

Remote electron effects and π - π interactions of α -diimine nickel complexes

Yizhan Wang*, Hailong He*, and Dan Peng✉

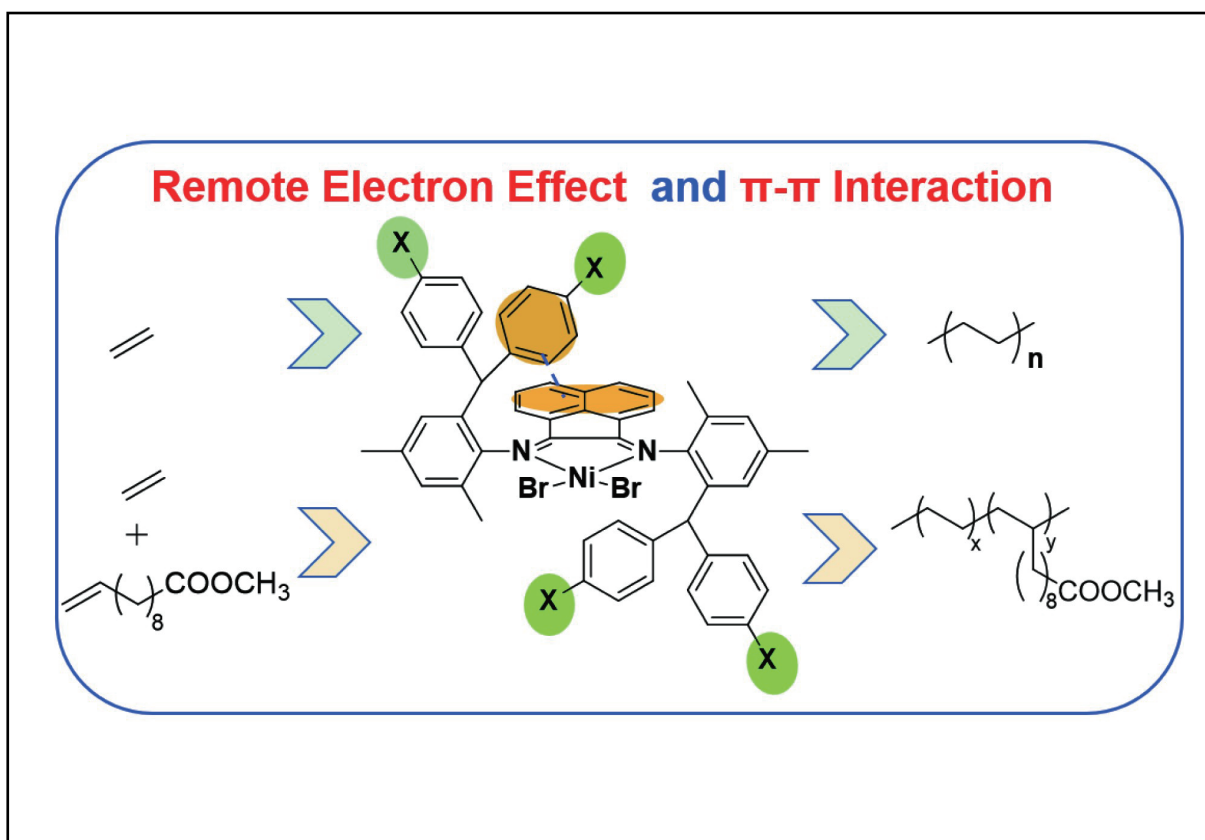
Hefei National Research Center for Physical Sciences at the Microscale, CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, China

* These authors contributed equally to this work

✉ Correspondence: Dan Peng, E-mail: pengdan@ustc.edu.cn

© 2024 The Author(s). This is an open access article under the CC BY-NC-ND 4.0 license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Graphical abstract



New types of α -diimine nickel catalysts with remote electron effects and π - π interactions were prepared and used in ethylene (co) polymerization.

Public summary

- Novel α -diimine nickel catalysts with different electronic effects were prepared.
- These α -diimine nickel catalysts showed high polymerization activities in ethylene polymerization, generating polyethylene products with adjustable molecular weight and branching density.
- These α -diimine nickel catalysts can also catalyze the copolymerization of ethylene and polar monomer, preparing functionalized polyolefin.

Remote electron effects and π - π interactions of α -diimine nickel complexes

Yizhan Wang*, Hailong He*, and Dan Peng✉

Hefei National Research Center for Physical Sciences at the Microscale, CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, China

* These authors contributed equally to this work

✉ Correspondence: Dan Peng, E-mail: pengdan@ustc.edu.cn

© 2024 The Author(s). This is an open access article under the CC BY-NC-ND 4.0 license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).



Cite This: *JUSTC*, 2024, 54(9): 0903 (6pp)



Read Online



Supporting Information

Abstract: The seminal report of α -diimine palladium and nickel catalysts in 1995 represented a major breakthrough in the preparation of functionalized polyolefin materials. Owing to the high abundance and low cost of nickel, nickel-based catalysts have great application prospects in the industrialization process of olefin coordination polymerization. In this work, various *N*-aryl substituents with different electronic effects were synthesized and introduced into α -diimine ligands. The as-prepared α -diimine nickel catalysts showed high polymerization activity (0.9×10^7 – 3.0×10^7 g·mol⁻¹·h⁻¹) in ethylene polymerization, generating polyethylene products with adjustable molecular weights (M_n values: 7.4×10^4 – 146.9×10^4 g·mol⁻¹) and branching densities (31/1000 C–68/1000 C). The resulting polyethylene products showed excellent mechanical properties, with high tensile strength (up to 25.0 MPa) and high strain at break values (up to 3890%). The copolymerization of ethylene and polar monomers can also be achieved by these nickel complexes, ultimately preparing functionalized polyolefins.

