

# Synthesis of Ultralow-Density Polyethylene Elastomers Using Triarylnaphthyl Iminopyridyl Ni(II) Catalysts

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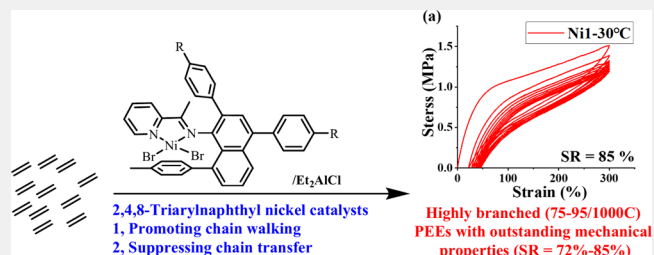
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**ABSTRACT:** Recently, the chain-walking ethylene polymerization strategy has garnered widespread attention as an efficient and straightforward method for preparing polyolefin elastomers. In this study, a series of 2,4,8-triarylnaphthyl iminopyridyl nickel catalysts were synthesized and used in ethylene polymerization. These catalysts demonstrated moderate catalytic activity ( $10^5$  g mol<sup>-1</sup> h<sup>-1</sup>), producing high-molecular-weight (up to 145.5 kg/mol) polyethylene materials with high branching degrees (75–95/1000C) and correspondingly low melting points. Detailed analysis using <sup>13</sup>C NMR spectroscopy revealed that the polyethylenes primarily featured methyl and long-chain branches. Mechanical testing of the polyethylene samples obtained from catalysts Ni1–Ni3 exhibited moderate stress at break (4.64–6.97 MPa) coupled with a very high strain at break (1650–3752%) indicating their very good ductility. Furthermore, these polyethylenes showcased great elastic recovery abilities, with strain recovery values ranging from 72% to 85%. In contrast, the polyethylene produced by Ni4 displayed notably inferior tensile strength (0.16 MPa) and tensile recovery (43%). To the best of our knowledge, this study represents the inaugural utilization of a nickel iminopyridyl catalyst in the preparation of a polyethylene thermoplastic elastomer.

**KEYWORDS:** 2,4,8-triarylnaphthyl, iminopyridyl Ni(II) catalysts, polyolefin elastomers, ultralow density, chain-walking



## INTRODUCTION

Polyethylene materials can be broadly categorized based on their density into ultralow-density polyethylene (ULDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), medium-density polyethylene (MDPE), and high-density polyethylene (HDPE). Among these, ULDPE stands out as the most recently commercialized addition to the polyethylene family.<sup>1</sup> Its polymerization mechanism bears resemblance to that of LLDPE, sharing a linear structure devoid of long-chain branching, earning it the moniker of the second-generation LLDPE. The industrial preparation of these materials involves metal-catalyzed copolymerization of ethylene with higher  $\alpha$ -olefins.<sup>1</sup> Notably, the percentage of  $\alpha$ -olefins used in ULDPE production is significantly higher compared to that of LLDPE. This unique composition imparts ULDPE with distinct properties, making it a versatile material with applications spanning multiple industries. Primary among these applications are films, including cast films, packaging films, and heat-shrinkable films. Additionally, ULDPE finds use in modifying polyolefin properties and is extensively utilized in various sectors such as automotive, packaging, wire and cable, medical devices, and household appliances.<sup>1</sup> Its trade name, polyolefin elastomers (POE), has gained widespread recognition due to its excellent thermoplastic elastomer characteristics, effectively positioning it as a viable alternative to earlier ULDPE formulations.

