imidazolidin-2-imine ligands (L1–L4) were prepared by the reaction of 8-aminoquinoline and 2-chloro-1,3-dialkylimidazolinium chloride (1–4), which was synthesized according to the literature (see the electronic supplementary information, ESI).
The nickel complexes Ni1–Ni4 were easily synthesized in good yield (> 70%) by the complexation of ligands and Ni(dme)Br2.[46–50]

Single crystal X-ray structure diffraction demonstrated the molecular structures of all the nickel complexes Ni1–Ni4 (Figs. 1–4). The nickel complexes displayed a distorted tetrahedral geometry at nickel center, and the five-membered (N, N) nickel chelate ring adopted a tetrahedral planar conformation. Theimidazolidin ring is almost perpendicular to the quinoline plane regardless of the substituent on the nitrogen atoms. The C10–N2–Ni1 angle of nickel complexes increased in the following order: Ni1 (117.8(8)°) < Ni3 (120.0(4)°) < Ni4 (122.5(2)°) < Ni2 (129.6(4)°), suggesting that the sterical hindrance around axial position of the nickel center can be effectively controlled by the substituent.

Copolymerization of Norbornene with Styrene

A detailed investigation of the N-S copolymerization catalyzed by nickel complexes Ni1–Ni4 in the presence of MAO has been conducted (Table 1). In comparison to NB homopolymerization, the copolymerization showed much lower activity to produce lower molecular weight copolymers. The change of Al/Ni molar ratio (500–2000) at 30 °C little affected the copolymerization activity, and the highest activity was observed with Ni3 under Al/Ni ratio of 1000. As temperature was raised from 0 °C to 90 °C, the catalytic activity improved from 128 kg·mol⁻¹·h⁻¹ to 288 kg·mol⁻¹·h⁻¹, demonstrating good thermal stability of the quinolinyl imidazolidin-2-imine nickel catalyst, although Mₙ of the resulting polymers decreased due to fast chain transfer reaction at high temperature.

To investigate the effects of the structure of nickel complexes, we conducted N-S copolymerization with Ni1, Ni2, Ni3, and Ni4 by changing comonomer feed ratio. Ni2 containing t-butyl substituent exhibited the highest activity in each comonomer feed ratio, indicating the electron-donating substituent with rational sterical hindrance is efficient for the increase of polymerization activity in this quinolinyl imidazolidin-2-imine nickel catalytic system. In each catalytic system, the increase of S concentration in the feed decreased the catalytic activity accompanied by the decrease of Mₙ. However, it is noteworthy that Mₙ of the polymers still re-

Fig. 1 Molecular structure of complex Ni1. H atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond lengths (Å) and angles (''): Ni1–Br1, 2.352(2); Ni1–Br2, 2.360(2); Ni1–N1, 1.998(9); Ni1–N2, 2.010(11); N2–C10, 1.370(17); N1–Ni1–Br1, 113.3(3); N1–Ni1–Br2, 107.1(3); N1–Ni1–N2, 82.8(4); N2–Ni1–Br1, 128.9(3); N2–Ni1–Br2, 105.7(3); C10–N2–Ni1, 117.8(8).

Fig. 2 Molecular structure of complex Ni2. H atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond lengths (Å) and angles (''): Ni1–Br1, 2.3653(12); Ni1–Br2, 2.3608(10); Ni1–N1, 2.007(4); Ni1–N2, 1.962(4); N2–C10, 1.356(7); N1–Ni1–Br1, 96.59(14); N1–Ni1–Br2, 140.00(13); N1–Ni1–N2, 82.09(18); N2–Ni1–Br1, 124.52(13); N2–Ni1–Br2, 110.48(14); C10–N2–Ni1, 129.6(4).

Fig. 3 Molecular structure of complex Ni3. H atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond lengths (Å) and angles (''): Ni1–Br1, 2.3720(12); Ni1–Br2, 2.3599(11); Ni1–N1, 2.014(5); Ni1–N2, 2.022(5); N2–C10, 1.338(7); N1–Ni1–Br1, 109.21(17); N1–Ni1–Br2, 104.58(15); C10–N2–Ni1, 120.0(4); N1–Ni1–N2, 81.9(2); N2–Ni1–Br1, 100.28(14); N2–Ni1–Br2, 143.80(14).

