Nickel catalysts with asymmetric steric hindrance for ethylene polymerization

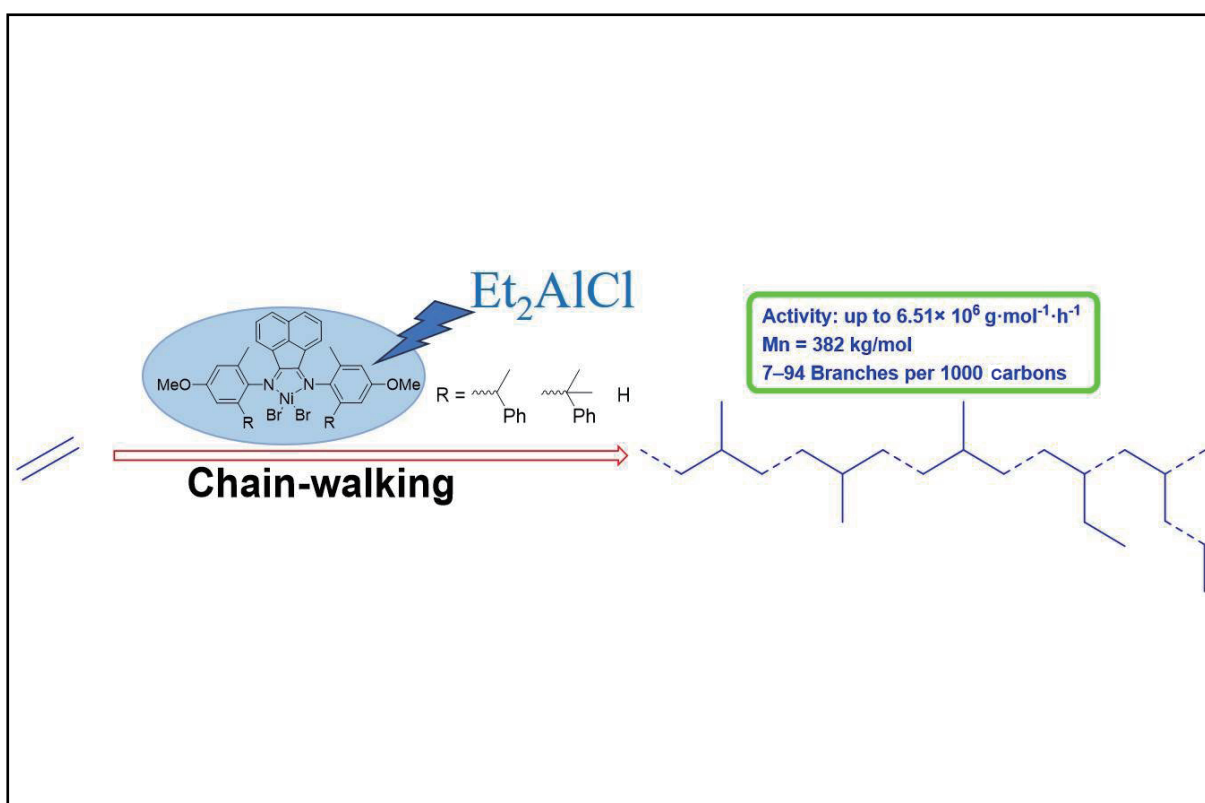Wanlu Tian[1,2], Fuzhou Wang[2] ✉, and Chen Zou[1] ✉

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Graphical abstract

Synthesis of branched polyethylene by ethylene polymerization catalyzed by nickel catalysts with asymmetric steric hindrance.

Public summary

■ A series of novel α-diimine nickel complexes with asymmetric steric hindrance were synthesized.

■ The nickel catalysts can withstand 90 °C and exhibit a high polymerization activity of 6.51×10^6 g·mol^{-1}·h^{-1}.

■ The nickel catalysts can be used to prepare high-molecular-weight polyethylene with an adjustable branching density distribution between 7 and 94 branches per 1000 carbons.

■ The polyethylene materials prepared from these α-diimine nickel catalysts exhibit excellent tensile properties.