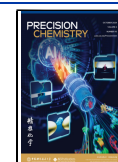
In the past decade, there has been a significant academic surge in the preparation of polyolefin elastomers (POEs) using chain-walking mechanisms, particularly with late-transition nickel and palladium catalysts.<sup>2</sup> This approach has circumvented the need for expensive, higher-order  $\alpha$ -olefins and has garnered considerable attention. Among these catalysts, nickel  $\alpha$ -diimine catalysts have emerged as the most promising for the preparation of chain-walking POEs due to their high activity, ease of tunability of product properties, and cost-effectiveness.<sup>3–7</sup> Various types of nickel  $\alpha$ -diimine catalysts have demonstrated exceptional abilities in the preparation of POEs (Chart 1). For instance, unsymmetric nickel  $\alpha$ -diimine catalysts (Chart 1A–C) and symmetric nickel  $\alpha$ -diimine catalysts (Chart 1D,E) containing flexible large substituents have both proven efficient in producing high molecular weight, highly elastic polyethylene materials.<sup>8–19</sup> Recently, our team employed innovative strategies in the design of catalysts for the synthesis of high-performance POEs. Specifically, we have implemented a rigid-flexible double-layer steric strategy for the

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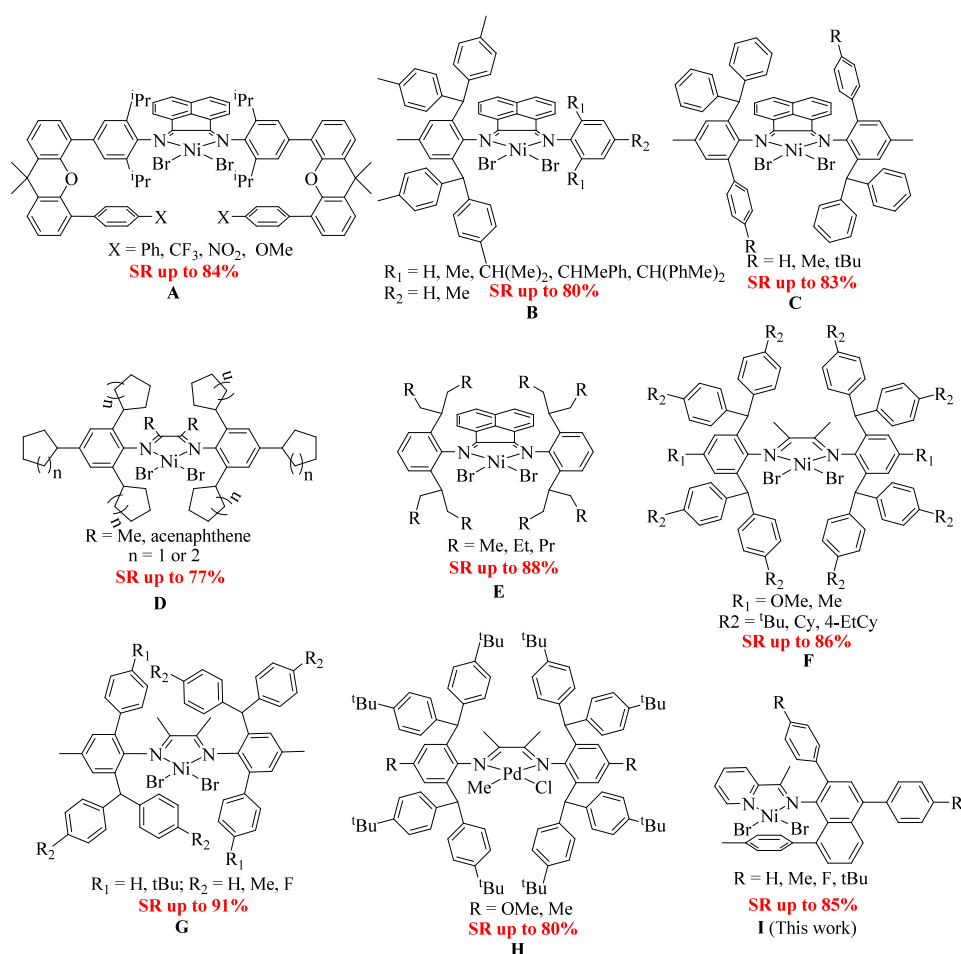
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**Chart 1.** Previously Reported Bulky  $\alpha$ -Diimine Catalysts (A–H) for the Synthesis of POEs with High Strain Recovery and Our Current Work (I)



