

Preparation of Highly Branched Polyethylene Using (α -Diimine) Nickel Complex Covalently Supported on Modified SiO₂

Hongliu Jiang, Qing Wu, Fangming Zhu, Haihua Wang

Institute of Polymer Science, School of Chemistry and Chemical Engineering, Sun Yat-Sen (Zhongshan) University, Guangzhou 510275, People's Republic of China

Received 5 May 2005; accepted 10 May 2006

DOI 10.1002/app.24972

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Bis(4-(4-amine-3,5-diisopropylbenzyl)-2,6-diisopropylphenylimino) acenaphthene NiBr₂ (Catalyst I) was synthesized. The complex covalently supported on Et₃Al-treated silica (SC) and used for ethylene polymerization was produced with cocatalyst of common inexpensive alkylaluminum compounds. Polyethylenes (PEs) with branching numbers of 12.94 (1000C) to 116.02 (1000C) were prepared in heptane. The polymerization conditions, such as the cocatalyst, Al/Ni ratio, and temperature, had significant effects on catalytic activity and properties of polyethylenes. Confirmed by high-temperature ¹³C NMR, the polyethylenes synthesized contain significant amounts of not only methyl but also ethyl,

propyl, butyl, pentyl, and other long branches (longer than six carbons). The branching degree of polyethylenes increased with temperature, while their molecular weight and melting point decreased correspondingly, resulting in linear semicrystalline to totally amorphous polymers. The formation of the branches could be illustrated by the chain walking mechanism, which controlled their specific spacing and conformational arrangements with one another. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1483–1489, 2007

Key words: (α -diimine)nickel complex; supported catalyst; branched polyethylenes; SiO₂

INTRODUCTION

The discovery of the homogenous α -diimine-based late transition metal catalyst in 1995 had a major impact on the polyolefin industries.¹ These catalysts can produce polyethylene with branch structures without the use of α -olefin comonomers and are well-suited for application in the copolymerization of α -olefins with polar monomers such as alkyl acrylates because of their lower oxophilicity.^{2–4} This is a significant advantage over homogeneous metallocene catalysts that are single site catalysts and can be fine-tuned to produce tailor-made polymers. As a result, the interest in the α -diimine-based late transition metal catalysts has greatly increased. However, when used in gas phase or slurry reactions to handle heterogeneous reactions, these catalysts often show problems such as reactor fouling and extremely high exothermic heat resulting from the homogeneous polymerization. To overcome these drawbacks, homogenous catalysts should be supported on carriers, without losing much of their advantages of high catalyst activity and desired polymer properties.

Supported metallocene catalysts have been widely investigated by both academic and industrial sectors.^{5–7} The late transition metal catalysts supported on different types of inorganic supports such as SiO₂, MgCl₂, clay as well as polymeric supports^{5,8–11} have been reported. Spherical SiO₂ is one of the most commonly used catalyst carrier because it leads to good polymer particle morphology.¹² Different supporting techniques have a significant effect on catalyst immobilization and characteristics of supported catalysts. In general, the immobilization of the catalyst on silica is achieved by two different methods, the direct immobilization of the catalyst on silica, and the immobilization of the catalyst on silica pretreated with aluminosilicate or alkylaluminum compounds activator. The first method usually significantly suppresses the catalytic activity of the catalyst and affects microstructure of the resulting polymer because this kind of immobilization generally changes the nature of the active centers through direct reaction of the catalyst with hydroxyls on the silica surface. This reaction forms some low active or inactive centers. In the second method, the catalyst is separated by the aluminosilicate or alkylaluminum compounds activator from the silica surface and directly reacts with the aluminosilicate or alkylaluminum activator that are similar to the homogeneous catalyst. This kind of immobilization is proved to be efficient in olefin polymerization, because it can widely maintain the original active

Correspondence to: Hai-hua Wang (ceswhh@zsu.edu.cn).

Contract grant sponsor: National Natural Science Foundation of China and SINOPEC; contract grant number: 20334030.