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Abstract: α-Diimide catalysts have attracted widespread attention due to their unique chain walking characteristics. A series of α-diimide nickel/palladium catalysts with different electronic effects and steric hindrances were designed and synthesized for olefin polymerization. In this work, we synthesized a series of asymmetric α-diimide nickel complexes with different steric hindrances and used them for ethylene polymerization. These nickel catalysts have high ethylene polymerization activity, up to 6.51×10^6 g·mol^{-1}·h^{-1}, and the prepared polyethylene has a moderate melting point and high molecular weight (up to 38.2×10^4 g·mol^{-1}), with a branching density distribution between 7 and 94 branches per 1000 carbons. More importantly, the polyethylene prepared by these catalysts exhibits excellent tensile properties, with strain and stress reaching 800% and 30 MPa, respectively.

Keywords: α-diimine; nickel complex; polyethylene; polymerization; asymmetric steric hindrance

CLC number: TQ426; TQ325.1   **Document code:** A

1   Introduction

Since the early 1930s, the first polyethylene product (low-density polyethylene) was generated by free radical polymerization[1]. More importantly, in the 1950s, Nata et al.[2] and Ziegler et al.[3] used coordination polymerization catalysts to achieve olefin polymerization under mild conditions, thereby promoting the vigorous development of the polyolefin industry. Over seventy years later, polyolefins were widely used in food packaging, healthcare, machinery, automotive manufacturing, and other applications due to their excellent chemical corrosion resistance and mechanical properties[4].

The transition metal catalysts required for coordinating polymerization to prepare polyolefins have attracted widespread attention from both industry and academia with the continuous development of the polyolefin industry[5]. Among them, late transition metal catalysts such as nickel and palladium have been widely studied in the copolymerization of olefins and polar monomers due to their high tolerance to polar groups and low hydrophilicity[6]. For example, these nickel/palladium catalysts include [N,N] catalysts[7], [N,O] catalysts[8,9], [P,O] catalysts[10–12], etc. Among them, α-diimine nickel/palladium catalysts (Fig. 1a) was first reported by Johnson et al.[13] in 1995 and is known for its unique chain walking mechanism; these catalysts can be utilized to synthesize polyolefins with branched chain structures and diverse polymer topologies.

Since then, domestic and foreign scholars have extensively designed and researched this type of highly distinctive [N,N]-type catalyst by designing and synthesizing a series of novel α-diimine nickel/palladium catalysts with varying degrees of electronic effects and steric hindrance[14–17]. For example, one important progress was the introduction of a diisopropylphenyl substituent, which significantly increased the axial steric hindrance of the metal center of the catalysts, thereby suppressing *β*-H elimination and improving the stability of the catalyst, allowing it to maintain high activity at 100 °C (Fig. 1b)[18]. Dai et al.[19] also studied the electronic effect of metal center coordination based on this large steric hindrance α-diimine palladium catalyst, further regulating the polymerization performance of the catalyst. In addition, Brookhart, Daugulis, and Coates et al.[20] synthesized a "sandwich" type with increased axial steric hindrance using an 8-(p-tolyl) naphthalene-1-amine α-diimine nickel catalyst (Fig. 1c), which can prepare polyethylene with a high branching density (up to 150 branches per 1000 carbons) in ethylene polymerization.

