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Research Article

Ethylene Polymerization through Neutral Nickel Complexes Bearing Cyclic Imides

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The catalyst synthesis of salicylaldimine Ni(II) complexes with bulky imide moieties, ethylene polymerization, and characterization of synthesized polyethylenes are described in this paper. These Ni(II) complexes are designed to bear 2-aminobiphenyl and 4-tritylaniline. Results confirmed relatively high activity (up to 4×10^4 g PE mol Ni^{-1} h^{-1}) of these catalysts in ethylene polymerization. Moreover, Ni(II) complexes demonstrated enhanced thermal stability, maintaining activity level up to 80°C. The generated polyethylenes possess moderate branching density and high melting temperatures. Less bulky 2-aminobiphenyl group resulted in higher branch content, while in Ni(II) complexes bearing 4-tritylaniline, more linear structure was observed. These semicrystalline polyethylenes showed mechanical properties similar to thermoplastics.

1. Introduction

Since the discovery of Brookhart in olefin polymerization field, Ni(II) and Pd(II) late transition metal catalysts have attracted significant attention due to their controlled structure and functional monomer tolerance in comparison to early transition metal catalysts [1–3]. Over decades, numerous Ni(II) and Pd(II) complexes have been synthesized and developed for olefin polymerization and copolymerization with variety of functional comonomers [1, 4–6]. Following the discovery of SHOP-type catalysts (Shell Higher Olefin Process) in order to highly selective preparation of α-olefins, neutral palladium and nickel complexes have been developed [7–10]. Zhang and Chen synthesize heterogeneous naphthoquinone-based nickel and palladium catalysts on the silica surface [11]. Also, they install an azobenzene functionality to catalyst preparation light-responsive palladium and nickel catalysts for the polymerization and copolymerization of ethylene [12]. Electronic effects and different ligands in iminopyridine-N-oxide nickel on the aniline moiety were studied for ethylene polymerization neutral catalysts; these catalysts demonstrated notable advantages in microstructure, activity, and stability [13].

In addition to [N,N] chelating ligands, [N,O]-, [P,N]-, and [P,O]-based ligands exhibited efficient olefin oligomerization and polymerization activity [1, 14, 15]. Moreover, very few [P,P] chelating ligands have been reported as ethylene polymerization catalysts due to low productivity and molecular weight [16, 17]. Among them, salicylaldimine and β-ketoiminato [N,O]-based nickel catalysts have shown success in ethylene polymerization and copolymerization with polar functional groups [5, 18, 19]. There are various ligand framework design results in specific catalytic behavior for olefin polymerization. Utilizing bulky group can enhance catalyst activity and molecular weight of polyethylene when positioned at the ortho position of phenoxy group in salicylaldimine complex [20, 21]. Moreover, electron withdrawing substituents increase catalytic activity [1–3]. Neutral nickel complexes with more bulky N-aryl imine moieties are effective in olefin polymerization due to block axial position of metal center [22].

As described above, neutral [N,O]-based catalytic performance has been improved through modification of electronic and steric properties of the ligand. Thus, here, we report the synthesis of neutral [N,O] nickel complexes bearing bulky 2-aminobiphenyl and 4-tritylaniline moieties followed by ethylene polymerization and characterization.
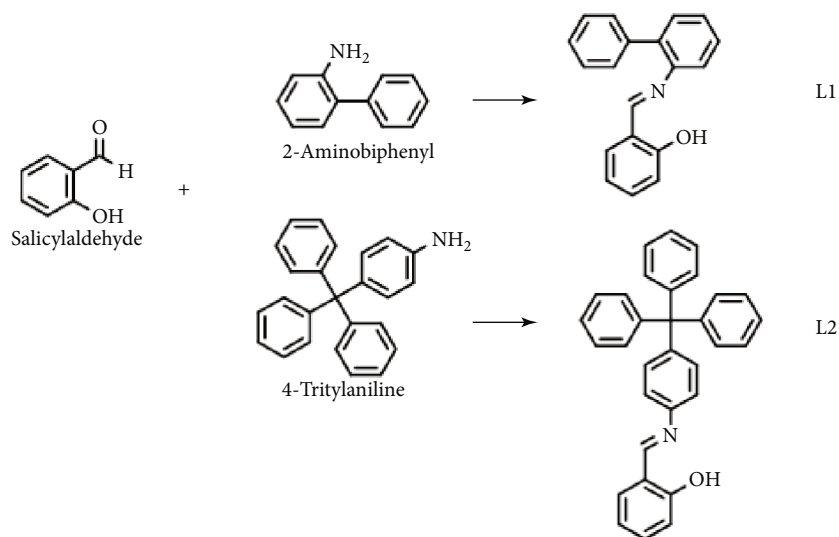
Scheme 1: Synthetic procedure for ligands L1 and L2.