Journal of Applied Polymer Science, Vol. 103, 1483–1489 (2007)
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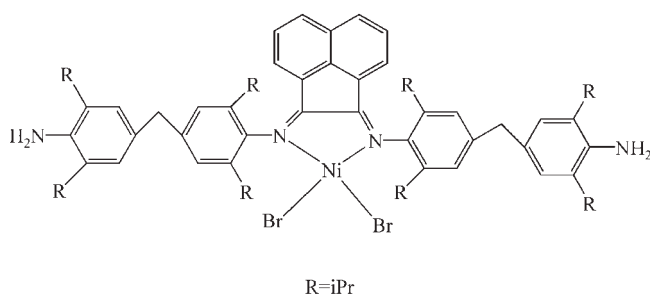
center of the homogeneous catalyst and produce polymers as those prepared by the homogeneous catalyst. Recently a new immobilization of catalysts whose ligands contains functionality for reaction with a second functional group on the surface of support to form covalent bond or a method to immobilize ligands on the supports, followed by addition of metal salts has been reported. Compared to the second way, the immobilization can keep the catalyst anchoring on the surface of support firmly and is less harmful to the active centers. A similar method for supporting zirconocene catalysts was reported earlier.¹³ More recently, covalently supported nickel-diimine catalysts¹⁴ and bis(imino)pyridyl Fe(II) catalysts¹⁵ were used successfully for ethylene polymerization.

In this study, we report the synthesis of highly branched polyethylenes by heterogeneous ethylene polymerization with a kind of (α -diimine) nickel complex (Scheme 1, denoted with the formula of NiLBr₂) covalently supported on Et₃Al-treated SiO₂ support in a slurry reactor, which is activated by general alkylaluminum compounds. The heterogenization technique to immobilize NiLBr₂ shows excellent activity, and no reactor fouling was observed during the whole olefin polymerization process. The effects of polymerization conditions on catalytic activity and properties of polyethylenes, and microstructures of the resulting branched polyethylenes, were discussed. The discussion subjects include the molecular weight, degree of branching, and branch type.

EXPERIMENTAL

Materials

All experiments were performed under nitrogen in Schlenk-type vessels, using anhydrous air-free reagents and solvents. Solvents were dried by refluxing with appropriate drying agents (sodium/benzophenone for toluene and diethyl ether, hexane, and CaH₂ for dichloromethane) and distilled under N₂ before use. (1,2-Dimethoxyethane) nickel (II) bromide [(DME)NiBr₂] was synthesized via a previously reported procedure.¹⁶ Diethylaluminum chloride (DEAC), triethyl aluminum (TEA), and triisobutyl aluminum (TIBA) were provide



Scheme 1 Nickel (II) diimine complex.

by the Institute of Chemical Engineering (Shanghai), and diluted to 350 g/L solutions in *n*-heptane before use. The ligand precursors, 4,4'-methylene-bis(2,6-diisopropylaniline) and acenaphthenequinone, were purchased from ACROS and used without purification. Silica (Grade 955) was provided by Davison (USA) and was calcinated under a nitrogen atmosphere at 600°C for 6 h before use. Ethylene was provided by Shanghai Jinshan Petroleum. The other chemicals were purchased commercially and used without further purification.

Instrumentation

¹H NMR spectra were recorded on a Bruker-500 spectrometer. Molecular weights and molecular weight distributions were determined by high-temperature GPC in 1,2,4-trichlorobenzene. The ¹³C NMR spectroscopic data for polyethylene were obtained using *o*-dichlorobenzene as the solvent with a Varian INOVA-500 NMR spectrometer at 130°C. Melting points were determined by DSC with a Perkin-Elmer 7 Series Thermal Analysis System. ICP-AES measurement for determining the loading of Ni in supported catalyst was performed on IRIS Advantage (HR) spectrometer.

Preparation of support

Calcinated SiO₂ (3.0 g) was introduced into a glass vessel equipped with a magnetic stirrer, and then 15 mL of *n*-heptane was added. Et₃Al (8 mL) solution in *n*-heptane was added to the mixture at 0°C and stirred for 2 h. The modified SiO₂ was separated by decantation, washing with *n*-heptane, and dried under vacuum at 60°C for 2 h.

Preparation of nickel catalyst

Synthesis of bis(4-(4-amine-3,5-diisopropylbenzyl)-2,6-diisopropylphenylimino) acenaphthene

4,4'-Methylene-bis(2,6-diisopropylaniline) (3.0 g) and acenaphthenequinone (0.54 g) were dissolved in 50 mL of toluene. A few drops of sulfuric acid were added and the solution was refluxed for 14 h, with continuous removal of water using a Dean-Stark. Upon cooling to temperature (RT), the solution was evaporated under vacuum, and the crude product was purified using column chromatography (silica, ethyl acetate/petroleum ether 1 : 9). Yield 1.2 g of yellow powder.