Keywords: α -diimine nickel catalyst; ethylene polymerization; π - π interaction effect; electronic effect; polar monomer

CLC number: O643.36; O632.12

Document code: A

1 Introduction

Polyethylenes play an important role in films, pipes and medical consumables because of their excellent properties, including easy processing, corrosion resistance and other advantages. However, traditional polyethylene materials have several limitations (adhesion, self-repair, antibacterial activity, degradability, etc.) in practical applications because of their nonpolar characteristics^[1]. Introducing a small number of polar functional groups into polyethylene can enhance the performance of the as-prepared polymer products and greatly broaden their application range^[2–4]. The coordination copolymerization of ethylene and polar monomers catalyzed by late transition metal catalysts is one of the most economical methods for preparing functional polyolefin materials^[5–8] and has been widely studied in recent decades^[9–12]. High-performance catalysts for copolymerization have been developed effectively through the introduction of substituents with different electrons and steric effects^[13,14].

The seminal report of α -diimine nickel and palladium catalysts in 1995 promoted the development of the field of olefin polymerization^[15]. Compared with palladium, nickel is more competitive in industry because of its high abundance in nature and low cost. Since the discovery of α -diimine nickel catalysts, approximately 2000 kinds of α -diimine nickel complexes with different ligand structures have been reported and successfully applied in ethylene polymerization^[16–20], and Fig. 1 shows several well-defined α -diimine nickel complexes with

structures reported in the literature^[21–23]. However, designing and synthesizing new types of catalyst structures to influence the microstructure and physical properties of polymer products is still highly scientific^[24–28].

The electronic and steric effects of α -diimine ligands are important factors affecting the properties of catalysts^[29–33]. In this work, various α -diimine ligands with different substituents based on acenaphthenequinone structures were synthesized, and the corresponding nickel catalysts were prepared. The effects of these nickel complexes on the polymerization activity, M_n value, branching density and mechanical properties of the as-synthesized polyethylenes were systematically studied.

2 Materials and methods

The chemical reagents were used as received from commercial sources without further purification. The synthesis of ligands was carried out in air. ¹H and ¹³C NMR spectra of the ligands were obtained with a Bruker 400 MHz instrument at room temperature. The air-sensitive nickel complexes were synthesized in a glove box. Elemental analysis, mass spectrometry and high-resolution mass spectrometry (HRMS) were performed at the Analytical Center of the University of Science and Technology of China. The molecular structures of the single crystals of the nickel complexes were obtained via X-ray diffraction. Ethylene polymerization and copolymerization were performed in a low-pressure reactor. The polyethylene products were precipitated by acidified methanol. The M_n

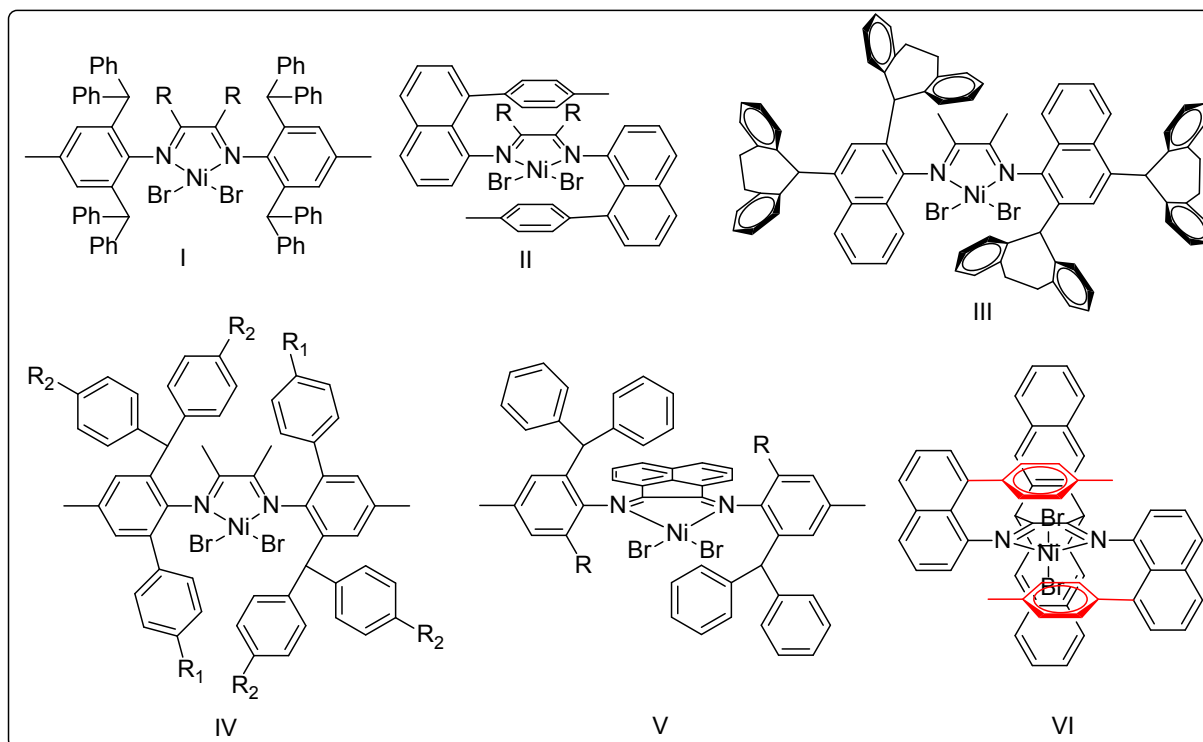


Fig. 1. Selected α -diimine nickel complexes.