Specific emphasis of the new study was placed on the clarification of trends in the volume and steric bulk of the new substituent ligand over ethylene polymerization and characterization of neutral [N,O] nickel complexes. As a part of novelty, in the research, bulky amine containing moieties (2-aminobiphenyl and 4-tritylaniline) has been selected to study the effect of steric hindrance of imide groups on ethylene polymerization and properties of synthesized polyethylenes. Results indicated that such complexes are capable of ethylene polymerization to thermoplastic polyethylene containing moderate branch numbers in the absence of Ni(COD)$_2$ activator. Given the characteristic, possibilities of structure alteration, and applications of polyolefins derived from neutral complexes, our findings are likely to be of interest to the vision of scientists and researchers.

2. Experimental

2.1. General Procedures. All manipulations involving sensitive materials were carried out under argon atmosphere using glovebox or Schlenk techniques. Synthesis and polymerization solvents were dried over CaH$_2$ and/or sodium, distilled, and kept over 3 Å molecular sieves before use. High purity ethylene gas was dried over activated molecular sieves for polymerization experiments. Tetrakis(triphenylphosphine)nickel(0) and chlorobenzene were purchased from Sigma-Aldrich.

Elemental analyses of samples were carried out using Elementar model Vario III microanalyzer. Nuclear magnetic resonance spectroscopy (^{1}H NMR) was performed using a Bruker Avance 500 spectrometer at ambient temperature in chloroform-d solvent unless otherwise stated. NMR chemical shifts were referenced to the residual solvent. DSC analysis was carried out at heating/cooling rate of 10°C min^{-1} under nitrogen atmosphere with a Mettler-Toledo DSC 1. Tensile properties were followed using a SANTAM universal testing instrument on a rectangular

specimen (60 mm long and 10 mm wide) cut from 1 mm compression-molded samples. Tension tests were performed in displacement-controlled mode according to ASTM D638. The strain rate was fixed at 300 mm min^{-1}. The average value was reported from five analysis per each sample.

2.2. Ethylene Polymerization. Ethylene polymerization was performed in a 300 ml pressure vessel equipped with mechanical stirrer. Followed by degassing with nitrogen at 100°C, 100 ml of toluene and catalyst solution (10 ml) were transferred into the reactor at 35°C. With stirring, the vessel heated to reach the desired temperature. After that, the vessel was pressurized with ethylene to desirable level and the reaction continued for 2 h. Polymerization was quenched in acidic methanol, filtered, and dried overnight in vacuum oven.

2.3. Ligands and Complexes Preparation. Preparation of L1: a mixture of salicylaldehyde (9.6 mmol) in ethanol was added 10 mmol of 2-aminobiphenyl and catalytic amount of *p*-toluenesulfonic acid and refluxed for 8 h. After filtration, solvent was removed under reduced pressure. The resulting orange solid was recrystallized from ethanol and dichloromethane to afford the desired product. Yield 2.43 g, 93%. Analysis calc. for C$_{19}$H$_{16}$NO: C, 83.3; H, 5.8; N, 5.1; O, 5.8. Found: C, 83.1; H, 5.8; N, 5.2; O, 5.9%.

Preparation of L2: the same procedure as above was employed by utilizing 4-tritylaniline. L2 was obtained as yellow solid. Yield 3.4 g, 80%. The reactions for these synthesis are given in Scheme 1. Anal. Calc. for C$_{32}$H$_{26}$NO: C, 87.3; H, 5.9; N, 3.2, O; 3.6. Found: C, 87.2; H, 5.9; N, 3.2; O, 3.7%.