preparation of ultrahigh molecular weight POEs (Chart 1F) and a hybrid steric strategy for the production of POEs exhibiting high elastic recovery, achieving elastic recovery up to 91% (Chart 1G).<sup>20,21</sup> Furthermore, we have explored the use of diarylmethyl  $\alpha$ -diimine palladium catalysts (Chart 1H) for the preparation of POEs and their biomass polar functionalized derivatives.<sup>22</sup> These advancements underscore the superiority of the  $\alpha$ -diimine system in controlling the branching density of the resulting polyethylene, which is crucial for the preparation of POE materials. Few other chain-walking ethylene polymerization systems have been able to meet the criteria for producing POE materials, often resulting in either low-branched polyethylene or polyethylene with insufficient molecular weight, such as the iminopyridine nickel system and neutral nickel salicylaldiminato system.<sup>23–30</sup> In this study, we have successfully prepared POEs via ethylene chain-walking polymerization using a novel class of 2,4,8-triarylnaphthyl iminopyridine nickel catalysts (Chart 1I). These materials demonstrate exceptional processing performance, rendering them promising candidates for a wide range of applications.

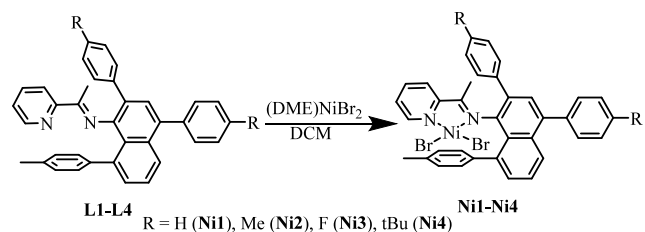
## 2. RESULTS AND DISCUSSION

### 2.1. Synthesis and Characterization of Ni(II) Complexes

The ligands L1–L4 were synthesized according to previously reported methodologies.<sup>31</sup> Subsequently, under nitrogen atmosphere and at room temperature, these ligands were

reacted with an equivalent amount of (DME)NiBr<sub>2</sub> (where DME = 1,2-dimethoxyethane) in anhydrous dichloromethane (DCM) for a duration of 12 h with constant stirring (Scheme 1). Following the reaction, the majority of the solvent was

#### Scheme 1. Synthesis of 2,4,8-Triarylnaphthyl Iminopyridyl Ni(II) Complexes



evaporated by using a rotary evaporator. The residue was then treated with a copious amount of anhydrous diethyl ether and sonicated to induce precipitation. The formation of a yellow powder was observed which, upon filtration, yielded the desired iminopyridyl Ni(II) complexes Ni1–Ni4. The isolated Ni(II) complexes exhibited good yields, ranging from 85% to 95%. Their purity and structural integrity were confirmed through elemental analysis, high-resolution MALDI-TOF mass spectrometry (Figures S1–4), and infrared spectroscopy.

## 2.2. Polyethylene Elastomer Synthesis

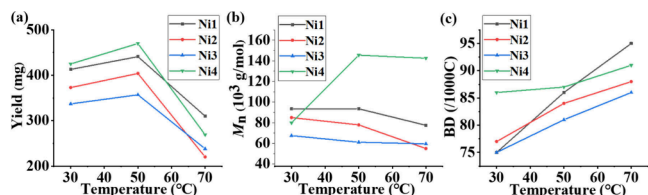
A series of 2,4,8-triaryl iminopyridyl Ni(II) complexes were activated with 200 equiv of Et<sub>2</sub>AlCl, paving the way for ethylene polymerization. Under controlled conditions of 6 atm ethylene pressure and temperatures ranging from 30 to 70 °C, these catalysts revealed moderate activity (10<sup>5</sup> g mol<sup>-1</sup> h<sup>-1</sup>) in the polymerization process, yielding polyethylene materials characterized by their high branching (75–95/1000C, Figures S5–16) and low melting points (–3.8–24.3 °C, Figures S17–20) (Table 1). As the reaction temperature gradually rose from