values and polymer dispersity indexes (PDIs) of the polyethylenes were determined via gel permeation chromatography (GPC) at 150 °C using 1,2,4-trichlorobenzene as the solvent. The T_m values of the polymer products were obtained via differential scanning calorimetry (DSC) analyses on a TA Instruments DSC Q20. Stress/strain experiments were performed at standard ambient temperature (25 °C) via a UTM2502 universal tester. The polyethylene samples were 28 mm long, 2 mm wide and 0.5 mm thick.

3 Results and discussion

The substituted anilines were obtained according to the literature procedures^[34]. The ligands (L1–L4) were prepared via acid-catalyzed condensation reactions in yields ranging from 85%–88% and were characterized via NMR analyses. The target α -diimine nickel complexes Ni1–Ni4 were prepared in high yields (85%–87%) via coordination reactions of the ligands with (DME)NiBr₂ at ambient temperature (Fig. 2). Single crystals of Ni2 and Ni3 were obtained by layering toluene solutions with *n*-hexane, and their contents were determined via X-ray diffraction (Fig. 3). The metal center adopted a twisted tetrahedral geometry, which resembled that reported in the literature for α -diimine nickel complexes^[35–37].

Ethylene polymerization. With Et₂AlCl as a cocatalyst, complexes Ni1–Ni3 all showed high catalytic activities in ethylene polymerization (level of 10⁷ g·mol⁻¹·h⁻¹, Table 1), affording polyethylenes with adjustable M_n values and moderate branching density. The highest catalytic activity was observed at 80 °C for Ni1–Ni3 (Table 1, entries 2, 5 and 8, up to 3.3×10⁷ g·mol⁻¹·h⁻¹). The maximum molecular weight of the as-prepared polyethylene products was 146.9×10⁴ g·mol⁻¹, which was generated by complex Ni1 at 50 °C (Table 1, entry

2). As the polymerization temperature increased from 50 °C to 100 °C, the M_n value of the polyethylene products decreased significantly, which may be due to the increasing rate of chain transfer and β -H elimination^[38–40]. Under the same conditions, the M_n value of the resulting polyethylene products synthesized from Ni1 with an electron-donating substituent (-OMe) is superior to that obtained from Ni3 with an electron-deficient substituent (-F) (Table 1, entries 1–3 vs. entries 7–9), which is mainly because the introduction of electron-donating substituents inhibited the rate of β -H elimination and chain transfer in the ethylene polymerization process^[41–44]. Interestingly, the M_n values of polyethylene obtained from Ni2 with electron-donating substituents (t-Bu) were dramatically lower than those of Ni1 (Table 1, entries 4–6 vs. entries 1–3). π - π interactions are responsible for this difference^[45,46]. In the structures of the acenaphthenequinone-based catalysts Ni1–Ni3, the π - π interactions between the aromatic ring in the diarylmethyl moiety and the acenaphthene planes demonstrated rigid conformations along with enhanced steric hindrance of the nickel center, leading to an improved M_n value of the resulting polyethylenes. For Ni2 complexes, the introduction of -t-Bu with large steric hindrance may weaken or eliminate this π - π interaction, which can also be observed from the single-crystal structure of Ni2 (Fig. 3a), leading to a much lower M_n value of the resulting polyethylene.

Mechanical properties. The physical and mechanical properties of the polymer products were also determined and are provided in Table 1. The polyethylene produced by Ni2 at 100 °C showed poor stretchability due to its low M_n value (Table 1, entry 6)^[47]. The other polyethylene products can be transferred into dog bone-shaped samples and exhibit good mechanical properties (Fig. 4). The polyethylene samples