¹H NMR (500 MHz, CDCl₃, δ ppm): 7.87, 7.85 (d, 2H), 7.35, 7.33, 7.32 (t, 2H); 7.11 (s, 4H); 6.93 (s, 4H); 6.77, 6.76 (d, 2H); 4.02 (s, 4H); 3.48 (s, 4H), 3.02, 3.01, 2.99, 2.98, 2.96, 2.95 (m, 8H); 1.28, 1.25 (d, 24H); 1.21, 1.19 (d, 12H); 0.95, 0.93 (d, 12H). ¹³C NMR (500 MHz, CDCl₃, δ ppm): 161.02, 145.36, 140.79, 137.94, 136.77, 135.17, 132.59, 131.64, 129.68, 128.69, 127.72, 124.57, 123.24, 123.01, 41.35, 28.57, 27.98, 23.41, 23.17, 22.50.

Anal. Calcd for $C_{62}H_{78}N_4$ (%): C, 84.68; H, 8.95; N, 6.37. Found (%): C, 84.80; H, 8.67; N, 6.34.

Synthesis of bis(4-(4-amine-3, 5-diisopropylbenzyl)-2,6-diisopropylphenylimino) acenaphthene $NiBr_2$

Bis(4-(4-amine-3,5-diisopropylbenzyl)-2,6-diisopropylphenylimino) acenaphthene (0.6 g) and (DME)- $NiBr_2$ (0.3g) were added into 30 mL of CH_2Cl_2 and the mixture was stirred for 14 h. After the solvent was removed under vacuum, the brown product was washed thrice with diethylether (yield 0.6 g, brown powder). Because of the paramagnetic nature of the complex, 1H NMR study was not feasible. Anal. Calcd for $C_{62}H_{78}N_4NiBr_2$ (%): C, 67.82; H, 7.17; N, 5.10. Found (%): C, 67.12; H, 6.72; N, 4.92.

Preparation of supported catalyst (SC)

SiO_2/Et_3Al (0.3g) was mixed with a solution of 0.0714 g of $NiLBr_2$ at $30^\circ C$ in 20 mL of CH_2Cl_2 . After 5 h the CH_2Cl_2 phase was subjected to vacuum, and the remaining solid was washed three times with CH_2Cl_2 . The contents of Ni of this supported catalyst are measured by ICP-OES method. The content of Ni is approximately 0.39 wt %. Scheme 2 shows a possible process of fixing $NiLBr_2$ on the SiO_2/Et_3Al support.

General procedure for polymerization of ethylene

The polymerization of ethylene was carried out in a 250-mL Schlenk flask equipped with a mechanical stirrer, the stirring rate of which is adjustable. The flask was dried by heating at $80^\circ C$ under vacuum for 1 h, during which the flask was swept with dry N_2 at least three times. After the flask was dried completely and cooled down to room temperature, the flask filled with 50 mL of *n*-pentane and the solvent saturated ethylene monomer at 1 atm. $AlEt_2Cl$ cocatalysts dis-

solved in *n*-pentane was injected into the reaction solution. The heterogeneous catalyst (0.04 g) was then added and the reactor was heated to the polymerization temperature within 2 min. After 1 h, the polymerization was quenched by addition of ethanol. The reaction solution was poured into the excess 10% HCl-EtOH solution, affording polyethylene as a suspended precipitate. The polymer was filtered and washed with ethanol several times, and dried in vacuum at $40^\circ C$ for 20 h.