By further adjusting the electronic effects and steric hindrance of the complex center, Wang et al.[21] synthesized a chiral α-diimine nickel catalyst with paraphenylethyl compounds that exhibited high ethylene polymerization activity (up to 2.85×10^6 g·mol^{-1}·h^{-1}·bar^{-1}) and produced polyethylene with a branching density of up to 117 branches per 1000 carbons at high temperatures. In addition, Coates et al.[22–24] introduced similar chiral structures into α-diimine nickel catalysts and used them for the polymerization of propylene and 1-butene to improve the regularity of the polymer. The steric hindrance of these nickel catalysts was significantly different from that of classical 2,6-diisopropyl nickel catalysts and 2,6-diisopropylphenyl nickel catalysts, with only half of the steric hindrance present. On the basis of these works, we designed new nickel catalysts with asymmetric steric hindrance and studied the polymerization performance and physical properties of the generated polyethylene in detail.
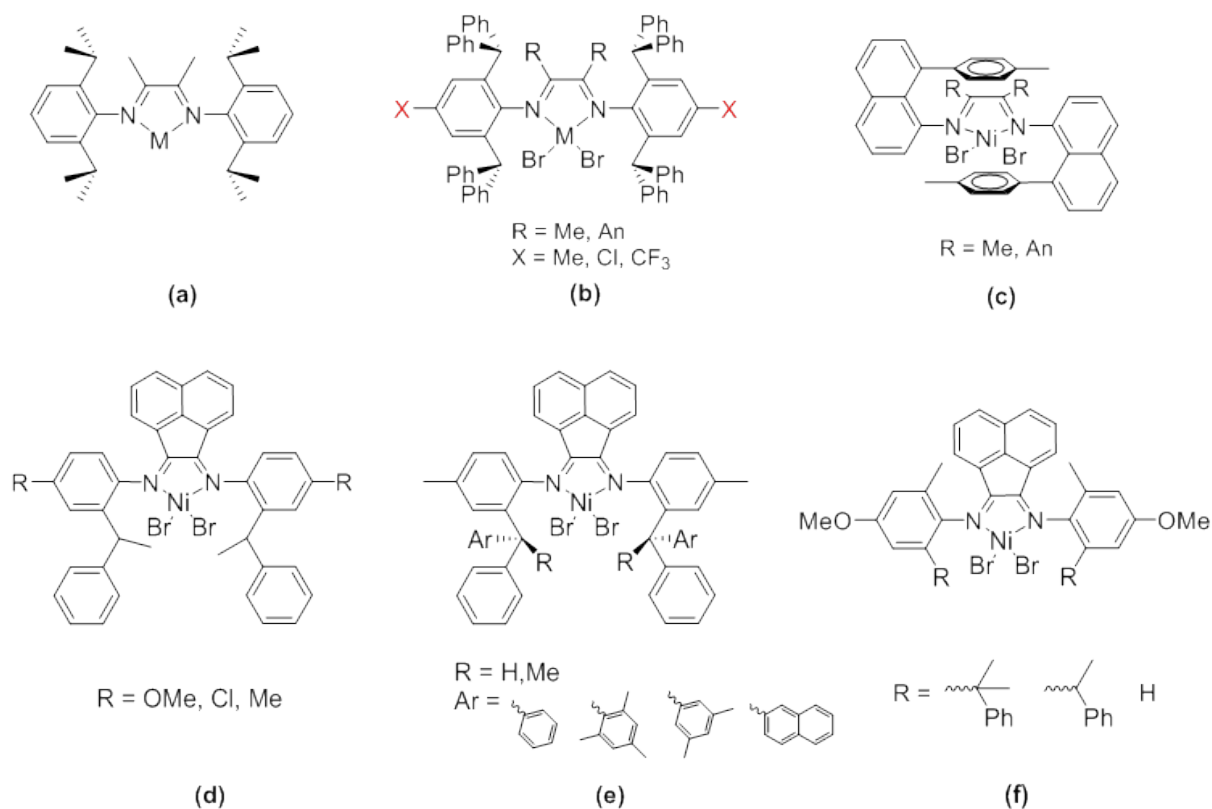
Fig. 1. Representative diimide catalysts (a–e) and novel structures used in this work (f).