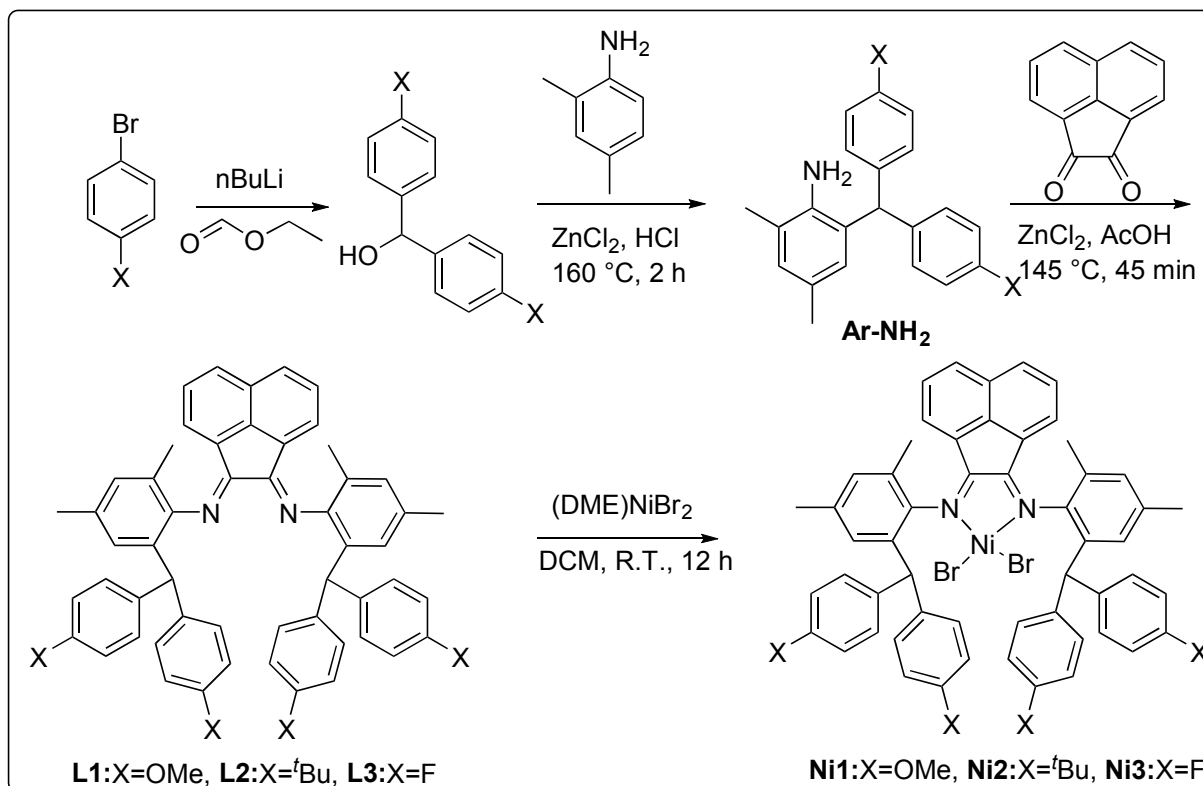


Fig. 2. Synthesis of α -diimine ligands L1–L3 and nickel catalysts Ni1–Ni3.

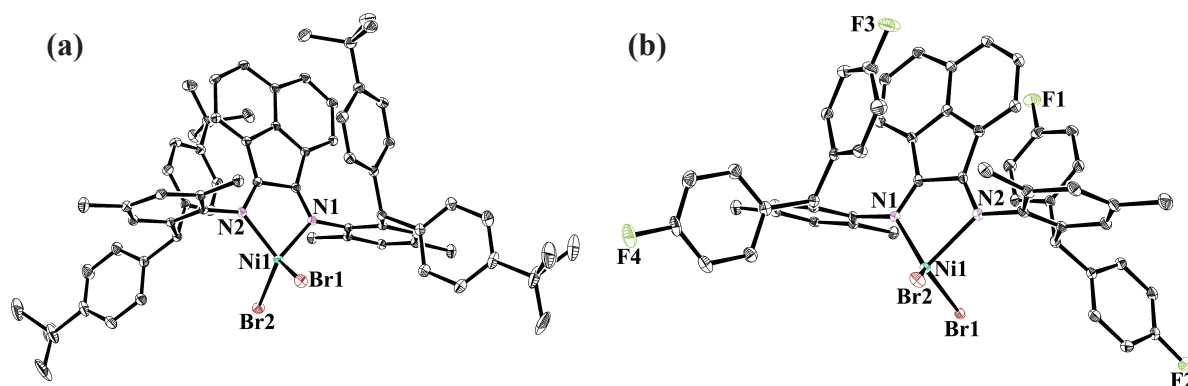


Fig. 3. (a) Molecular structures of Ni2 (CCDC number 2348877). The selected bond lengths (\AA) and angles ($^\circ$) were as follows: Ni1–N1 2.025(2), Ni1–N2 2.025(2), Ni1–Br1 2.3315(4), Ni1–Br2 2.3315(4), N1–Ni1–N2 82.40(14), Br2–Ni1–Br1 115.38(3). (b) Molecular structures of Ni3 (CCDC number 2348878). The selected bond lengths (\AA) and angles ($^\circ$) were as follows: Ni1–N12.034(2), Ni1–N2 2.209(2), Ni1–Br1 2.4368(5), Ni1–Br2 2.3539(5), N1–Ni1–N2 80.15(9), Br2–Ni1–Br1 130.943(18).

generated from Ni1 at 50°C have a high branching density and melting point (T_m), affording high tensile strength (25.0 MPa) and moderate strain at break values (745%, Fig. 4a). When the polymerization temperature was increased to 80°C and 100°C , the tensile strength of the prepared polyethylene products decreased (25.0 MPa and 5.9 MPa), whereas the strain at break increased (1400% and 2078%, Fig. 4a). Compared with that of Ni1, the tensile strength of polyethylene prepared from Ni2 and Ni3 at 80°C is lower (3.2 MPa and 14.8 MPa, Fig. 4b and c). The difference in mechanical properties may be due to the different topological structures of the polymers (molecular weight and branching density). Finally, these polyethylene samples also exhibited elastic properties, the cyclic recovery value of which reached 70% (Table 1,

entry 3, Fig. 4d).