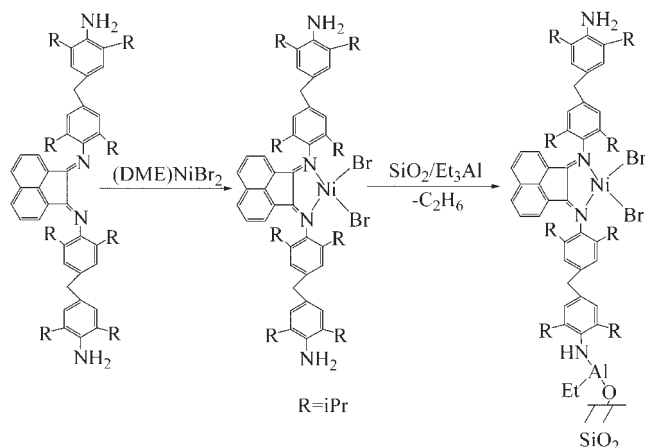
RESULTS AND DISCUSSION

Stability of the supported catalyst

As we all know, to ensure the immobilized Ni complex not to be removed from the support by washing with solvent, it is important for the supported catalysts to form a covalent bond between the Et_3Al -modified support surface and nickel α -diimine catalyst. To explain the process, it is suggested that the washed supported catalyst should show no difference with the original heterogeneous catalyst in polymerization, in which Al-N bond is believed to form. Thus, the following experiment was designed. In a flame-dried Schlenk-type apparatus, 0.04 g supported catalyst was dissolved in 50 mL of toluene under N_2 atmosphere. After vigorously stirring at $50^\circ C$ for about 30 min, the mixture was filtered under N_2 atmosphere. The solid and the liquid were used to catalyze the ethylene polymerization in the usual procedure, respectively. After polymerization for about 30 min, the solid-catalyzed polymerization yielded polyethylenes, while for the liquid only a trace of polyethylene was produced. Therefore, it may be concluded from the result that the synthesized supported catalyst is supported on the support.

Effects of the cocatalyst

To evaluate the performance of the supported catalyst, ethylene polymerization was conducted. As for $NiLBr_2/SiO_2/Et_3Al$ supported catalyst, the effect of cocatalysts (DEAC, TEA, and TIBA) on ethylene polymerization under the conditions of Al/Ni ratio 800 and temperature $50^\circ C$ was investigated. On the basis of our experiment results, we found that the role of cocatalysts in the ethylene polymerization is of great interest, DEAC can effectively initiate ethylene to polymerize, but TEA and TIBA cannot initiate it at all. In general, it is the cationic form of organometallic complexes that is of interest in polymerizations. Reaction of halocomplexes with methyl aluminoxanes (MAO) in the presence of ethylene or other olefins is presumed to form catalytical cationic active species.¹⁷ $AlEt_2Cl$ is also presumed to react with supported nickel α -diimine complex in the presence of ethylene to



Scheme 2 Synthesis of supported complex.

form similar catalytical cationic active species while TEA and TIBA probably make the complex of NiLBr₂ reduce excessively and cannot form the cationic species. In our previous study, for α -diimine-based late transition metal catalyst, a similar result was reported.¹⁰

Effects of polymerization conditions

Table I shows the effects of the Al/Ni ratio on catalytic activity of ethylene polymerization and properties of polyethylenes. The activity increases with the increase of Al/Ni ratio, with a highest activity of 1.92×10^6 g PE/(mol of Ni h) at Al/Ni ratio 800, but slightly decreases as Al/Ni ratio increases further. For late transition metal catalysts, it is believed that aluminum alkyl cocatalysts are responsible for activation.¹⁸ The suitable amount of AlEt₂Cl commences making nickel α -diimine complex to form cationic nickel species, and thus initiate ethylene to polymerize. Concentration of cationic nickel species increases with Al/Ni ratio, and reaches the highest point at 800. Further increase in the amount of aluminum reagent will speed up chain transfer on AlEt₂Cl, thus decreasing the catalytic activity of polyethylene formation. Molecular weights and molecular weight distributions of all obtained polyethylenes were determined by high-temperature GPC. As shown in Table I, the polymers have higher molecular weights and rather broader molecular weight distributions of 3.18–3.87. Molecular weight of polyethylenes decreases with the increase of Al/Ni ratio. M_w of 3.49×10^5 is obtained at Al/Ni ratio 200. It reaches 1.96×10^5 as Al/Ni ratio is increased to 800. AlEt₂Cl is regarded as a chain transfer reagent in ethylene polymerization. Therefore, chain transfer rate will increase with Al/Ni ratio and thus lead to the decrease in the molecular weight of polyethylenes. Al/Ni ratio has a slight effect on branches

of polyethylenes, branches increase from 88.62 (1000C) to 91.69 (1000C) as Al/Ni ratio increases from 200 to 800.