The microstructure of the ligands obtained was performed by nuclear magnetic resonance test (^{1}H NMR), and the results are shown in Figures 1 and 2. As can be seen in the sample spectrum, the peak of the NH$_2$ reaction group in 2-aminobyphenyl (3.7 ppm) was removed after reaction with salicylic aldehyde, and no interaction of the peak of
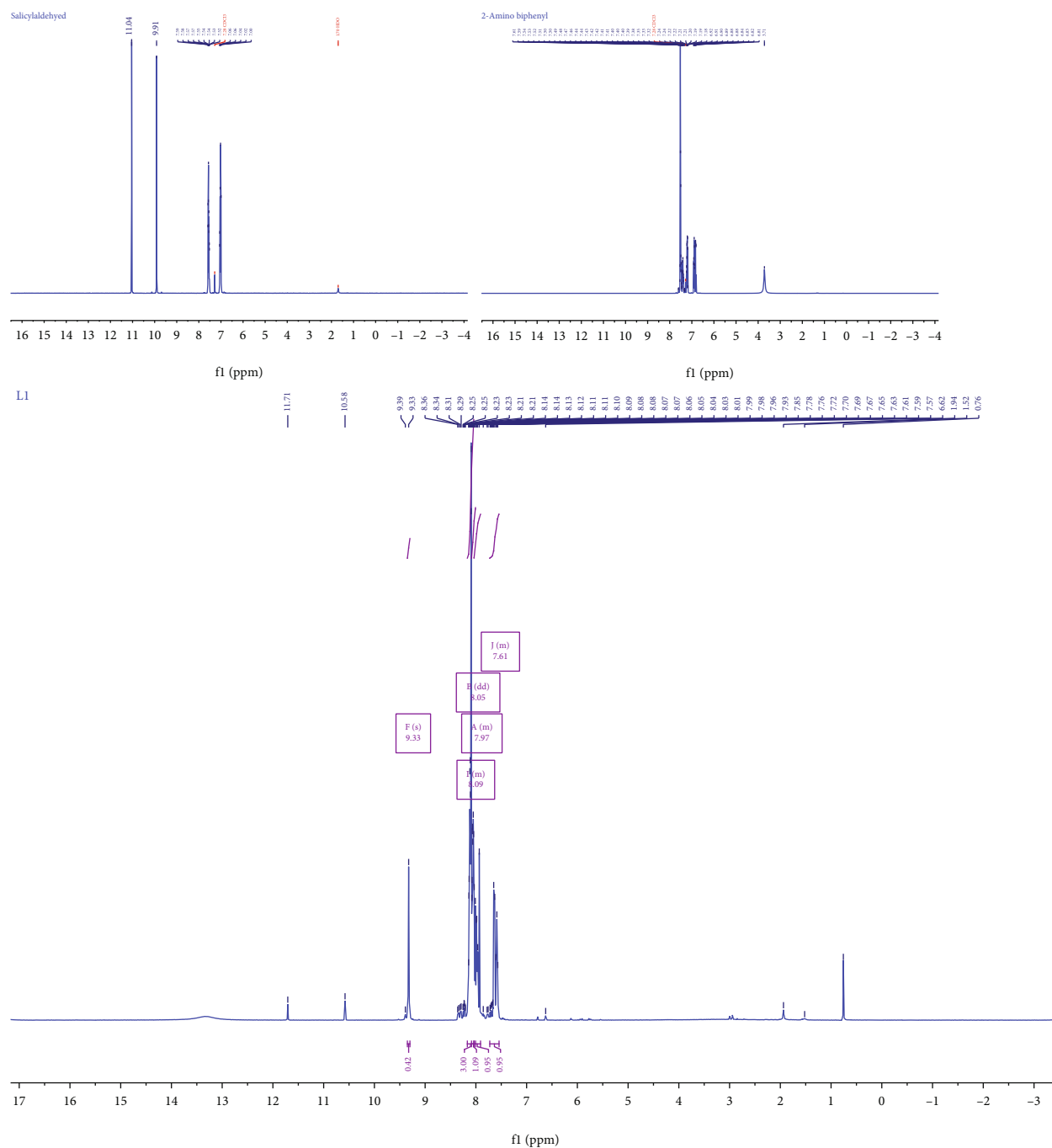
FIGURE 1: Comparison of magnetic resonance spectra nuclei of salicylic aldehyde, 2-aminobyphenyl, and ligand (L1).

the aldehyde group (9.9 ppm) in salicylic aldehyde was observed in the final product.

In the case of 4-tert-aniline, it seems that the peak of the amine group attached to the phenyl ring is in the form of wide peaks in the range of 3.5 to 4.5 ppm; due to the reaction with the aldehyde group, this peak is removed in the final product.

Nickel complex (Ni1) synthesis: a solution of L1 (0.5 g, 1.8 mmol) in 30 ml of dried tetrahydrofuran was added sodium hydride (65 mg, 2.7 mmol) under mild stirring con-

dition at ambient temperature and reaction continued for 3 h. After that, $(PPh_3)_2Ni(Ph)Cl$ solution in tetrahydrofuran (1.8 mmol in 10 ml) was introduced to ligand sodium salt solution and stirred for 24 h. The complex solution was filtered and concentrated to 5 ml, followed by addition of cold hexane (40 ml) and separation of complex crystals. Drying under vacuum for 24 h resulted in 1.27 g (yield 76%) of Ni1.