Ethylene copolymerization. Finally, catalysts Ni1–Ni3 can also catalyze the copolymerization of ethylene and the polar monomer methyl 10-undecenoate, resulting in the preparation of ester-functionalized polyolefin materials. Complex Ni2 had the highest incorporation ratio of the polar monomer (1.1 mol%, Table 2, entry 2). This may be due to the weakening of the π – π interactions in the Ni2 structure. The Ni1 catalyst shows the highest polymerization activity ($2.1 \times 10^4 \text{ g} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$), moderate incorporation ratio of the polar monomer (0.9 mol%) and highest polymer molecular weight ($31.3 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$, Table 2, entry 1), which may be attributed to the electron-donating effect and π – π interactions of the Ni1 complex with the –OMe substituent. The Ni3

Table 1. Ethylene polymerization using Ni1–Ni3^a.

Entry ^a	Catalyst	T(°C)	Yield(g)	Activity ^b (10 ⁷ g·mol ⁻¹ ·h ⁻¹)	M _n ^c (10 ⁴ g·mol ⁻¹)	PDI	B ^d	T _m (°C) ^e	Stress(MPa) ^f	Strain(%) ^f	SR(%) ^g
1	Ni1	50	1.00	3.0	146.9	1.9	32	113.1	25.0±0.3	745±19.8	33
2	Ni1	80	1.10	3.3	88.2	2.0	51	70.6	22.6±0.2	1400±36.1	36
3	Ni1	100	0.50	1.5	81.4	1.5	68	69.7	5.9±0.5	2078±27.5	70
4	Ni2	50	0.89	2.7	44.0	1.9	42	83.2	5.6±0.5	460±25.5	69
5	Ni2	80	1.02	3.1	13.3	4.0	59	73.1	3.2±0.3	1440±33.7	65
6	Ni2	100	0.81	2.4	7.4	4.0	67	–	–	–	–
7	Ni3	50	0.80	2.4	60.2	1.9	31	90.5	16.8±1.2	471±15.3	25
8	Ni3	80	0.82	2.5	53.4	1.9	58	65.0	14.8±0.3	677±11.2	35
9	Ni3	100	0.31	0.9	10.5	3.3	63	61.3	7.7±0.2	788±30.5	57

^a Polymerization conditions: 0.2 μ mol nickel catalyst in 2 mL CH₂Cl₂, 18 mL heptane, 8 atm ethylene, 500 eq. Et₂AlCl, time = 10 min. ^b The activity was determined from the mass of the polymer product and was the average of at least two runs. ^c Determined by GPC. ^d Branching density determined by ¹H NMR at 120 °C. ^e T_m values were determined via DSC. ^f Strain and stress at break values. ^g Strain recovery values: SR = 100 ($\epsilon_a - \epsilon_r$)/ ϵ_a .