A series of experiments were done to determine the effect of temperature variation on SC performance and properties of polyethylene. Table I shows the results of polymerizations performed at four different temperatures (0, 25, 50, and 75°C). Three effects are observed. First, at 50°C, a significant change in the productivity of catalysts is observed, with the highest activity of 1.92×10^6 g PE/(mol of Ni h) for polyethylene formation, and decreases regardless if the temperature decreases or increases. Ethylene polymerization rate decreases with the decrease in polymerization temperature, but an increase in temperature also lowers the activity of the supported catalyst due to deactivation. Second, the molecular weight of polyethylenes decreases with increase in temperature. M_w of 1.36×10^6 is obtained at 0°C and it reaches 1.96×10^5 as temperature is increased to 50°C. Third, T_m of polyethylene evidently decreases with the increase in temperature. This is due to the fact that chain-transfer rates increase with polymerization temperature. These results agree with the effects observed by Brookhart et al.¹⁹ However, broadening of the molecular weight distributions is evident with the supported catalyst systems. A molecular polydispersity of 2.90–5.28 is observed in the supported system. The molecular weight broadening due to support is a known phenomenon and likely results from the interactions between catalyst and support, which leads to the formation of multiactive sites having slightly different chain transfer rates.²⁰

From the data in Table I, although the activity of SC is slightly lower than that of catalyst I, a good catalytic activity of SC with AlEt₂Cl was obtained. The molecular weight of the obtained polyethylene is much

TABLE I
Results of Ethylene Polymerization with SC/DEAC^a and I/DEAC

Run	Catalyst	Polymerization temperature (°C)	n_{Al}/n_{Ni} ^b (mol/mol)	Activity ^c	Branches (1000 C) ^d	M_w (10^{-5}) ^e	MWD	T_m (°C) ^f
1	SC	0	800	0.31	12.94	13.61	5.10	118.72
2	SC	25	800	1.08	37.07	12.67	5.28	114.19
3	SC	50	800	1.92	91.69	2.91	3.55	–
4	SC	75	800	0.55	116.02	1.56	2.91	–
5	I	50	800	2.14	98.51	1.82	2.42	–
6	SC	50	200	0.71	88.62	3.49	3.87	–
7	SC	50	500	1.55	90.20	1.96	3.21	–
8	SC	50	1000	1.42	97.45	2.07	3.18	–

^a Polymerization conditions: [Ni], 0.0479–0.0567 mmol/L; pressure of C₂H₄, 1 atm; polymerization time, 1 h; solvent, heptane.

^b n_{Al} , molar number of Al; n_{Ni} , molar number of Ni.

^c 10^6 g of PE/mol of Ni h.

^d Number of branches per 1000 carbon atoms in the polyethylene main chain, as determined by high-temperature ¹³C NMR.

^e Weight-average molecular weight, as determined by GPC measurement at 140°C in 1,2,4-trichlorobenzene.

^f Melting temperature, as determined by DSC.

higher and molecular polydispersity is broader for the supported catalyst SC than for the homogeneous catalyst I, because the β -hydrogen transfer was suppressed. The supported catalyst SC produced polyethylene with slightly less total branching than did the homogeneous catalyst I.

Study on microstructures of the resulting branched polyethylenes

For nickel α -diimine complexes, the branched polyethylene products are produced only with a single feed of ethylene, without the intermediacy of α -olefins. Branching of polyethylene products is thought to form according to the mechanism of "chain walking."¹⁷ However, the results obtained by us in the support system indicate no marked effect on the basic modes of chain growth and branching. DSC measurement demonstrates that some polyethylene samples do not have melting point, while others show very broad one, implying that all polyethylene under our experiment conditions is branched polyethylene. The DSC curves of polyethylenes with different degrees of branching prepared with the support system at various values of T_m are shown in Figure 1. T_m decreased with an increased degree of branching of polyethylene and gave rise to linear semicrystalline to totally amorphous polymers. The polyethylenes produced at 0 and 25°C had a higher T_m value of 118.72°C [Fig. 1(a)] and 114.19°C [Fig. 1(b)], respectively, whereas the highly branched polyethylenes prepared at 50 and 75°C showed no melting peak [Fig. 1(c, d)]. The DSC curves also become broader as the degree of branching increases, as shown in Figure 1. The DSC curve of branched polyethylene produced at 25°C shows a much broader melting peak than at 0°C. The broadening of the DSC curve, and the disappearance of the