Nickel complex (Ni2) synthesis: Ni2 complex was prepared similar to Ni1 procedure using sodium salt of L2
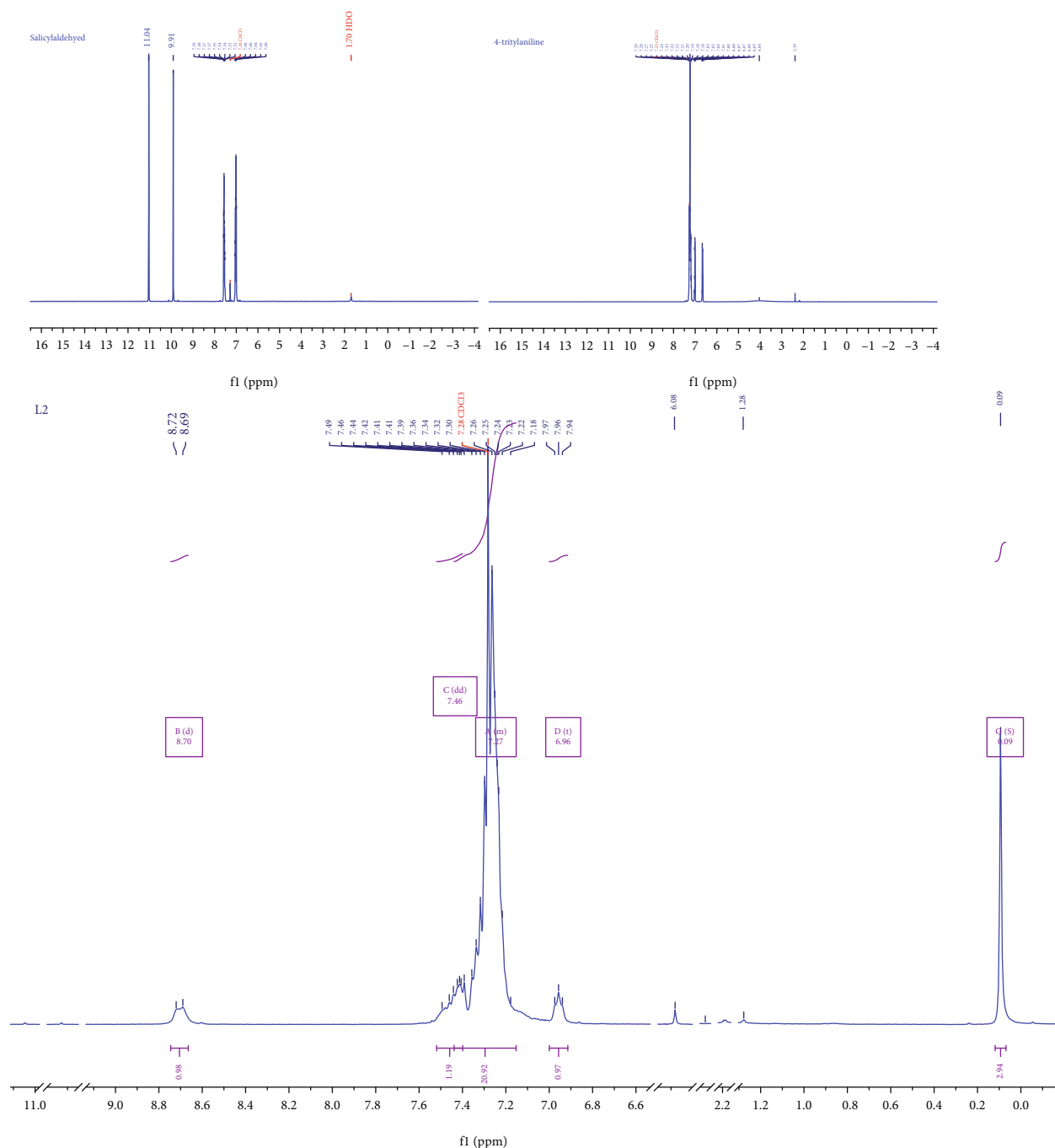
FIGURE 2: Comparison of magnetic resonance spectra nuclei of salicylic aldehyde, 4-tert-aniline, and ligand (L2).

(0.55 g, 1.2 mmol) and (PPh$_3$)$_2$Ni(Ph)Cl (835 mg, 1.2 mmol). **Ni2** was obtained as light green crystals (yield 0.96 g, 73%). Chemical structures of Ni1 and Ni2 complexes are given in Scheme 2.

3. Results and Discussion

3.1. Ethylene Polymerization. Ligand structure has been proved to be effective in polymer chain structure. To ascertain the effect of bulky imide moieties on polymerization activity and chain structure, ethylene polymerization was performed under different temperature and pressure conditions, and the results are summarized in Table 1.

From the obtained data, it can be shown that polymerization activity of Ni1 bearing less bulky 2-aminobiphenyl group is higher than Ni2 over studied polymerization conditions. Less steric hindrance might facilitate ethylene insertion by active species and cause improved polymerization activity in Ni1. As polymerization temperature increases, due to reduced solubility of monomer and
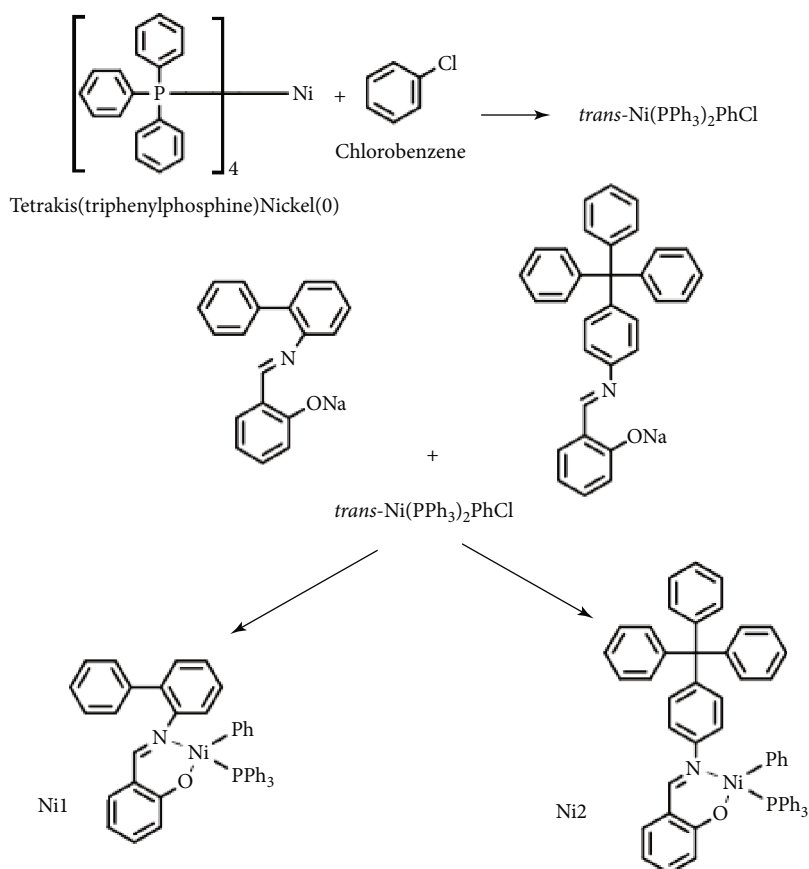
SCHEME 2: Chemical structures of Ni1 and Ni2 complexes.