**Table 1. Polyethylene Elastomer Synthesis<sup>a</sup>**

entry	complex	T (°C)	yield (mg)	act. <sup>b</sup>	M <sub>n</sub> <sup>c</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>c</sup>	brs <sup>d</sup>	T <sub>m</sub> <sup>e</sup>
1	Ni1	30	413	2.07	93.4	2.11	75	16.5
2	Ni1	50	441	2.21	93.5	2.25	86	7.9
3	Ni1	70	310	1.55	77.5	2.34	95	–1.5
4	Ni2	30	373	1.86	85.0	2.09	77	19.1
5	Ni2	50	404	2.02	77.9	2.47	84	7.6
6	Ni2	70	220	1.10	55.0	2.51	88	–2.8
7	Ni3	30	337	1.68	67.5	2.29	75	24.3
8	Ni3	50	357	1.78	61.1	2.74	81	14.7
9	Ni3	70	238	1.19	59.5	2.67	86	2.7
10	Ni4	30	425	2.13	79.8	2.14	86	11.1
11	Ni4	50	470	2.35	145.5	1.60	87	2.8
12	Ni4	70	269	1.34	142.5	1.85	91	–3.8

<sup>a</sup>Reaction conditions: Ni(II) complexes = 2 μmol, Et<sub>2</sub>AlCl = 200 equiv, toluene = 20 mL, ethylene = 6 atm, polymerization time = 1 h. <sup>b</sup>Activity is in unit of 10<sup>5</sup> g mol<sup>-1</sup> h<sup>-1</sup>, <sup>c</sup>M<sub>n</sub> is in unit of kg mol<sup>-1</sup>, determined by GPC in trichlorobenzene at 150 °C vs polystyrene standards. <sup>d</sup>B = Number of branches per 1000C, as determined by <sup>1</sup>H NMR spectroscopy. <sup>e</sup>Melting point (T<sub>m</sub>) is determined by differential scanning calorimetry (DSC), broad peak.

30 to 50 °C, a discernible enhancement in the catalytic activity for ethylene polymerization was observed across various catalysts. Nevertheless, a sharp decline in activity became apparent when the temperature was elevated to 70 °C, indicating a significant loss of catalytic potency at this higher temperature (as illustrated in Figure 1a). This observation



**Figure 1.** Plots of yield (a), molecular weight (b), and branching density (c) of the polyethylene obtained versus temperature with Ni1–Ni4.

underscores the good thermal stability of these iminopyridyl nickel catalysts within the 30 to 50 °C range, followed by a notable deterioration in stability at 70 °C, leading to pronounced catalyst deactivation. Furthermore, the reduced solubility of ethylene at elevated temperatures contributed, in part, to this observed phenomenon. Under these precisely controlled conditions, the nickel catalysts facilitated the production of a diverse array of high molecular weight polyethylenes (Figures S21–24), exhibiting varying degrees of branching (with M<sub>n</sub> values reaching up to 145.5 kg mol<sup>-1</sup>).

Interestingly, the molecular weight exhibited a nonlinear trend with increasing temperature. Initially, it rose steadily as the temperature increased from 30 to 50 °C but then exhibited a downward trajectory as the temperature surpassed 50 °C (Figure 1b). This behavior can be attributed to the concurrent acceleration of both chain transfer and chain growth rates with increasing temperature. Between 30 and 50 °C, the rate of chain growth outweighed that of chain transfer, resulting in a higher molecular weight. However, this trend reversed between 50 and 70 °C, leading to a decrease in the molecular weight. The degree of branching in the resulting polyethylenes was profoundly influenced by the catalysts' chain walking and chain growth capabilities. Notably, as the polymerization temperature escalated, so did the degree of branching in the polyethylene (Figure 1c). This observation suggests a direct correlation between the relative rates of chain walking and chain growth with increasing temperature. Consequently, the melting points of these polymers decreased correspondingly with an increase in branching. It is worth mentioning that among the catalysts tested, Ni3 stood out due to its consistently lower activity and branching degree compared to its counterparts. This distinct behavior can be attributed to the presence of an electron-withdrawing fluorine substituent in Ni3, which potentially raises the energy barrier for ethylene insertion and diminishes its chain walking proficiency.