2 Results and discussion
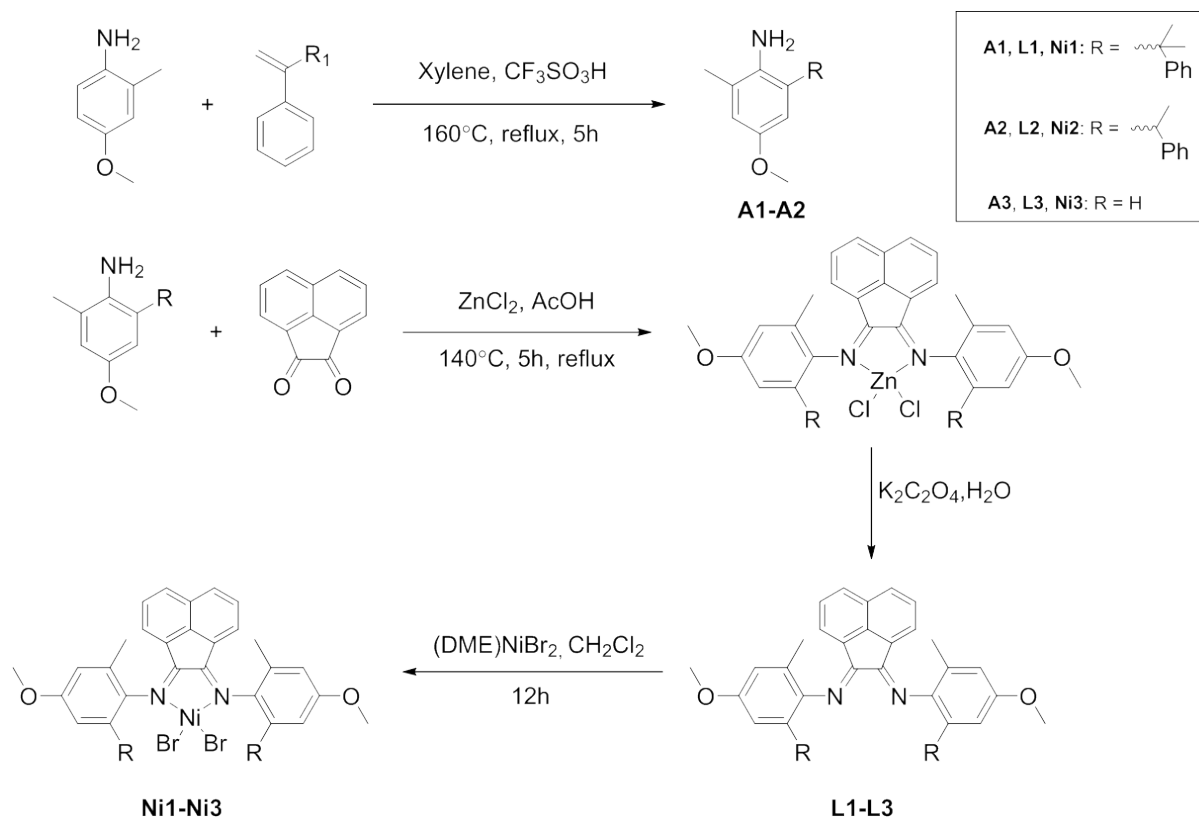
2.1 Synthesis and characterization

According to Scheme 1, aniline derivatives were prepared from precursors and *p*-anisidine by Friedel-Crafts alkylation. Subsequently, acetic acid was used as a catalyst, and ligand L1−L3 in high yield was easily prepared by the condensation of two equivalent aniline derivatives and one equivalent of 1,2-acenaphthenedione (Scheme 1). The ligands were reacted with equimolar amounts of (DME)NiBr$_2$ to prepare the corresponding α-diimine nickel complex Ni1–Ni3, which was a reddish-brown solid in almost quantitative yield. These complexes were characterized by elemental analysis, ^{1}H NMR and ^{13}C NMR. The purity and identity of the two ortho-phenyl-substituted nickel complexes were determined by elemental analysis and XRD.

Single crystals of complexes Ni1 and Ni2 were prepared by treating toluene solution with *n*-pentane at 0 °C on the top layer (Figs. 1 and 2, Tables S1 and S2). X-ray crystallographic analysis showed that the nickel dibromide complexes Ni1 and Ni2 (Figs. 2 and 3) crystallized symmetrically at two nickel centers with a twisted tetrahedral geometry at the center of the bromine-bridged dimer, where each nickel atom is connected to two bridged bromine atoms and an α-diimine ligand. The two nickel atoms in complexes Ni1 and Ni2 are connected by a quaternary ring.

2.2 Ethylene polymerization

Under fixed aggregation conditions and with the assistance of the AlEt$_2$Cl catalyst, the effect of the Ni1–Ni3 catalysts on ethylene polymerization was investigated by altering the temperature (0–90 °C) while maintaining a [Al]/[Ni] ratio of 500 (Table 1). As shown in Table 1, Ni1 exhibited a high activity of up to 6.51×10^6 g·mol^{-1}·h^{-1} and produced polyethylene with a high molecular weight of up to 38.2×10^4 g·mol^{-1} (Table 1, Entries 1–4). For Ni1, as the polymerization temperature increased, the polymerization activity, molecular weight and melting point changed. The polymerization activity reached its maximum value at 30 °C, while the molecular weight of the polymer decreased with increasing temperature (from 38.2×10^4 g·mol^{-1} to 16.6×10^4 g·mol^{-1}), the melting point of the polyethylene decreased with increasing polymerization temperature (from 128.2 to 114.0 °C), and the branching density increased to 41 branches per 1000 carbons. Compared with Ni1, Ni2 was obtained by replacing 2-phenylpropan-2-yl with 1-phenylethyl, and the steric hindrance of the nickel metal center decreased due to the reduction in the number of methyl groups. Compared with those of Ni1, the polymerization activity of Ni2 and the molecular weight of the prepared polyethylene slightly decreased, while the branching density increased to 61 branches per 1000 carbons (Table 1, Entries 5–8). Compared to Ni1 and Ni2, Ni3 obtained by completely removing the substituent at this position significantly reduced the ethylene polymerization activity, especially at high temperatures (90 °C), where it almost became inactive. The molecular weight of the polymer was reduced by more than half compared to that of Ni1 and Ni2 (with a maximum value of only 16.2×10^4 g·mol^{-1}). However, due to the sharp decrease in the steric hindrance of Ni3, chain transfer and chain walking accelerated, and the branching density of polyethylene increased to 94 branches per 1000 carbons (Table 1, Entries 9–12). Furthermore, we investigated the tem-

