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Polymerizations of Propylene with Unsymmetrical (α-Diimine)nickel(II) Catalysts

Manseong Jeon, Chul Jong Han, and Sang Youl Kim*

Polyolefin Materials Research Center, Department of Chemistry and School of Molecular Science (BK21), Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea

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Abstract: New unsymmetrical (α-diimine)nickel(II) catalysts having different pendent groups at the *ortho* positions on aromatic rings were synthesized and subjected to propylene polymerizations with MAO (methylaluminoxane). Structural analyses of the resulting polypropylenes by ^{1}H and ^{13}C NMR showed that the ortho substituents on aromatic rings of (α-diimine)nickel(II) catalyst affected significantly the polypropylene microstructure. While C_s symmetric catalyst afforded a syndiotactic polypropylene (rr triad content=66%) due to the syndiospecific chain end control, C_1 symmetric catalysts produced much less stereoregular polypropylenes (rr triads content <50%), presumably because of collision of the isospecific site control with the syndiospecific chain end control.

Keywords: (α-diimine)nickel(II) catalysts, late transition metal complex, poly(propylene) (PP), tacticity, unsymmetrical ligands.

Introduction

Recently olefin polymerization catalysts based on late transition metals have attained much research interest mainly because of their tolerance to polar functional groups.[1,2] Especially (α-diimine)nickel(II) catalysts have gained remarkable attention because of their easy synthesis, air stability, and novel polymerization characteristics. The catalysts showed good activity for ethylene polymerizations, α-olefin polymerizations, internal olefin polymerizations, ethylene/polar functional monomer copolymerizations, and polar functional monomer polymerizations when they were activated with MAO or other cationizing reagents.[3] Steric bulkiness of ortho substituents on aromatic rings of the (α-diimine) nickel(II) catalyst has been known to affect the molecular weight of resulting polyolefin as well as the catalyst activity.[4] Higher molecular weight polyolefin was produced as the steric bulkiness of ortho substituents increases, because it retards a rate of associative olefin displacement.[5]

Pellecchia *et al.* reported that the (α-diimine)nickel(II) catalyst promoted syndiospecific polymerization of propylene at -78 °C (rr triad content = 80%).[6,7] The propylene polymerization proceeded through 1,2-insertion and syndiospecific chain end control.[8] Isolated 2,1-insertion during 1,2-insertions resulted in adjacent methyl and 2,1 insertion followed by β-hydride elimination and reinsertion resulted in 1,3-inserted monomer unit as shown in Scheme I. Theoretical calculations have suggested that the syndiospecific chain end control in this catalyst system originate from a chiral orientation of a growing chain.[9] They have also reported on the effect of the ortho substituents on aromatic rings of (α-diimine)nickel(II) catalyst on the polypropylene microstructure.[10] In particular C_2 symmetric (α-diimine)nickel(II) catalysts afforded polypropylenes having high mm triad contents. So dual mechanism of steric control (partly isospecific site control, partly syndiospecific chain end control) has been suggested for the C_2 symmetric (α-diimine)nickel(II) catalysts.

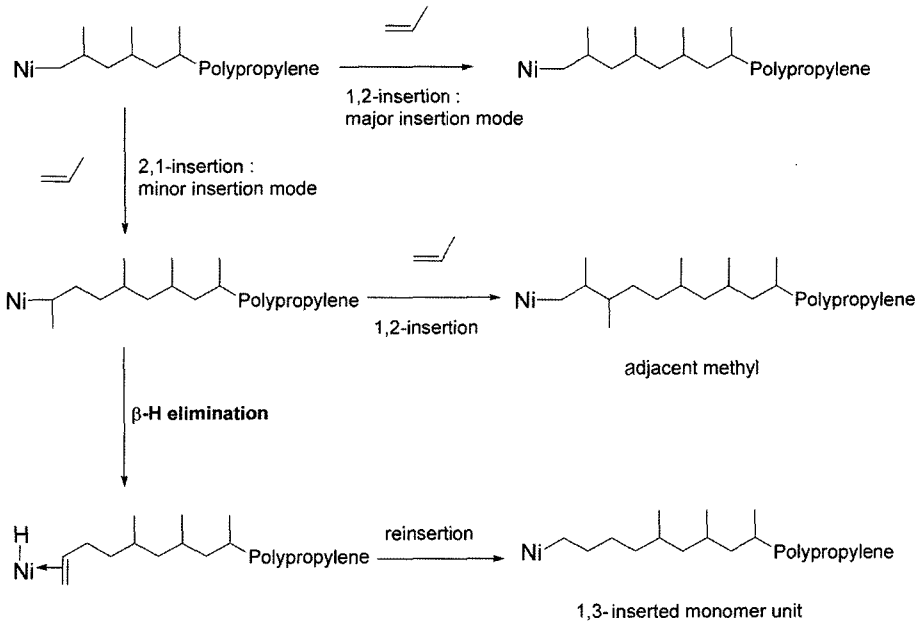
Recently Coates *et al.* reported new C_2 symmetric (α-diimine)nickel(II) catalysts which showed isospecific propylene polymerization behavior at -78 °C and living polymerization behavior at temperatures above -40 °C.[11]