TABLE 1: Ethylene polymerization results[a].

Entry	Temperature[b]	Pressure	Yield[c]	Activity[d]	Tm[e]	Xc[e]	Branches[f]
Ni1-1	60	6	2.1	3.5	107	31.7	55
Ni1-2	60	8	2.4	4	112	34.2	62
Ni1-3	80	8	1.95	3.25	118	27.6	73
Ni2-1	60	6	1.42	2.36	118	44	22
Ni2-2	60	8	1.62	2.7	118	46	38
Ni2-3	80	8	1.23	2.05	118	41.3	47

[a]General conditions: Ni = 30 μmol, toluene = 100 ml, and time = 2 h. [b]Reaction temperature $^\circ$C. [c]Yield (g). [d]Activity (Act.) = 10^4 g PE mol Ni^{-1} h^{-1}. [e]Melting temperature ($^\circ$C) and crystallinity (%) provided by DSC. [f]Branching numbers per 1000C by NMR.

accelerated deactivation of active sites, polymerization yield reduces. However, both complexes exhibit acceptable polymerization activity at 80°C. On the other hand, increase in ethylene pressure under similar polymerization temperature condition results in increased activity. This observation for Ni1 and Ni2 can be attributed to accelerated monomer insertion compared to transfer reactions due to higher monomer concentration in polymerization media.

The effect of polymerization conditions on microstructure of polyethylene was determined by NMR spectroscopy, and the results are tabulated in Figures 3 and 4 along with

Table 1. As supported by literature data, branching degree tends to increase over polymerization temperature increment [23, 24]. What is interesting is that compared to Ni2, Ni1 complex tends to produce more branches as temperature changes from 60°C (branches per 1000 C's) to 80°C (branches per 1000 C's). As data exhibit, ethylene polymerization using Ni2 results in linear chain structure as the prepared samples comprised of 22-47 branches per 1000 C's. ^{13}CNMR spectroscopy and results are tabulated in Figures 5 along with Table 1.

According to the data in Table 1, the major share of side branches in synthetic samples belongs to methyl branches,
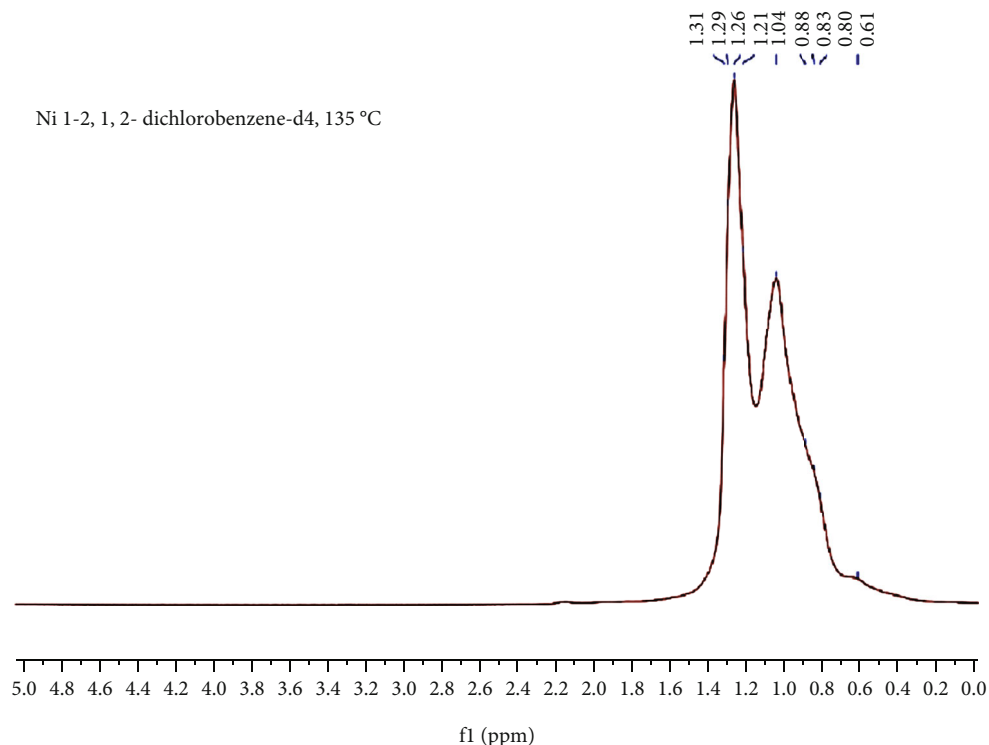
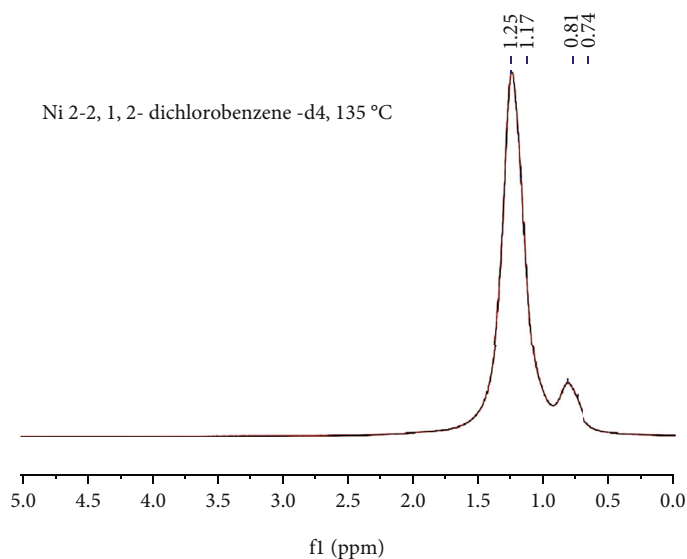FIGURE 3: ^{1}H NMR spectrum for Ni1-2 in 1,2-dichlorobenzene-d4.