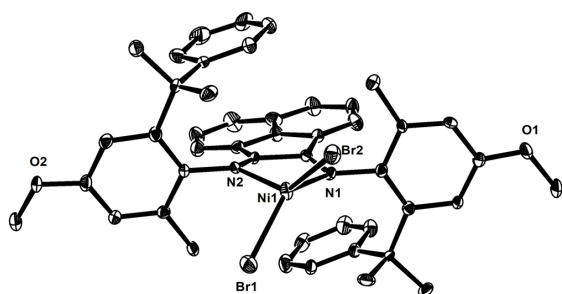**Scheme 1.** Synthetic route to nickel complexes Ni1−Ni3.

Fig. 2. Crystal structure of Ni1. The selected bond lengths (Å) and angles (°) were as follows: Br2–Ni1 = 2.3442(13), Br1–Ni1 = 2.3577(13), Ni1–N1 = 2.043(5), Ni1–N2 = 0.055(6), Br2–Ni1–Br1 = 110.57(5), N1–Ni1–N2 = 83.0(2), N1–Ni1–Br2 = 97.94(17), N1–Ni1–Br1 = 134.85(18), and N2–Ni1–Br1 = 99.18(16).
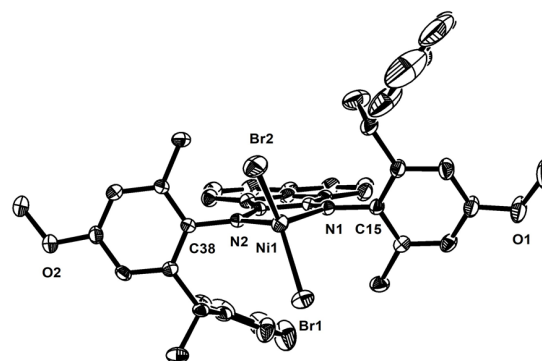

Fig. 3. Crystal structure of Ni2. The selected bond lengths (Å) and angles (°) are as follows: Br1–Ni1 = 2.3451(9), Ni1–Br2 = 2.3256(9), Ni1–N2 = 2.020(4), Ni1–N1 = 2.020(4), Br2–Ni1–Br1 = 122.07(4), N2–Ni1–Br1 = 115.23(10), N2–Ni1–Br2 = 107.94(10), N1–Ni1–Br1 = 101.99(10), N1–Ni1–Br2 = 120.38(10), and N1–Ni1–N2 = 82.98(15).

perature-dependent polymerization activity of the Ni1 and Ni2 catalysts at 90 °C (Fig. 4), and the results showed that the Ni1 and Ni2 catalysts could maintain their polymerization activity for up to 40 min at 90 °C, with Ni1 exhibiting the best performance.

2.3 Mechanical properties of synthesized polyethylene

Subsequently, as shown in Fig. 5, we investigated the tensile properties of polyethylene prepared with these nickel catalysts and found that the stress distribution of these polyethylene materials was between 15 and 30 MPa and that the strain distribution was between 400% and 800%. These polyethylene materials exhibit excellent tensile properties, which may be attributed to their high molecular weight (M_n greater

than 17.3×10^4 g·mol^{-1}). For the polyethylene samples prepared from Ni1 and Ni2, the sample with the highest stress was obtained at 30 °C, while the polyethylene sample obtained at 0 °C had the lowest stress, which may be related to its branching density.

3 Conclusions

We synthesized a series of novel α-diimine nickel complexes with asymmetric steric hindrance and studied their catalytic performance for ethylene polymerization. The polymerization activity of these catalysts can reach up to 6.51×10^6

Table 1. Ethylene homopolymerization catalyzed by nickel catalyst Ni1−Ni3[a].