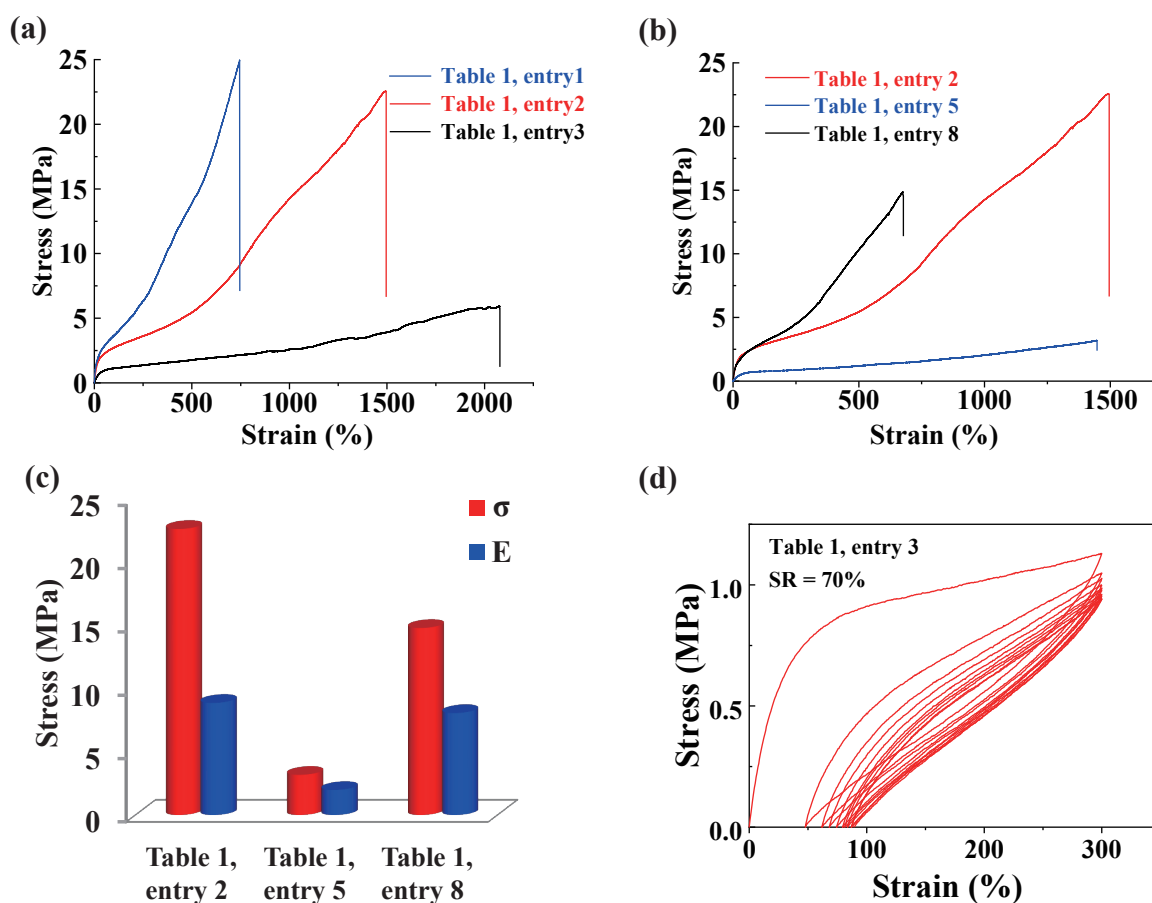


Fig. 4. (a) Stress–strain curves of the polymer samples obtained from Ni1 at 50 °C, 80 °C and 100 °C. (b) Stress–strain curves of the polymer samples obtained from Ni1–Ni3 at 80 °C. (c) Fracture stress and Young’s modulus of the polymer samples generated from Ni1–Ni3 at 80 °C. (d) Strain recovery curve of the polymer sample from Table 1, entry 3.





catalyst has the lowest molecular weight (2.0×10^4 g·mol⁻¹, Table 2, entry 3) and incorporation ratio of the polar monomer (0.3 mol%), possibly because the Ni3 catalyst, which is electron deficient, is easily poisoned by the polar monomer. In addition, the copolymerization of ethylene and 0.5 M 6-chlorohex-1-ene catalyzed by Ni2 was also performed (Table 2, entry 4, incorporation ratios: 0.4 mol%). In summary, the electronic and π - π interactions of catalysts can

greatly influence their catalytic activities in the copolymerization of ethylene and polar monomers, the M_n values and the incorporation ratios of the resulting copolymers.

4 Conclusions

In this work, various new types of α -diimine nickel complexes with different N-aryl moieties were prepared and

Table 2. Ethylene copolymerization using Ni1–Ni3^a.

Entry	Catalyst	Comonomer	Yield (g)	Activity (10 ⁵ g·mol ⁻¹ ·h ⁻¹)	X ^b	M _n ^c (10 ⁴ g·mol ⁻¹)	PDI ^c	T _m ^d (°C)
1	Ni1		2.10	2.1	0.9	31.3	1.6	117.5
2	Ni2		1.50	1.5	1.1	8.9	1.6	110.4
3	Ni3		0.82	0.8	0.3	2.0	2.4	101.0
4 ^e	Ni2		1.80	1.8	0.4	27.7	1.7	114.3

^a Polymerization conditions: 10 μmol Ni in 2 mL CH₂Cl₂, 18 mL heptane, 8 atm ethylene, 1.0 M methyl 10-undecenoate, total volume of heptane, CH₂Cl₂ and polar monomer = 20 mL, 50 °C, 500 eq. Et₂AlCl, 60 min. ^b Comonomer incorporation ratio determined by ¹H NMR at 120 °C. ^c Determined by GPC.

^d T_m values were determined via DSC. ^e 0.5 M 6-chlorohex-1-ene.

studied for use in ethylene polymerization and copolymerization with methyl 10-undecenoate. The above nickel catalysts mediate ethylene polymerization with high activities (10⁷ g·mol⁻¹·h⁻¹), and the M_n value of the as-prepared polyethylene products can be adjusted by the polymerization conditions, remote electronic effects and π–π interactions of these nickel complexes. The as-synthesized polyethylene samples also exhibited mechanical properties with high tensile strength (up to 25.0 MPa) and high strain at break values (up to 3890%), along with elastic properties (cyclic recovery value: 25%–70%). Furthermore, these nickel complexes can catalyze the copolymerization of ethylene and polar monomers (methyl 10-undecenoate and 6-chlorohex-1-ene) with a moderate incorporation ratio of polar monomers (0.3–1.1 mol%). The study of remote electronic effects and π–π interactions in this work provides new inspiration for the design and synthesis of olefin polymerization catalysts.

Supporting information

The supporting information for this article can be found online at <https://doi.org/10.52396/JUSTC-2024-0059>.

Acknowledgements

This work was supported by the National Key R&D Program of China (2021YFA1501700) and Fundamental Research Funds for the Central Universities (WK9990000142).

Conflict of interest

The authors declare that they have no conflict of interest.

Biographies

Yizhan Wang is currently a master's student in the Department of Polymer Science and Engineering, University of Science and Technology of China, under the supervision of Prof. Changle Chen. His research mainly focuses on the preparation of α-diimine nickel catalysts and their applications in olefin polymerization.

Hailong He is currently a graduate student in the Department of Polymer Science and Engineering, University of Science and Technology of China, under the supervision of Prof. Changle Chen. His research mainly focuses on the preparation of nickel and palladium catalysts and their applications in olefin polymerization.

Dan Peng is currently a postdoctoral researcher in the Hefei National Research Center for Physical Sciences at the Microscale, University of Science and Technology of China (USTC). She received her Ph.D. de-

gree from USTC under the tutelage of Prof. Changle Chen in 2023. Her research interests include the preparation of polyolefin materials and their applications.