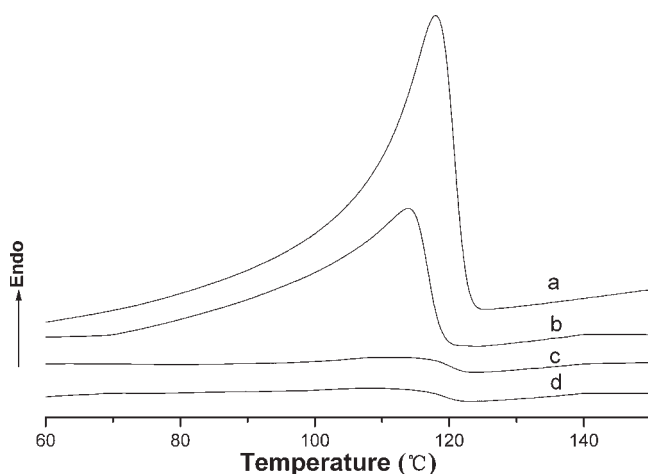


Figure 1 DSC thermograms for polyethylenes produced with supported catalyst at reaction temperature 0°C (a), 25°C (b), 50°C (c) and 75°C (d), Al/Ni = 800.

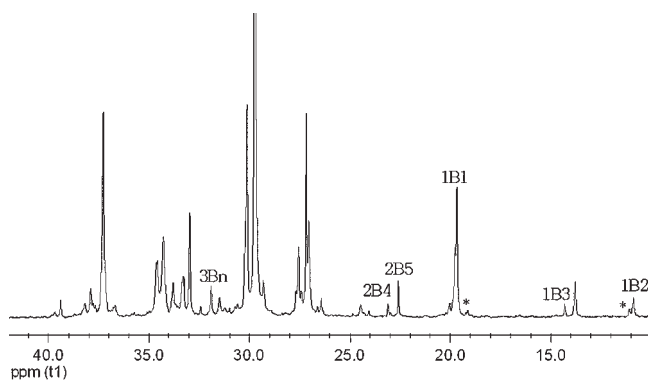


Figure 2 The high-temperature ^{13}C -NMR spectroscopy of polyethylene produced with supported catalyst at the following polymerization conditions: 50°C, Al/Ni = 800. The two peaks indicated by the asterisk (*) represent branches containing a *sec*-butyl end, the shortest branch-on-branch observed in polyethylenes.

melting peak found at high branching numbers in the polymers could be due to the chain density. Increasing chaining density decreases lamellar thickness of the crystal structure and thus lowers melting temperature of the polymer.²⁰

The microstructures of the branched polyethylenes obtained with supported (α -diimine)nickel catalyst are analyzed using high-temperature ^{13}C NMR spectroscopy. The analysis shows that some polyethylenes have extensive branching, and a branched structure consists mainly of methyl branches. A representative ^{13}C NMR spectrum of polyethylene prepared with the support catalyst at 50°C is shown in Figure 2.

The assignments of each resonance peak were done based on chemical shift calculations performed using Linderman and Adams method.²¹ The corresponding branches resonance peaks can be found in our polymer spectrum. The characteristic chemical shifts at 19.74 (1B₁), 32.99 (brB₁), 10.95 (1B₂), 39.42 (brB₂), 14.38

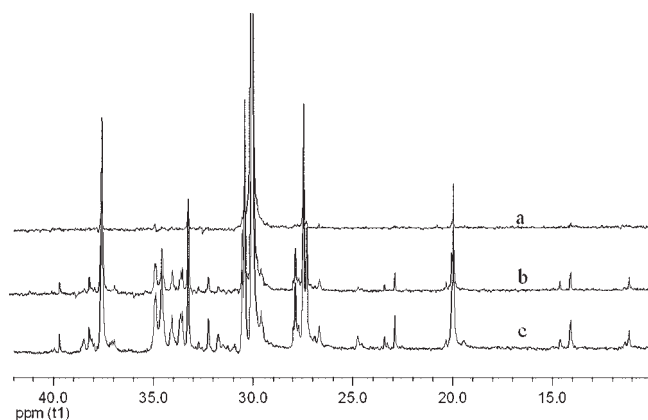


Figure 3 The high-temperature ^{13}C -NMR spectroscopy of polyethylenes produced with supported catalyst at reaction temperature 0°C (a), 25°C (b) and 75°C (c), Al/Ni = 800.

TABLE II
The Effects of Different Temperatures on Branches Distribution of Polyethylenes

Temperature (°C)	Branches ^a (1000 C)	Branches distribution (%)					
		Methyl	Ethyl	Propyl	Butyl	Pentyl	Long branches (n ≥ 6)
0	12.94	100.00	0	0	0	0	0
25	37.07	77.49	7.80	3.45	1.81	5.99	3.45
50	91.69	58.17	10.48	3.62	3.16	11.56	13.01
75	116.02	45.03	16.40	3.74	4.22	16.75	13.83

^a Determined by high-temperature ¹³C NMR measurement as branches/1000 carbons.