In this study, new unsymmetrical α-diimine ligands which contain 2,6-diisopropylphenyl on one side and other alkyl substituted phenyl on the other side were synthesized using $TiCl_4$ as a dehydration agent.[12,13] New C_s symmetric and C_1 symmetric (α-diimine)nickel(II) catalysts were synthesized from these ligands and subjected to propylene polymerizations with MAO to investigate the effect of ortho substituents on aromatic rings of (α-diimine)nickel(II) catalyst on the polypropylene microstructure.

Experimental

Manipulations of sensitive materials were carried out under a dry nitrogen atmosphere using Schlenk flasks or a glove box.

*Corresponding Author. E-mail: kimsy@kaist.ac.kr



Scheme I. Representative polypropylene microstructures.

Materials. Toluene was refluxed over sodium and distilled under nitrogen atmosphere. Chlorobenzene and CH_2Cl_2 were distilled over CaH_2 and stored over 4 Å molecular sieves. MAO was purchased from Aldrich as a 10 wt% solution in toluene and used as received. Acenaphthenequinone, 2-*tert*-butylaniline, 2,6-diisopropylaniline, 2,6-dimethylaniline, 2-isopropyl-6-methylaniline, and nickel(II) bromide ethylene glycol dimethyl ether complex ((DME)$NiBr_2$) were purchased from Aldrich, and used without further purification. 1,4-Diazabicyclo[2,2,2]octane (DABCO) was sublimed in vacuo at 40 °C. Chloroform-d was dried over 4 Å molecular sieves and stored in a glove box.

Characterization. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance 300 or 400 spectrometers. Chemical shifts are reported relative to residual $CHCl_3$ in $CDCl_3$ (δ 7.24 for ^1H, δ 77.00 for ^{13}C). Elemental analysis was performed on FISONS EA1110 Analyzer. Mass spectra were obtained with JMS-HX110/110A (Jeol Ltd.) at Korea Basic Science Institute using fast atom bombardment (FAB) technique. Gel permeation chromatographic analysis were performed with Senshu Scientific High Temperature GPC (SSC-7100) equipped with Shodex HT 803 and HT 804 columns and RI detector using 1,2,4-trichlorobenzene as a solvent at 135 °C. A calibration curve was made with polystyrene standards.

((2,6-Diisopropylphenyl)imino)-acenaphthenone (1). Acenaphthenequinone (3.2 g, 18 mmol) and Na_2SO_4 (15 g) were stirred at 45 °C in 500 mL of methanol. 2,6-Diisopropylaniline (3.1 g, 16 mmol) and formic acid (0.60 mL) in 100 mL of methanol were added dropwise to the acenaphthenequinone solution for 3 h. After 10 h, the solvent was removed by rotary evaporator. The crude product was purified by column chromatography (20% ethyl acetate/hexane, silica gel) to afford 5.5 g of red-orange solid (yield=84%). ^1H NMR (300 MHz, $CDCl_3$): δ=8.13 (d, 2H, An *H*), 7.95 (d, 1H, An *H*), 7.77 (t, 1H, An *H*), 7.36 (t, 1H, An *H*), 7.24 (m, 3H , Ar *H*), 6.59 (d, 1H, An *H*), 2.81 (hep, 2H, C*H*$(CH_3)_2$), 1.12, 0.86 (2d, 12H, CH(C*H*$_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$, selected resonances): δ= 189.45 (*C*=O), 160.37 (*C*=N), 28.21 (*C*H$(CH_3)_2$), 23.25 (CH(*C*$H_3)_2$); EA (CHN) analysis calcd for $C_{24}H_{23}NO$ (MW: 341.45) : C, 84.42; H, 6.79; N, 4.69. Found; C, 83.91; H, 7.00; N, 4.13.