FIGURE 4: ^{1}H NMR spectrum for Ni2-2 in 1,2-dichlorobenzene-d4.

and therefore, it is expected that the polymers will show linear behavior (melting point above 100) in the thermal analysis. The presence of bulky 2-aminobiphenyl group has increased the share of short branches (methyl, ethyl, and propyl) compared to longer branches (butyl, amyl, and long branches) to tetrakis(triphenylphosphine). As the polymerization temperature increases to 80°C, the share of longer branches in each sample increases, which indicates the increase in isomerization reactions.

3.2. Thermal Analysis. In order to assess the melting and crystallization behavior of synthesized polyethylenes, thermal analysis using differential scanning calorimetry was performed, and corresponding melting and cooling graphs and attributed data are demonstrated in Figure 6 and Table 1.

For all samples, broad melting point higher than 110°C was observed which can be attributed to variety of branches in chain structure and relatively linear polymer backbone that induce crystal formation with different crystallite size
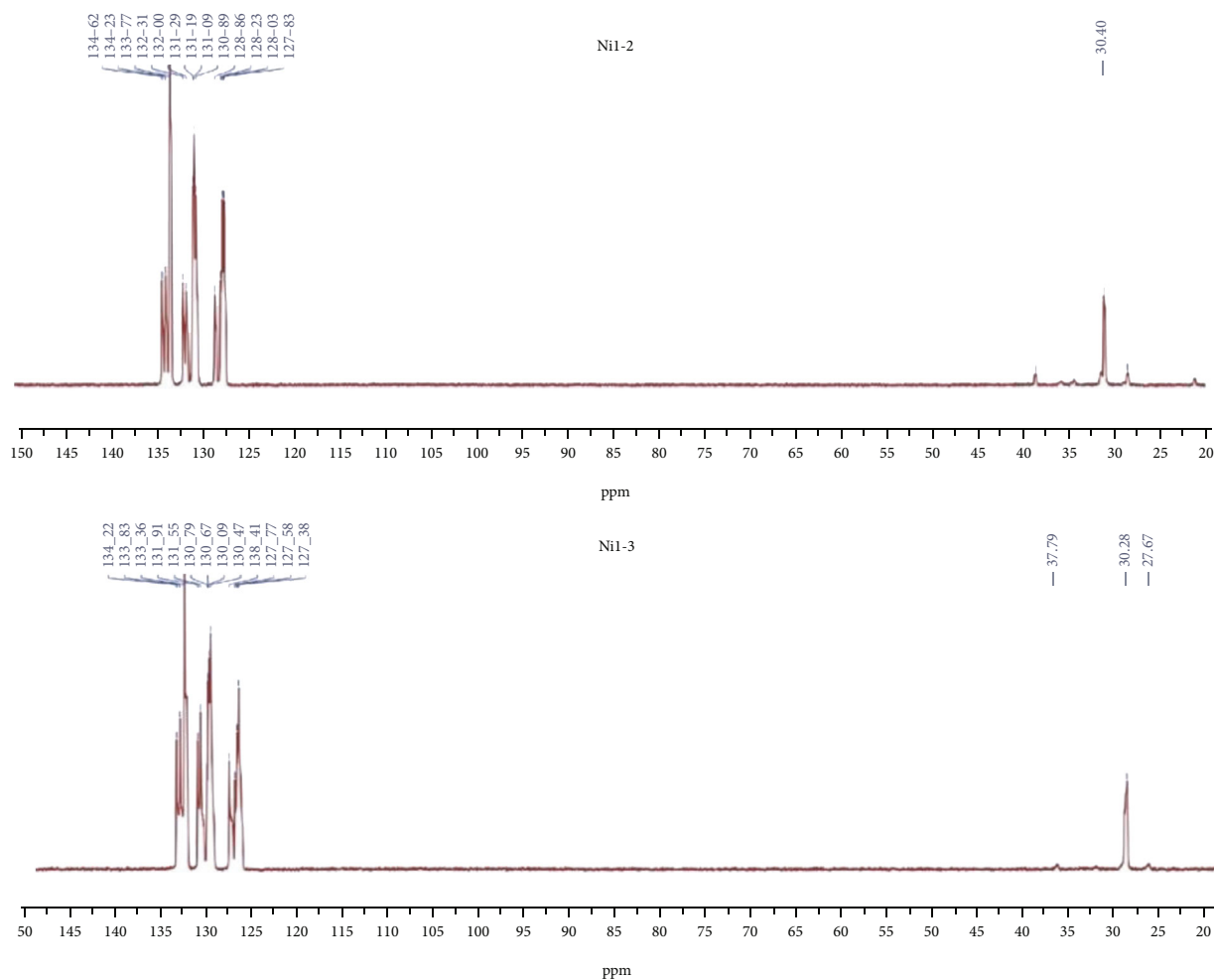
Figure 5: ^{13}CNMR spectrum for synthetic polyethylene.