## 2.3. Polymer Mechanical Properties

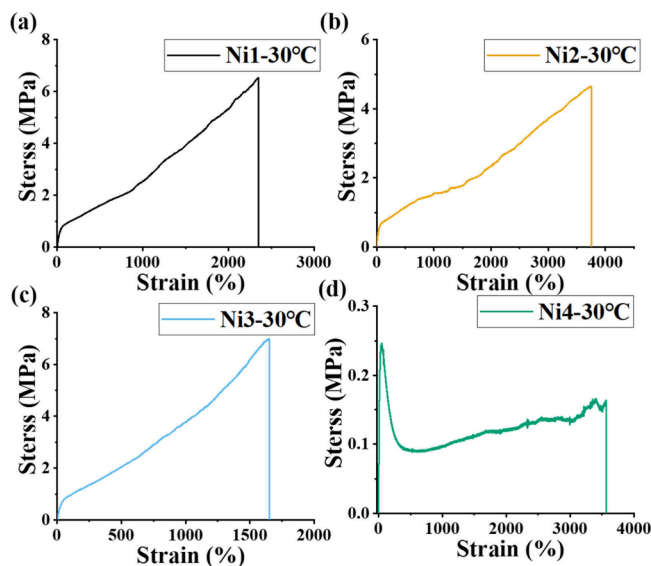
The branching degree of polyethylenes is a critical factor that profoundly influences their physical properties, including crystallinity, melting point, and mechanical behavior.<sup>2</sup> In the context of ethylene polymerization catalyzed by iminopyridyl Ni(II) systems, the resulting polyethylene's branching degree is governed by the intricate balance between chain walking and chain growth reactions. Operating within an optimal ratio range is essential to achieving polyethylene materials that exhibit superior mechanical properties. Notably, the presence of both suitable crystallinity and high molecular weight in these materials leads to a unique combination of elastomeric characteristics reminiscent of rubber and high-temperature processability typically associated with plastics. Polyethylenes produced by catalysts Ni1–Ni4, characterized by high branching degrees, low melting points, extremely low polyethylene density and elevated molecular weights, potentially possess thermoplastic elastomer properties (Table 1 and 2). To elucidate their mechanical behavior, tensile tests were systematically conducted on polyethylenes synthesized by catalysts Ni1–Ni4 at 30 °C. The tests of polyethylenes synthesized by catalysts Ni1–Ni3 revealed moderate stress at

**Table 2. Mechanical Properties of Polyethylene Elastomer<sup>a</sup>**

entry	precat.	T/°C	strain (%) <sup>b</sup>	stress (MPa) <sup>b</sup>	SR (%) <sup>c</sup>	ρ <sup>d</sup>
1	Ni1	30	2349	6.53	85	0.858
2	Ni2	30	3752	4.64	72	0.861
3	Ni3	30	1650	6.97	80	0.862
4	Ni4	30	3563	0.16	43	0.857

<sup>a</sup>Conditions: performed at 5 mm/min by means of a Universal Test Machine (UTM2502) at room temperature (25 °C). <sup>b</sup>Strain and stress at break values. <sup>c</sup>The strain recovery (SR) values can be calculated by SR = 100(ε<sub>a</sub> – ε<sub>r</sub>)/ε<sub>a</sub>, where ε<sub>a</sub> is the applied strain and ε<sub>r</sub> is the strain in the cycle at zero load after the 10th cycle. <sup>d</sup>Density of polyethylene samples is in unit of g/mL, determined by a full-automatic electronic density meter.

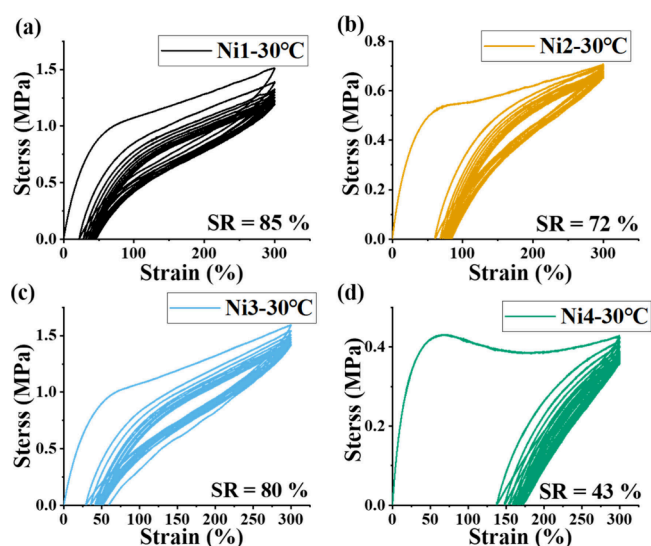
break values in the range of 4.6 to 7.0 MPa, coupled with remarkably high strain at break values spanning from 1650% to 3752% (Figure 2a–c). Conversely, the polyethylene obtained