((2,6-Diisopropylphenyl)imino)-((2,6-dimethylphenyl) imino)-acenaphthene (2b). 2,6-Dimethylaniline (0.71 g, 5.9 mmol) and DABCO (2.0 g , 18 mmol) were dissolved in 45 mL of chlorobenzene. $TiCl_4$ (0.83 g, 4.4 mmol) in 5 mL of chlorobenzene was added to this solution dropwise at 90 °C for 20 min, followed by the addition of **1** (1.0 g, 2.9 mmol) in 10 mL of chlorobenzene. The solution was stirred at 150 °C for 24 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate was evaporated. The product was purified by column chromatography (10% ethyl acetate/hexane/2% triethylamine, silica gel) to afford 0.72 g of orange solid (yield=56%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, 1H, An *H*), 7.84 (d, 1H, An *H*), 7.35 (q, 2H, An *H*), 7.24 (m, 3H, Ar *H*), 7.14 (m, 2H, Ar *H*), 7.07 (m, 1H, Ar *H*), 6.72 (d, 1H, An *H*), 6.65 (d, 1H, An *H*), 3.01 (hep, 2H, C*H*$(CH_3)_2$), 2.14 (s, 6H, C*H*$_3$), 1.23, 0.98 (2d, 12H, CH(C*H*$_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$, selected resonances): δ= 160.89 (*C*=N), 160.68 (*C*=N), 28.49 (*C*H$(CH_3)_2$), 23.20, 23.00 (CH(*C*$H_3)_2$), 17.64 (*C*H_3); EA (CHN) analysis calcd for $C_{32}H_{32}N_2$ (MW: 444.61) : C, 86.44; H, 7.25; N, 6.30. Found; C, 86.11; H, 7.46; N, 6.36.

((2,6-Diisopropylphenyl)imino)-((2-isopropyl-6-methylphenyl)imino)-acenaphthene (2c). The above procedure was repeated with 2-isopropyl-6-methylaniline and **1** to afford 0.35 g of orange-yellow solid (yield=25%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.87 (d, 1H, An *H*), 7.84 (d, 1H, An *H*), 7.35 (q, 2H, An *H*), 7.24 (m, 4H, Ar *H*), 7.14 (d, 2H, Ar *H*), 6.69 (d,1H, An *H*), 6.64 (d, 1H, An *H*), 3.05 (m, 3H, C*H*$(CH_3)_2$), 2.12 (s, 3H, CH_3), 1.24, 0.97 (2t, 18H, CH(CH_3)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$, selected resonances): δ=160.91 (*C*=N), 160.85 (*C*=N), 28.66, 28.63, 28.43 (*C*H$(CH_3)_2$), 23.61, 23.50, 23.19, 23.01, 22.89, 22.60 (CH(*C*H_3)$_2$), 17.85 (*C*H_3); EA (CHN) analysis calcd for $C_{34}H_{36}N_2$ (MW: 472.66) : C, 86.40; H, 7.68; N, 5.93. Found; C, 85.85; H, 8.05; N, 5.91.