[25]. Increase in polymerization temperature for Ni1 and Ni2 complexes results in reduction in crystalline content along with melting and crystallization peak intensities due to branch formation amplification. As pressure increases, linear chain production and reduction in branch content cause higher melting temperature accompanied with onset temperature of crystallization shifting toward higher temperatures. For Ni1 samples, the melting temperature varies from 107 to 118°C, indicating the possibility of formation of long chain branches. As regards melting characteristics of Ni2 polyethylene samples, it can be concluded that manipulation of polymerization conditions does not exert significant effects on melting point of polyethylenes. However, the crystalline content increases about 10% by reducing polymerization temperature or increasing ethylene pressure from 6 to 8 bar.

3.3. Mechanical Analysis. Chain structure and molecular feature of polymer chain can significantly affect mechanical properties of such materials. Thus, to study the changes in mechanical behavior of polyethylene samples, uniaxial stretching at room temperature was performed and stress-

strain curves of synthesized samples are depicted in Figures 7 and 8.

As it can be seen, synthesized polyethylenes using Ni1 exhibit tensile strength in the range from 7 to 9 MPa and strain-at-break value ranging from 800 to 1000%, which are comparable with reported data on elastomeric PEs. As the crystallinity increases due to reduction in polymerization temperature or ethylene pressure increase, both stress-at-break and modulus tend to rise in value. On the contrary, produced polymers with **Ni2** complex demonstrate thermo-plastic features as the stress-at-break and strain-at-break value changing in range of 8 to 12 MPa and 500 to 700%, respectively. This behavior can be attributed to enhanced portion of linear molecules and tie formation of polymer backbones in matrix of polyethylene.