Entry	Catalyst	T(°C)	Yield[b] (g)	Activity[b] (10^6)	M_n[c] (10^4)	PDI[c]	Branch[d]	T_m[e] (°C)
1	Ni1	0	2.65	3.18	38.2	1.8	7	128.2
2	Ni1	30	5.43	6.51	33.6	2.1	21	118.0
3	Ni1	60	2.52	3.02	21.9	2.0	40	114.4
4	Ni1	90	2.01	2.41	16.6	2.1	41	114.0
5	Ni2	0	2.35	2.82	37.6	1.8	15	120.2
6	Ni2	30	4.11	4.93	29.7	1.9	26	117.0
7	Ni2	60	2.76	3.31	17.3	2.1	46	113.6
8	Ni2	90	0.90	1.08	14.8	2.1	61	80.9
9	Ni3	0	1.10	1.32	16.2	2.3	36	115.1
10	Ni3	30	1.94	2.33	12.8	2.6	51	106.1
11	Ni3	60	0.80	0.96	11.9	3.1	72	69.1
12	Ni3	90	0.02	0.02	11.5	3.2	94	–

[a] 1 μmol of catalyst in CH_2Cl_2 (2 mL), [Al]/[Ni] = 500. $V_{n\text{-heptane}}$ = 20 mL, $t_{polymerization}$ = 10 min, $P_{ethylene}$ = 8 atm. [b] Activity is in units of 10^6 g·mol^{-1}·h^{-1}. [c] Determined by Gel Permeation Chromatography (GPC) in 1,2,4-trichlorobenzene at 150 °C. [d] Branches per 1000 carbons, determined by ^{1}H NMR. [e] Determined by differential scanning calorimetry.
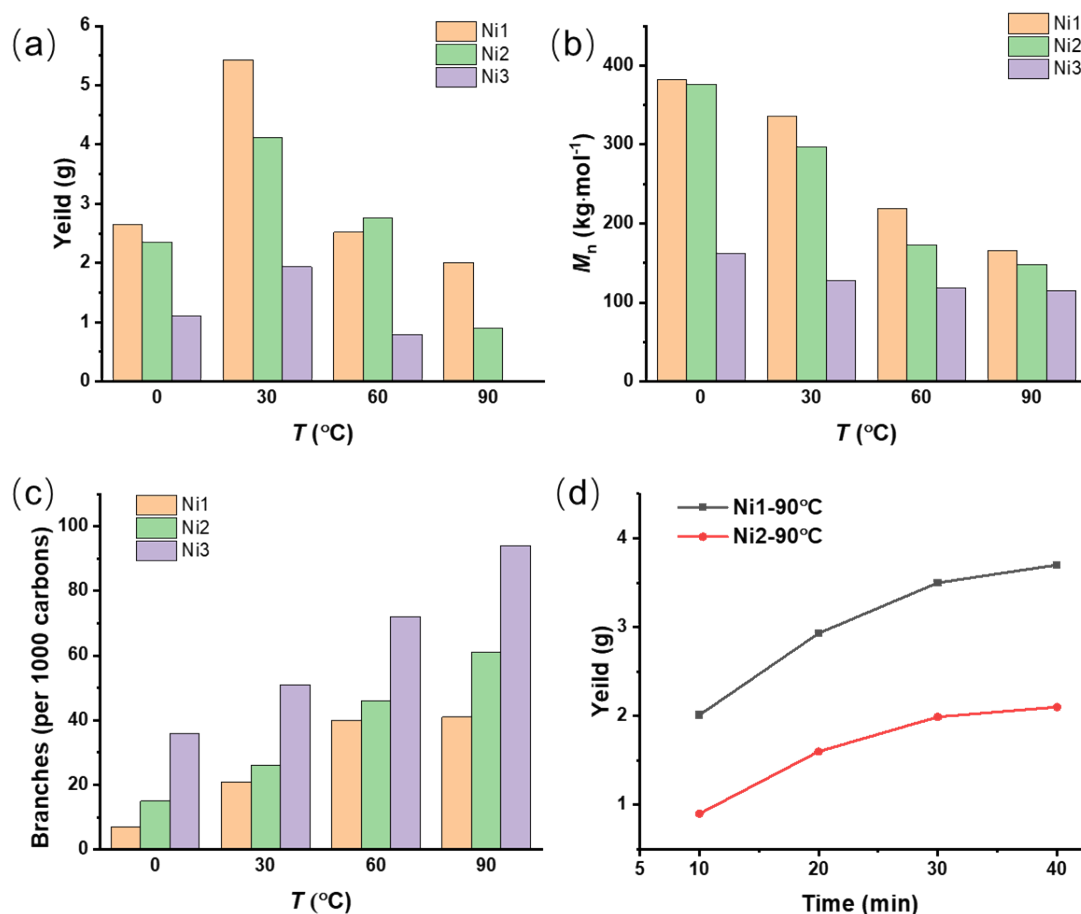