Fig. 4 Molecular structure of complex Ni4. H atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond lengths (Å) and angles (''): Ni1–Br1, 2.3468(6); Ni1–Br2, 2.3549(6); Ni1–N1, 1.996(3); Ni1–N2, 2.012(2); N2–C10, 1.318(4); N1–Ni1–Br1, 107.82(8); N1–Ni1–Br2, 101.91(7); N1–Ni1–N2, 82.90(10); N2–Ni1–Br1, 122.49(7); N2–Ni1–Br2, 107.06(7); C10–N2–Ni1, 122.5(2).
Table 1  N polymerization and copolymerization with S using nickel complexes.\(^a\)

| Entry | Cat. | Temp. (°C) | Al/Ni | S (mol%) | Time (min) | Yield (g) | \(M_r\) \((g\cdot mol^{-1})\) | \(M_w/M_n\) | \(T_g\) (°C) | \(f_0\) (mol%) | Conv. (%) \(N/S\) |
|-------|------|------------|-------|----------|-------------|-----------|----------------|-------------|-------------|----------------|-----------------|
| 1     | Ni3  | 30         | 1000  | 0        | 2           | 1.22      | 7320          | 31.6        | 2.52        | 9              | 0               | 9               |
| 2     | Ni3  | 30         | 500   | 40       | 60          | 0.58      | 116           | 5.1         | 2.66        | 9              | 9               | 9               |
| 3     | Ni3  | 30         | 1000  | 40       | 60          | 0.64      | 128           | 5.4         | 2.54        | 335            | 9               | 9               |
| 4     | Ni3  | 30         | 1500  | 40       | 60          | 0.53      | 106           | 3.5         | 2.43        | 9              | 9               | 9               |
| 5     | Ni3  | 30         | 2000  | 40       | 60          | 0.52      | 104           | 3.4         | 2.97        | 9              | 9               | 9               |
| 6     | Ni3  | 300       | 1000  | 40       | 60          | 0.11      | 22            | 7.8         | 2.61        | 337            | 9               | 9               |
| 7     | Ni3  | 50         | 1000  | 40       | 60          | 1.16      | 232           | 2.0         | 3.22        | 335            | 9               | 9               |
| 8     | Ni3  | 70         | 1000  | 40       | 60          | 1.37      | 274           | 0.9         | 3.81        | 331            | 9               | 9               |
| 9     | Ni3  | 90         | 1000  | 40       | 60          | 1.44      | 288           | 0.7         | 3.64        | 325            | 9               | 9               |
| 10    | Ni1  | 30         | 1000  | 20       | 10          | 0.24      | 288           | 8.5         | 2.52        | 367            | 1.01            | 3.88/0.33       |
| 11    | Ni1  | 30         | 1000  | 40       | 10          | 0.15      | 180           | 4.3         | 2.49        | 332            | 2.57            | 6.46/0.26       |
| 12    | Ni1  | 30         | 1000  | 60       | 10          | 0.08      | 96            | 2.9         | 2.61        | 311            | 6.25            | 4.94/0.22       |
| 13    | Ni1  | 30         | 1000  | 80       | 10          | 0.10      | 36            | 1.9         | 2.74        | 273            | 12.47           | 3.38/0.12       |
| 14    | Ni2  | 30         | 1000  | 20       | 5           | 0.20      | 480           | 9.6         | 2.53        | 9              | 1.24            | 6.53/0.33       |
| 15    | Ni2  | 30         | 1000  | 40       | 10          | 0.23      | 276           | 5.7         | 2.66        | 341            | 3.56            | 9.75/0.54       |
| 16    | Ni2  | 30         | 1000  | 60       | 10          | 0.11      | 132           | 3.8         | 2.47        | 329            | 7.05            | 6.75/0.34       |
| 17    | Ni2  | 30         | 1000  | 80       | 10          | 0.05      | 60            | 1.7         | 2.34        | 283            | 12.97           | 5.75/0.22       |
| 18    | Ni3  | 30         | 1000  | 20       | 10          | 0.17      | 204           | 9.1         | 2.36        | 365            | 1.10            | 5.56/0.25       |
| 19    | Ni3  | 30         | 1000  | 40       | 10          | 0.11      | 132           | 5.2         | 2.51        | 334            | 2.73            | 4.75/0.20       |
| 20    | Ni3  | 30         | 1000  | 60       | 10          | 0.04      | 48            | 3.5         | 2.42        | 295            | 7.06            | 2.44/0.13       |
| 21    | Ni3  | 30         | 1000  | 80       | 10          | 0.02      | 24            | 1.4         | 2.25        | 258            | 12.86           | 2.25/0.08       |
| 22    | Ni4  | 30         | 1000  | 20       | 10          | 0.16      | 192           | 13.1        | 2.45        | 9              | 1.42            | 5.25/0.30       |
| 23    | Ni4  | 30         | 1000  | 40       | 10          | 0.13      | 156           | 7.4         | 2.21        | 354            | 4.09            | 5.46/0.35       |
| 24    | Ni4  | 30         | 1000  | 60       | 10          | 0.04      | 48            | 4.4         | 2.59        | 327            | 7.54            | 2.44/0.13       |
| 25    | Ni4  | 30         | 1000  | 80       | 10          | 0.01      | 12            | 1.8         | 2.27        | 255            | 16.54           | 1.09/0.05       |