**Figure 2.** Stress–strain curves for polyethylenes generated with (a–d) Ni1–Ni4 at 30 °C.

from Ni4 under identical conditions exhibited a significantly lower stress at a break of 0.16 MPa and an exceptionally high strain at a break of 3563% (Figure 2d). These findings suggest that under comparable conditions polyethylene elastomers produced by Ni1–Ni3 catalysts demonstrate superior ultimate tensile strength and toughness when compared to those synthesized by Ni4. This observed difference can be attributed to the higher branching degree and lower melting point exhibited by the Ni4-derived polyethylenes, which likely lead to reduced crystallinity and consequently weaker physical cross-linking strength. These POE materials, with their excellent flexibility and plasticity, have a wide range of applications in various fields such as medical devices, sports equipment, daily necessities, vehicle and marine engineering, electronics and electrical systems, construction, and civil engineering, as well as textiles and paper manufacturing.

To gain deeper insights into the elastic properties of these materials, hysteresis experiments were performed on polyethylene samples produced by catalysts Ni1–Ni4 at 30 °C. During these tests, the samples were subjected to repeated cycles of stretching up to 300% strain and subsequent stress recovery to 0 MPa. The results indicated that the polyethylene samples obtained from catalysts Ni1–Ni3 exhibited impressive elastic recovery performance, with strain recovery (SR) values ranging from 72% to 85% (Figure 3a–c). However, it is worth noting that the significantly lower SR (43%) observed for the Ni4-derived sample (Figure 3d) may be associated with its comparatively reduced physical cross-linking strength. Furthermore, a detailed quantitative analysis of the branch types and corresponding concentrations in polyethylene obtained from Ni3 at 30 °C was conducted using  $^{13}\text{C}$  NMR spectroscopy (Figure 4). This analysis revealed that the polyethylene primarily contained methyl and long-chain branches, with the preponderance being methyl branches.<sup>32–34</sup>



**Figure 3.** Plots of hysteresis experiments of ten cycles at 300% strain for polyethylenes generated by Ni1–Ni4 at 30 °C (a–d).

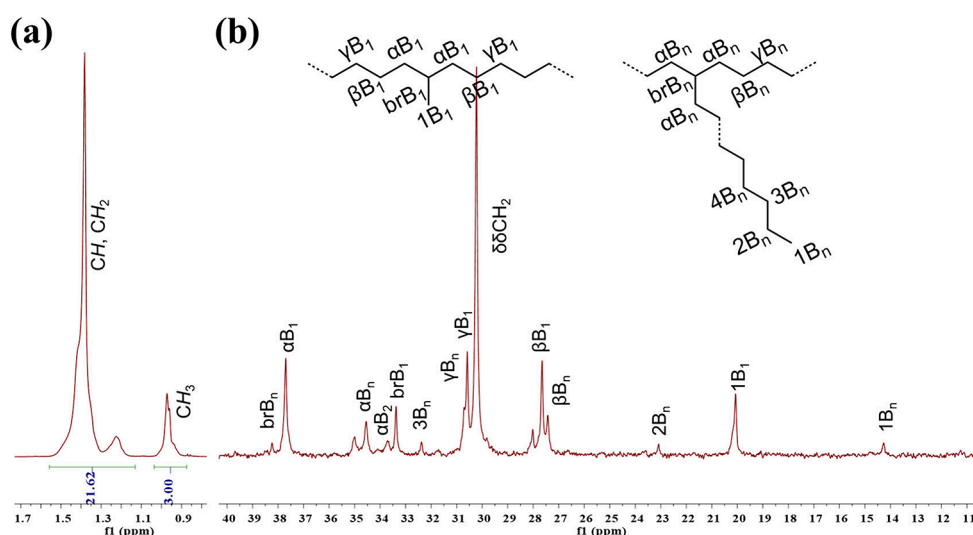
#### 2.4. Comparison with Reported Nickel Iminopyridine Catalysts