References

- [1] Tan C, Chen M, Zou C, et al. Potentially practical catalytic systems for olefin-polar monomer coordination copolymerization. *CCS Chemistry*, **2024**, *6*: 882–897.
- [2] Franssen N M G, Reek J N H, de Bruin B. Synthesis of functional ‘polyolefins’: state of the art and remaining challenges. *Chemical Society Reviews*, **2013**, *42*: 5809–5832.
- [3] Chung T C. Functionalization of Polyolefins. New York: Academic Press, **2002**.
- [4] Tan C, Chen C L. Nickel catalysts for the synthesis of ultra-high molecular weight polyethylene. *Science Bulletin*, **2020**, *65*: 1137–1138.
- [5] Soshnikov I E, Chen C L, Bryliakov K P. Ni catalyzed ethylene copolymerization with polar monomers. *Science China Chemistry*, **2019**, *62*: 653–654.
- [6] Xiong S, Shoshani M M, Zhang X, et al. Efficient copolymerization of acrylate and ethylene with neutral P, O-chelated nickel catalysts: mechanistic investigations of monomer insertion and chelate formation. *Journal of the American Chemical Society*, **2021**, *143*: 6516–6527.
- [7] Hu X Q, Kang X H, Jian Z B. Suppression of chain transfer at high temperature in catalytic olefin polymerization. *Angewandte Chemie International Edition*, **2022**, *61*: e202207363.
- [8] Li M Y, Cai Z G, Eisen M S. Rational design of aldimine imidazolidin-2-imine/guanidine nickel catalysts for norbornene (co)polymerizations with enhanced catalytic performance. *Journal of Catalysis*, **2023**, *420*: 58–67.
- [9] Tan C, Chen C L. Emerging palladium and nickel catalysts for copolymerization of olefins with polar monomers. *Angewandte Chemie International Edition*, **2019**, *58*: 7192–7200.
- [10] Tan C, Zou C, Chen C L. Material properties of functional polyethylenes from transition-metal-catalyzed ethylene-polar monomer copolymerization. *Macromolecules*, **2022**, *55*: 1910–1922.
- [11] Boan N K, Hillmyer M A. Post-polymerization functionalization of polyolefins. *Chemical Society Reviews*, **2005**, *34*: 267–275.
- [12] Muhammad Q, Tan C, Chen C L. Concerted steric and electronic effects on α-diimine nickel- and palladium-catalyzed ethylene polymerization and copolymerization. *Science Bulletin*, **2020**, *65*: 300–307.
- [13] Yuan W B, Li W M, Dai S Y. Preparation of polyethylene thermoplastic elastomers using C₅-symmetric nickel catalysts in ethylene polymerization. *Polymer*, **2023**, *285*: 126322.
- [14] Yan Z P, Chang G R, Zou W P, et al. Synthesis of lightly branched ultrahigh-molecular-weight polyethylene using cationic benzocyclohexyl nickel catalysts. *Polymer Chemistry*, **2023**, *14*: 183–190.
- [15] Johnson L K, Killian C M, Brookhart M. New Pd(II)- and Ni(II)-based catalysts for polymerization of ethylene and α-olefins. *Journal*