(1B₃), 23.14 (2B₄), 37.94 (brB₄), 22.63 (2B₅), 31.94 (3B_n), and 29.34 (4B_n) for the supported catalyst manifests that some polyethylenes have methyl, ethyl, propyl, butyl, pentyl, and long branched chains (*n* ≥ 6). However, at 0°C a linear semicrystalline polyethylene is prepared, for which only signals of methyl branches [Fig. 3(a)] were seen in its ¹³C NMR spectrum. Some small resonances attributable to ethyl, propyl, butyl, and pentyl branches can be observed [Fig. 3(c)] for branched polyethylene obtained at 75°C. It is very surprising that long branches (longer than six carbons) are confirmed by the presence of the 3B_n and 4B_n car-

bon resonances at 31.95 and 29.34 ppm, and a pair of resonances attributable to a branch terminated with a *sec*-butyl group are also found in Figures 2 and 3(c). This is the smallest branch-on-branch possible in an ethylene polymerization. The above nomenclature used to designate the different carbon types is that of Usami and Takayama.²² Branches are named by *x*B_{*n*}, where *B* designates a branch chain, *n* is the length of the branch, *x* is the carbon number starting with the methyl group of the branch chain and the end methyl noted as *n* = 1. According to the equation proposed by Usami and Takayama:

$$N(\text{total branches}/1000 \text{ C}) = \frac{1000(I_{\text{Me}}/0.90 + I_{\text{Et}}/0.84 + I_{\text{Pr}}/0.83 + I_{\text{Bu}}/0.90 + I_{\text{Pe}}/0.90 + I_{\text{Lg}}/0.80)}{I_{\text{main}} + 5.5(I_{\text{Et}}/0.84) + I_{\text{Pr}}/0.83 + 8.0(I_{\text{Bu}}/0.90 + I_{\text{Pe}}/0.90 + I_{\text{Lg}}/0.80)}$$

where *N* is total branches (1000C). *I*_{Me}, *I*_{Et}, *I*_{Pr}, *I*_{Bu}, *I*_{Pe}, and *I*_{Lg} are the corresponding integral intensity of ¹³C NMR chemical shift of 1B₁, 1B₂, 1B₃, 2B₄, 2B₅, and 3B_{*n*}, respectively. The proportion of various branches content is as follows:

$$\text{Me} : \text{Et} : \text{Pr} : \text{Bu} : \text{Pe} : \text{Lg} = (I_{\text{Me}}/0.90) : (I_{\text{Et}}/0.84) : (I_{\text{Pr}}/0.83) : (I_{\text{Bu}}/0.90) : (I_{\text{Pe}}/0.90) : (I_{\text{Lg}}/0.80)$$

Therefore, concentration and distribution of various branched chains of the supported catalyst can be calculated. The results are shown in Table II. Table II shows the effect of different temperatures on branches degree and distribution of polyethylenes. At 0°C there is lower branches degree and almost all methyl branches incorporated in the polyethylene backbone, but no incorporation of long branches can be observed in the ¹³C NMR spectrum. As the temperature increases, the methyl branch content decreases, and that of long branches and branches degree increases. At 50°C, 58.17% of methyl branch and 13.01% of long branches were incorporated in polyethylene backbone. It can be clearly seen that the chain walking mechanism appeared to be pronounced in the supported catalyst system too. An increase in polymerization temperature raises the rate of chain walking and results in the formation of more branching polyethyl-

ene, which leads to a low melting point. Overall, the ¹³C NMR (Table II) of the polyethylene produced by these catalytic systems shows that these results are consistent with the results reported by Brookhart and coworkers.¹

CONCLUSIONS

In this report, a highly active supported Ni(II) α -diimine complex has been studied. The amino-functionalized (α -diimine) nickel complex was synthesized without the need for protecting groups. By reaction of the functional groups with modified silica, the catalyst was covalently anchored on the support. The tethered complex could be used to polymerize ethylene with high activity, using diethylaluminum chloride as inexpensive cocatalyst at lower Al/Ni ratios, and high branched polyethylenes can be obtained. The presence of short and long branches in the product makes this synthesis valuable for these branches to improve rheological properties, thus facilitating the processing of these polymers.

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