When further compared with reported nickel iminopyridine catalysts of similar structures, Ni1 in this work demonstrated superior performance under similar polymerization conditions, capable of producing polyethylene with a higher molecular weight and branching density than most reported catalysts (Figure 5). The attainment of higher molecular weight and branching density is likely a crucial factor in generating exceptional elastomers. It is noteworthy that the RC-4 catalyst is also capable of producing polyethylene with a high molecular weight and high branching density, possibly due to its possession of both 8-aryl naphthyl and 2-diphenylmethyl substituents. However, the polyethylene obtained from this catalyst has not been further tested for elastomer mechanical properties; thus, it is unknown whether it can be used for the production of polyethylene elastomers.

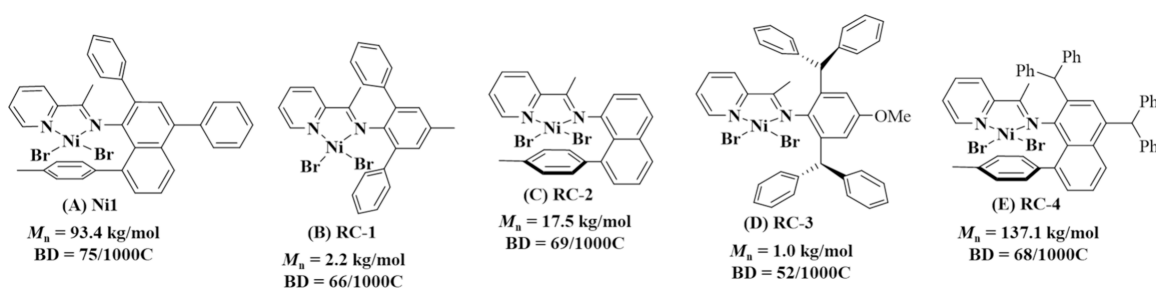
### 3. CONCLUSIONS

In summary, we report the synthesis of a series of 2,4,8-triarylnaphthyl iminopyridyl nickel catalysts and their subsequent application in ethylene polymerization. These catalysts exhibited moderate activity ( $10^5 \text{ g mol}^{-1} \text{ h}^{-1}$ ) and produced high-molecular-weight (up to 145.5 kg/mol) polyethylene materials characterized by high branching degrees (75–95/1000C) and low melting points. Further analysis via  $^{13}\text{C}$  NMR spectroscopy revealed that the molecular chains of the resulting polyethylenes are predominantly branched with methyl and long chain groups.

Mechanical testing of the polyethylene samples produced by catalysts Ni1–Ni3 demonstrates moderate stress at break values (4.64–6.97 MPa) coupled with remarkably high strain at break (1650–3752%). Additionally, these polyethylenes exhibit excellent elastic recovery capabilities, with strain recovery (SR) values ranging from 72% to 85%. In contrast, the polyethylene obtained from Ni4 exhibited significantly lower tensile strength (0.16 MPa) at break and recovery values (43%). To our knowledge, this is the first instance of preparing polyethylene thermoplastic elastomer using a nickel iminopyridyl catalyst. In future work, we will further investigate the



**Figure 4.** Detailed analysis of  $^1\text{H}$  (a) and  $^{13}\text{C}$  (b) NMR spectrum of the polyethylene elastomer from Table 1, entry 7. Assignments are numbered according to refs<sup>32–34</sup>.



**Figure 5.** Comparison of polyethylene molecular weight and branching density produced by representative reported catalysts RC-1–4 and Ni1.

impact of catalyst structure and polymerization conditions on the properties of these elastomers.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/prechem.4c00057>.

Full experimental details for the synthetic procedures, materials, analytical methods, EA and mass spectra (Figures S1–4) of synthetic compounds, NMR (Figures S5–16), DSC (Figures S17–20), and GPC (Figures S21–24) curves of PEEs (PDF)

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## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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