\(N\) = 5 \(\mu\)mol, solvent = toluene, total volume = 20 mL, \([M]\) = 2 \(mol\cdot L^{-1}\). \(^a\) Activity = \(kg\) polymer \(mol\_Ni^{-1} \cdot h^{-1}\). \(^b\) Determined by GPC using universal polystyrene standard. \(^c\) Determined by DSC. \(^d\) S incorporation determined by \(^1^H\)-NMR. \(^e\) Not determined under 380 °C. \(^f\) Not determined.

Fig. 5  Fineman-Ross plots for copolymerizations of N and S with Ni1 (a), Ni2 (b), Ni3 (c), and Ni4 (d) \((F = [N]/[S])\) in feed and \(f = [N]/[S]\) in copolymer.

https://doi.org/10.1007/s10118-020-2400-3
mained at a high level (> 1.3 × 10^4 g·mol⁻¹), which seemed to be enough to form self-standing films. The molecular weight distribution of polymers was narrow with unimodal GPC curve (see ESI), indicating that all the copolymerizations were carried out with single-site catalysts. Although Ni4 exhibited lower activity, Mₙ of the copolymers obtained was higher than those of the polymers obtained with Ni1, Ni2, and Ni3 at each comonomer feed ratio, respectively, probably due to bulkier substituent of Ni4 on the imidazolidinyl ring around the axial position of active site.[51]

The microstructure of N-S copolymer was analyzed with ¹H-NMR and ¹³C-NMR spectroscopies, and the comonomer content in the copolymer was calculated from ¹H-NMR according to the literature.[51] In each catalytic system, the content increased with the increasing S concentration in the feed, and the highest content (up to 16.54 mol%) in the copolymer was observed with Ni4.

The monomer reactivity ratios (r₁ = kₙ₁/kₙ₅ and r₂ = k₅₅/k₉₅) were then evaluated for each system by Fineman-Ross plots (Fig. 5), since the copolymerization time was shortened to keep low monomer conversions as shown in Table 1. The values were obtained to be r₁ = 44.8 and r₂ = 0.04 for Ni1, r₁ = 19.57 and r₂ = 0.05 for Ni2, r₁ = 22.47 and r₂ = 0.04 for Ni3, and r₁ = 17.14 and r₂ = 0.06 for Ni4. All the catalytic systems gave copolymers with a preference for the insertion of norbornene, although the reactivity ratios were slightly dependent on the complex used. The products of reactivity ratios (r₁/r₂) obtained with each catalytic system (> 1.0) indicated a tendency of the random copolymerization of N and S regardless of the complex used.

**Copolymerization of Norbornene with para-Chlorostyrene**

The ability of nickel to promote the incorporation of the functionalized styrene derivative was verified by using CS comonomer, which offered the reactive site for further functionalization of N-S copolymer.[52] The copolymerization of N with CS was carried out with nickel complexes (Table 2). The copolymerization exhibited much higher activities (up to 1070 kg·mol⁻¹·h⁻¹) than N-S copolymerization in each catalytic system. Similar to the N-S copolymerization, Ni4 afforded higher molecular weight copolymers (up to 25.8 × 10^4 g·mol⁻¹) with the highest comonomer content. We therefore selected Ni4 to investigate the effect of comonomer feed ratio, where low comonomer concentration was also kept by shortening the copolymerization time. The ¹H-NMR and ¹³C-NMR spectra of poly(N-CS) prepared by Ni4 (Table 2, entry 8) were shown in Fig. 6 and Fig. 7, respectively. The resonances of all the aliphatic protons (H₁-₉) and the aromatic protons (H₁₀-H₁₄) were observed at the range of 0.80–2.50 and 6.17–7.27 ppm, respectively. The resonances of all the aliphatic carbons were assigned as follows: δ = 27.29–33.32 ppm, C₇: δ = 35.14 ppm, C₈: δ = 36.27–43.84 ppm, C₁₄: δ = 45.90 ppm, Cₛ₉: δ = 52.31 ppm.