4. Conclusions

In summary, we have described the synthesis of Ni(II) nickel complexes bearing cyclic imides with the aim to investigate the effect of bulky imide ligands on catalytic properties and structure of polyethylenes. These catalysts in the absence of
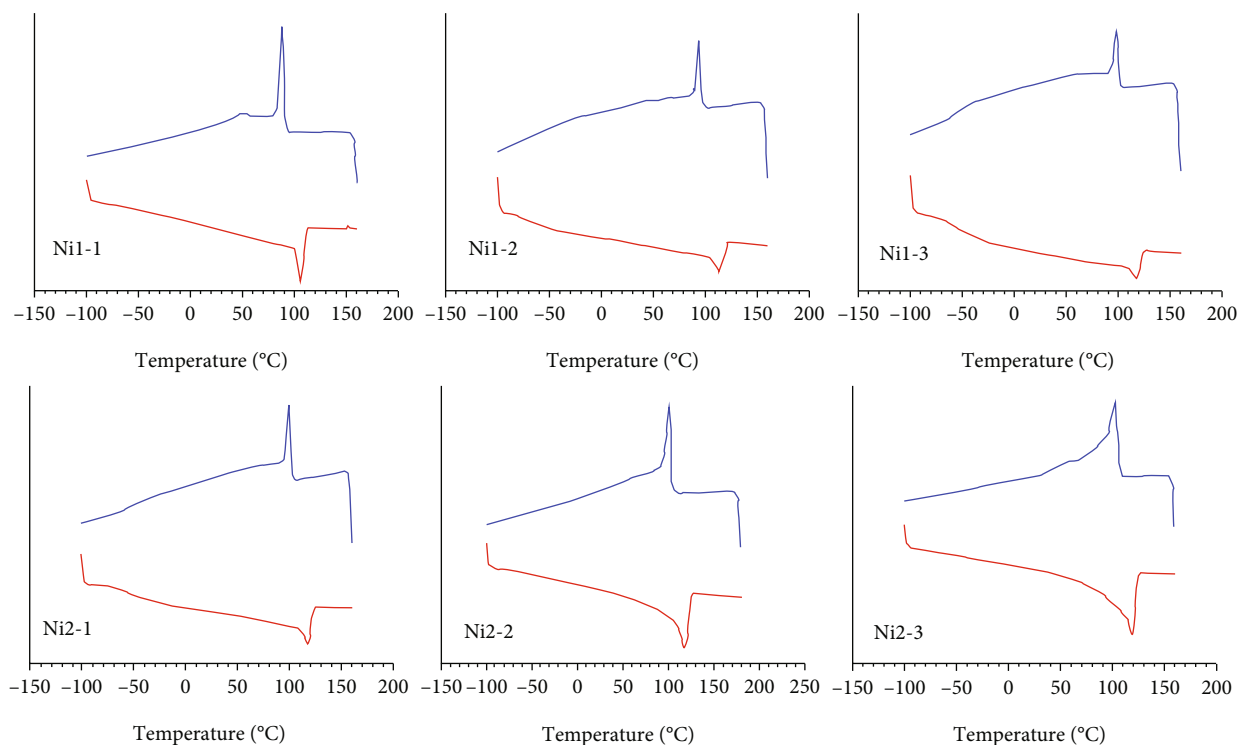
Figure 6: DSC scans for melting and cooling from the melt through polymerization condition variation.
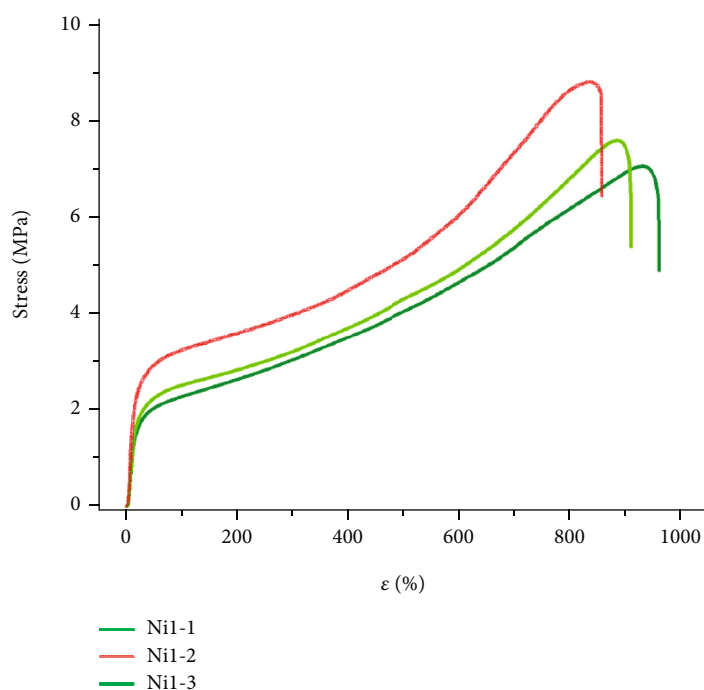

Figure 7: Stress-strain curves for Ni1 polyethylenes.

$Ni(COD)_2$ activator demonstrated satisfactory level of polymerization activity up to 80°C. The introduction of bulky imide moieties seemed to improve the thermal stability of catalyst. The introduction of bulky 4-tritylaniline group resulted in production of more linear structure accompanied with superior mechanical properties compared to 2-aminobiphenyl group. Aside from polymerization temperature and ethylene pressure which seemed to affect branching
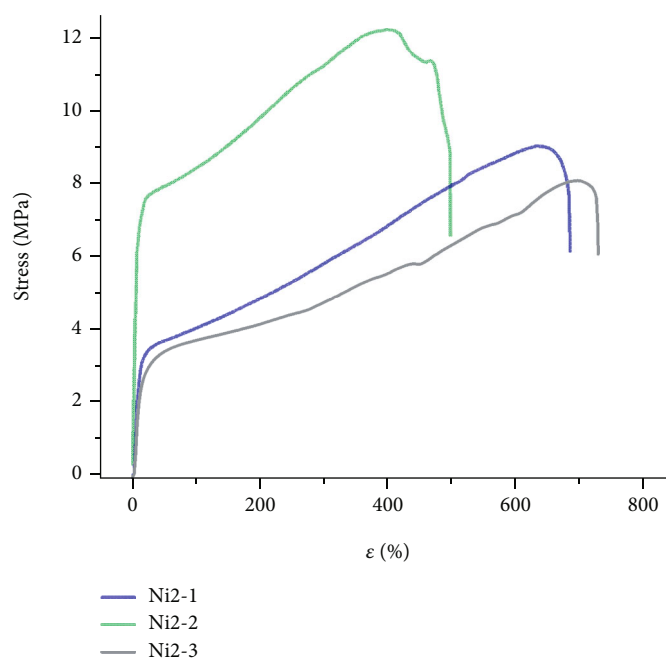
FIGURE 8: Stress-strain curves for Ni2 polyethylenes.

density, the presence of 2-aminobiphenyl group in Ni(II) complex caused higher branch content in produced polyolefins.

Data Availability

The DSC, CHN, and NMR dates used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare no conflict of interest.

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