Fig. 4. The polymerization performance of catalysts. (a) Polymer weight comparisons of generated polyethylene at 0 °C, 30 °C, 60 °C and 90 °C. (b) Molecular weight comparisons of generated polyethylene at 0 °C, 30 °C, 60 °C and 90 °C. (c) Branching density comparisons of generated polyethylene at 0 °C, 30 °C, 60 °C and 90 °C. (d) Time-dependent studies (polymer yields vs polymerization time) at 90 °C.

g·mol^{-1}·h^{-1} and can be used to prepare high-molecular-weight polyethylene with adjustable branching density distributions

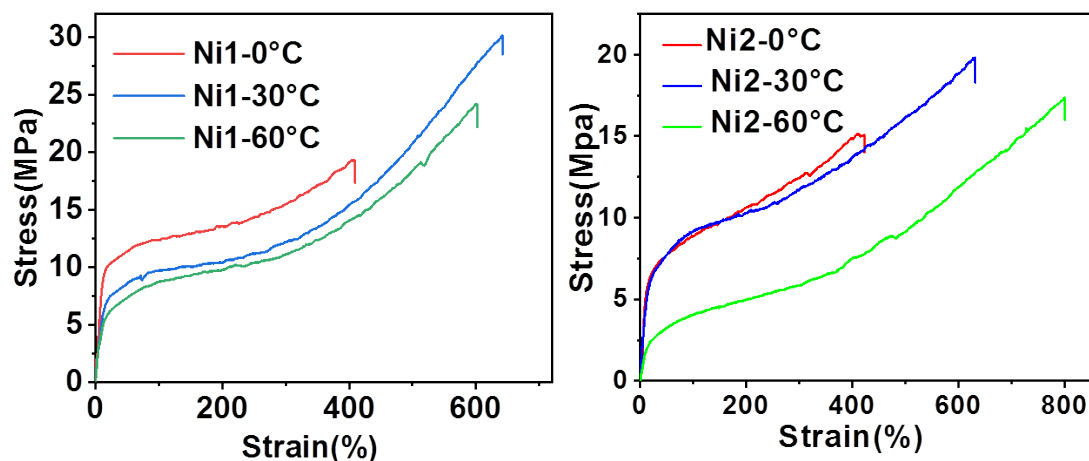between 7 and 94 branches per 1000 carbons. More importantly, the polyethylene prepared from these α-diimine nickel

Fig. 5. Tensile curve of polyethylene prepared with nickel catalysts.

catalysts exhibited excellent tensile properties.

Supporting information

The supporting information for this article can be found online at https://doi.org/10.52396/JUSTC-2024-0001. The supporting information includes 34 figures. Experimental details, figures, and characterization data for the nickel catalysts and polymers are provided in the supporting information.

Conflict of interest

The authors declare that they have no conflict of interest.

Biographies

Wanlu Tian is currently a graduate student in the Institutes of Physical Science and Information Technology, Anhui University. His research mainly focuses on the synthesis and characterization of polyolefins from new types of later transition metal catalysts.

Fuzhou Wang is currently an Associate Professor in the Institutes of Physical Science and Information Technology, Anhui University. He received his M.S. degree from Northwest Normal University in 2013. He carried out his doctoral work in polymer chemistry at Hiroshima University under the direction of Prof. Takeshi Shiono from 2013 to 2017. In 2018, he joined Anhui University as an Associate Professor. His current research mainly focuses on olefin polymerization by late transition metal catalysts.

Chen Zou is currently an Associate Professor at the University of Science and Technology of China, mainly engaged in research on polyolefin catalysts and functionalized polyolefin materials. He graduated with a Bachelor's degree from Qingdao University of Science and Technology in 2012 and a doctoral degree from the University of Science and Technology of China in 2016.

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