((2,6-Diisopropylphenyl)imino)-((2-*tert*-butylphenyl)imino)-acenaphthene (2d). The above procedure was repeated with 2-*tert*-butylaniline and **1** at 100 °C for 17 h to afford 1.0 g of orange solid (yield=75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.85 (d, 2H, An *H*), 7.53 (d, 1H, An *H*), 7.30 (q, 2H, Ar *H*), 7.24 (m, 5H, Ar *H*), 6.99 (d, 1H, An *H*), 6.80 (d, 1H, An *H*), 6.61 (d, 1H, An *H*), 3.05 (hep, 2H, C*H*$(CH_3)_2$), 1.34 (s, 9H, C(CH_3)$_3$), 1.23, 0.95 (2d, 12H, CH(CH_3)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$, selected resonances): δ=161.32 (*C*=N), 159.53 (*C*=N), 35.35 (*C*$(CH_3)_3$), 29.81 (C(*C*H_3)$_3$), 28.36 (*C*H$(CH_3)_2$), 23.39 (CH(*C*H_3)$_2$); EA (CHN) analysis calcd for $C_{34}H_{36}N_2$ (MW: 472.66) : C, 86.40; H, 7.68; N, 5.93. Found; C, 85.50; H, 7.98; N, 5.86.

((2,6-Diisopropylphenyl)imino)-((2,6-dimethylphenyl)imino)-acenaphthene nickel(II) dibromide (3b). (DME) $NiBr_2$ (0.13 g, 0.41 mmol), **2b** (0.20 g, 0.45 mmol), and CH_2Cl_2 (10 mL) were placed in a Schlenk flask under nitrogen atmosphere, and stirred at room temperature for 24 h. The solution was filtered to remove insoluble material and the solvent was evaporated *in vacuo*. The solid was washed three times with Et_2O and dried in vacuo to afford 0.24 g of red-brown powder (yield=89%). FAB-MS: *m/z*=660 (M^+), 581, 583 (M^+ - Br), 500, 502 (M^+ - 2 Br), 445 (M^+ - $NiBr_2$).

((2,6-Diisopropylphenyl)imino)-((2-isopropyl-6-methylphenyl)imino)-acenaphthene nickel(II) dibromide (3c). The above procedure was repeated with **2c** to afford 0.28 g of red-brown powder (yield=71%). FAB-MS: *m/z*=688 (M^+), 611, 609 (M^+-Br), 530, 528 (M^+-2 Br), 472 (M^+-$NiBr_2$).

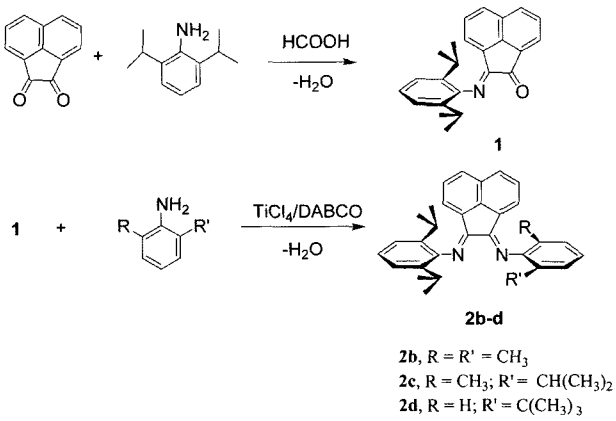
((2,6-Diisopropylphenyl)imino)-((2-*tert*-butylphenyl)imino)-acenaphthene nickel(II) dibromide (3d). The above procedure was repeated with **2d** to afford 0.32 g of red-brown powder (yield=80%). FAB-MS: *m/z*=688 (M^+), 611, 609 (M^+-Br), 530, 528 (M^+-2 Br), 472 (M^+-$NiBr_2$).

Polymerization of Propylene. The polymerizations were carried out in 50 mL, magnetically stirred Schlenk flasks, which were thermostated at -45 °C and charged with the (α-diimine)nickel(II) catalyst (30 μmol) and toluene (30 mL) under nitrogen. The nitrogen atmosphere was replaced by propylene. Liquid propylene (10 mL) and MAO (3.48 mL, [Al]/[Ni]=200) were added. The polymerization mixture was stirred for 5 h, and then quenched by addition of 10 vol% HCl/methanol solution. Polypropylene precipitated from the solution was filtered and washed with fresh methanol. The resulting polymer was dried under vacuum at 70 °C overnight.