- of the American Chemical Society, **1995**, *117*: 6414–6415.
- [16] Wang F Z, Chen C L. A continuing legend: the brookhart-type α -diimine nickel and palladium catalysts. *Polymer Chemistry*, **2019**, *10*: 2354–2369.
- [17] Guo L H, Dai S Y, Sui X L, et al. Palladium and nickel catalyzed chain walking olefin polymerization and copolymerization. *ACS Catalysis*, **2016**, *6*: 428–441.
- [18] Popeney C S, Levins C M, Guan Z. Systematic investigation of ligand substitution effects in cyclophane-based nickel(II) and palladium(II) olefin polymerization catalysts. *Organometallics*, **2011**, *30*: 2432–2452.
- [19] Rhinehart J L, Mitchell N E, Long B K. Enhancing α -diimine catalysts for high-temperature ethylene polymerization. *ACS Catalysis*, **2014**, *4*: 2501–2504.
- [20] Wu R K, Wu W K, Stieglitz L, et al. Recent advances on α -diimine Ni and Pd complexes for catalyzed ethylene (Co)polymerization: A comprehensive review. *Coordination Chemistry Reviews*, **2023**, *474*: 214844.
- [21] Dai J J, Dai S Y. Impact of *o*-aryl halogen effects on ethylene polymerization: steric vs. electronic effects. *Dalton Transactions*, **2024**, *53*: 9286–9293.
- [22] Lu W Q, Ding B H, Zou W P, et al. Direct synthesis of polyethylene thermoplastic elastomers with high molecular weight and excellent elastic recovery via a hybrid steric bulky strategy. *European Polymer Journal*, **2023**, *201*: 112577.
- [23] Ding B H, Jiang L H, Kang X H, et al. Enhancing suppression of chain transfer via catalyst structural evolution in ethylene (co)polymerization. *Chinese Journal of Chemistry*, **2023**, *41*: 1509–1516.
- [24] Na Y N, Wang X B, Lian K B, et al. Dinuclear α -diimine Ni^{II} and Pd^{II} complexes that catalyze ethylene polymerization and copolymerization. *ChemCatChem*, **2017**, *9*: 1062–1066.
- [25] Zhang D F, Nadres E T, Brookhart M, et al. Synthesis of highly branched polyethylene using “sandwich” (8-*p*-tolyl naphthyl α -diimine)nickel(II) catalysts. *Organometallics*, **2013**, *32*: 5136–5143.
- [26] Rhinehart J L, Brown L A, Long B K. A robust Ni(II) α -diimine catalyst for high temperature ethylene polymerization. *Journal of the American Chemical Society*, **2013**, *135*: 16316–16319.
- [27] Lian K B, Zhu Y, Li W M, et al. Direct synthesis of thermoplastic polyolefin elastomers from nickel-catalyzed ethylene polymerization. *Macromolecules*, **2017**, *50*: 6074–6080.
- [28] Hu X Q, Wang C Q, Jian Z B. Comprehensive studies of the ligand electronic effect on unsymmetrical α -diimine nickel(II) promoted ethylene (co)polymerizations. *Polymer Chemistry*, **2020**, *11*: 4005–4012.
- [29] Wang Y Y, Wang C Q, Hu X Q, et al. Benzosuberyl substituents as a “sandwich-like” function in olefin polymerization catalysis. *Chinese Journal of Polymer Science*, **2021**, *39*: 984–993.
- [30] Peng D, Xu M H, Tan C, et al. Emulsion polymerization strategy for heterogenization of olefin polymerization catalysts. *Macromolecules*, **2023**, *56*: 2388–2396.
- [31] Zhong L, Li G L, Liang G D, et al. Enhancing thermal stability and living fashion in α -diimine–nickel-catalyzed (co)polymerization of ethylene and polar monomer by increasing the steric bulk of ligand backbone. *Macromolecules*, **2017**, *50*: 2675–2682.
- [32] Nie N, Yu F, Liu B Y, et al. Homo- and hetero-polymerization of ethylene catalyzed by α -diimine nickel complexes with hydroxyl groups. *European Polymer Journal*, **2024**, *210*: 112962.
- [33] Zhong L, Du C, Liao G F, et al. Effects of backbone substituent and intra-ligand hydrogen bonding interaction on ethylene polymerizations with α -diimine nickel catalysts. *Journal of Catalysis*, **2019**, *375*: 113–123.
- [34] Li A K, Ma H Y, Huang J L. Zirconium complexes bearing bis(phenoxy-imine) ligands with bulky *o*-bis(aryl)methyl-substituted aniline groups: synthesis, characterization and ethylene polymerization behavior. *Applied Organometallic Chemistry*, **2013**, *27*: 341–347.
- [35] Li S K, Xu G Y, Dai S Y. A remote nonconjugated electron effect in insertion polymerization with α -diimine nickel and palladium species. *Polymer Chemistry*, **2020**, *11*: 2692–2699.
- [36] Liao Y D, Zhang Y X, Cui L, et al. Penttiptyceny substituents in insertion polymerization with α -diimine nickel and palladium species. *Organometallics*, **2019**, *38*: 2075–2083.
- [37] Lu Z, Xu X W, Luo Y, et al. Unexpected effect of catalyst’s structural symmetry on the branching microstructure of polyethylene in late transition metal polymerization catalysis. *ACS Catalysis*, **2023**, *13*: 725–734.
- [38] Nie N, Wang Y Z, Tan C, et al. The synthesis of hyperbranched ethylene oligomers by nickel catalysts with oxazole structure. *Journal of Catalysis*, **2023**, *428*: 115164.
- [39] Zhong L, Zheng H D, Du C, et al. Thermally robust α -diimine nickel and palladium catalysts with constrained space for ethylene (co)polymerizations. *Journal of Catalysis*, **2020**, *384*: 208–217.
- [40] Wang X L, Zhang Y P, Wang F, et al. Robust and reactive neutral nickel catalysts for ethylene polymerization and copolymerization with a challenging 1,1-disubstituted difunctional polar monomer. *ACS Catalysis*, **2021**, *11*: 2902–2911.
- [41] Gao J X, Yang B P, Chen C L. Sterics versus electronics: Imine/phosphine-oxide-based nickel catalysts for ethylene polymerization and copolymerization. *Journal of Catalysis*, **2019**, *369*: 233–238.
- [42] Peng D, Pang W M, Xu G Y, et al. Facile synthesis of sterically demanding SHOP-type nickel catalysts for ethylene polymerization. *Applied Organometallic Chemistry*, **2019**, *33*: e5054.
- [43] Peng D, He H L, Pang W M, et al. Synthesis of UHMWPE by neutral phosphine-phenolate based nickel catalysts. *Polymer*, **2023**, *280*: 126019.
- [44] Wang H, Lu W Q, Zou M M, et al. Direct synthesis of polyethylene thermoplastic elastomers using hybrid bulky acenaphthene-based α -diimine Ni(II) catalysts. *Molecules*, **2023**, *28*: 2266.
- [45] Gong Y F, Li S K, Tan C, et al. π - π interaction effect in insertion polymerization with α -Diimine palladium systems. *Journal of Catalysis*, **2019**, *378*: 184–191.
- [46] Guo L H, Hu X Y, Lu W Q, et al. Investigations of ligand backbone effects on bulky diarylmethyl-based nickel(II) and palladium(II) catalyzed ethylene polymerization and copolymerization. *Journal of Organometallic Chemistry*, **2021**, *952*: 122046.
- [47] Bi Z X, Zhou J J, Zhu N N, et al. Heterogeneous nickel catalysts for the synthesis of ethylene-based polyolefin elastomers. *Macromolecules*, **2024**, *57*: 1080–1086.