**Table 2.** Copolymerizations of N and CS with nickel complexes Ni1–Ni4.*

| Entry | Cat. | Temp. (°C) | CS (mol%) | Time (min) | Yield (g) | Act. a | Mₙ = 10^4 (g·mol⁻¹) | PDI c | Tg (°C) | f₁₂ b (mol%) | Conv. (%) N/CS |
|-------|------|------------|-----------|------------|----------|-------|------------------|------|----------|-------------|----------------|
| 1     | Ni1 | 30         | 40        | 10         | 0.63     | 756   | 21.3             | 2.41 |         | −1          | 0.54           |
| 2     | Ni2 | 30         | 40        | 10         | 0.89     | 1070  | 17.8             | 2.90 | 371      | 1.22        |
| 3     | Ni3 | 30         | 40        | 10         | 0.50     | 600   | 24.6             | 2.83 | 377      | 0.85        |
| 4     | Ni4 | 30         | 40        | 10         | 0.45     | 540   | 25.8             | 2.46 | 375      | 1.51        |
| 5     | Ni4 | 30         | 20        | 5          | 0.30     | 720   | 42.4             | 2.69 | −1       | 0.57        | 9.88/0.23     |
| 6     | Ni4 | 30         | 40        | 5          | 0.22     | 528   | 23.6             | 2.53 | 373      | 1.57        | 9.50/0.22     |
| 7     | Ni4 | 30         | 60        | 5          | 0.13     | 312   | 17.7             | 2.43 | 368      | 3.22        | 8.25/0.18     |
| 8     | Ni4 | 30         | 80        | 5          | 0.05     | 120   | 7.8              | 2.41 | 352      | 7.86        | 5.88/0.13     |
| 9     | Ni4 | 60         | 60        | 10         | 0.44     | 528   | 7.9              | 3.01 | 345      | 6.18        | −1            |
| 10    | Ni4 | 60         | 80        | 10         | 0.23     | 276   | 3.6              | 3.39 | 325      | 11.7        | −1            |

* Ni = 5 mmol, MAO = 5 mmol, solvent = toluene, total volume = 20 mL, [M] = 2 mol/L, temperature = 40 °C. a Activity = kg polymer·mol⁻¹·h⁻¹. b Determined by GPC using universal polystyrene standard. c Determined by DSC. d CS incorporation determined by ¹H-NMR. e Not determined under 380 °C. f Not determined.

**Fig. 6.** ¹H-NMR spectrum of N-CS copolymer obtained by Ni4 with 80 mol% of CS (Table 2, entry 8).

**Fig. 7.** ¹³C-NMR spectrum of N-CS copolymer obtained by Ni4 with 80 mol% of CS (Table 2, entry 8).
Transparencies of Copolymer Films

The transparencies of N-S (Table 1, entry 20) and N-CS (Table 2, entry 7) copolymer films processed by solution casting were evaluated, and the UV-Vis spectra of the prepared films are shown in Fig. 10. The result showed that the transmittance of copolymer films remained about 90% in the visible light region (350–750 nm) regardless of the comonomer used, indicating that these copolymers could be used as an optical transparent polymer material.

![Fig. 10 UV-Vis spectra of N-S and N-CS copolymer thin films (Table 1, entry 20 and Table 2, entry 7).](https://doi.org/10.1007/s10118-020-2400-3)

CONCLUSIONS

A class of quinolinyl imidazolidin-2-imine based nickel complexes was developed for the synthesis of low birefringent COCs via copolymerization of N and S with high activity. The installation of bulky 2,6-disopropylanilin substituent on the imidazolidine ligand (Ni4) improved the molecular weight and the comonomer content of the copolymers. The complexes were also able to promote copolymerization of N and CS with increased activities of up to 1070 kg·mol⁻¹·h⁻¹, affording high molecular weight (M₄₅ up to 4.2 × 10⁴ g·mol⁻¹) functionalized copolymers. The comonomer content in the copolymer was controllable by changing comonomer feed ratio. The linear relationship between comonomer content and glass transition temperature was observed. The evaluation of monomer reactivity ratios in the copolymerizations of N with S or CS indicated the production of the expected copolymers and a preference for the insertion of N monomer regardless of the last inserted monomer at the growing polymer chain. The performance of these nickel catalysts demonstrates a straightforward ligand design for the development of the late transition metal catalysts in the olefin (co)polymerization.

Electronic Supplementary Information

Electronic supplementary information (ESI), which includes synthesis and characterization of the ligands and corresponding complexes, polymerization data and polymer characterization, and X-ray crystallography, is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-020-2400-3.
ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (No. 21774018), the Fundamental Research Funds for the Central Universities (No. 2232020A-05), and the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning.

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