Results and Discussion

One of the efficient methods to control the steric bulkiness of ortho substituents on aromatic rings of a (α-diimine)nickel (II) catalyst is making the catalyst based on an unsymmetrical α-diimine ligand. Some papers describing a synthesis of the unsymmetrical α-diimine ligands have been published.[14] But there was no report on the synthesis of unsymmetrical α-diimine ligands composed of acenaphthenequinone and properly substituted aniline units. For the synthesis of the unsymmetrical α-diimine ligand, acid catalyzed condensation reaction between one diketone and two different anilines is necessary. However the acid catalyzed reaction usually produces a mixture of two symmetric α-diimines and one unsymmetrical α-diimine, and the separation of the unsymmetrical α-diimine by flash chromatography is quite difficult because of small difference between the α-diimines. The separation was possible only when one of the two aniline units contains another functional group.[15] We synthesized unsymmetrical α-diimine ligands in two steps in which the first step is a monocondensation reaction and the second step is an irreversible α-diimine synthesis reaction. For the selective synthesis of unsymmetrical α-diimines, the second step should be irreversible. If the second step is reversible, it is inevitable to have a mixture of two symmetric α-diimines and one unsymmetric α-diimine which is difficult to separate.[13b]

New unsymmetrical α-diimine ligands **2b-d** which contain 2,6-diisopropylphenyl on one side and other alkyl substituted phenyl on the other side were synthesized in two steps as shown in Scheme II. Acid catalyzed reaction of acenaphthenequinone with 2,6-diisopropylaniline gave monocon-



Scheme II. Synthesis of α-diimine ligands **2b-d**.

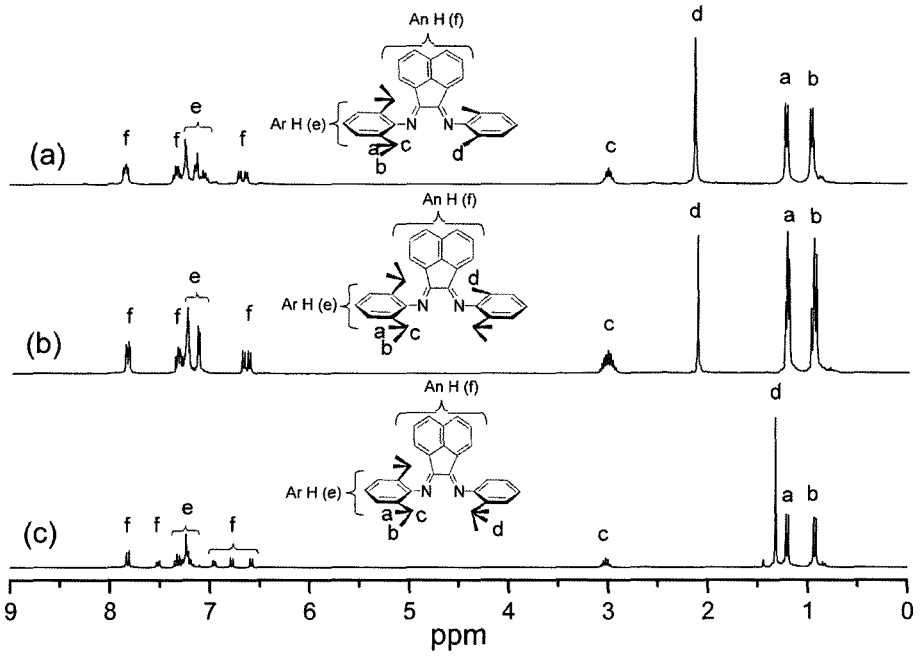


Figure 1. ^{1}H NMR spectra of α-diimine ligands (a) **2b**, (b) **2c**, and (c) **2d**.

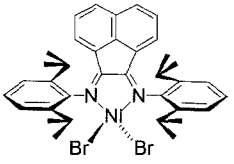
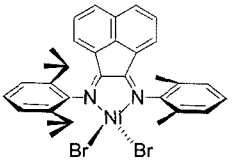
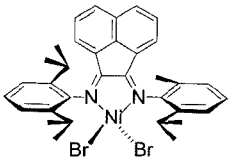
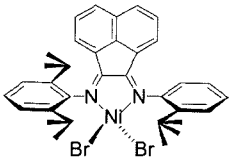
densation product **1**, which was further reacted with properly substituted aniline derivatives via $TiCl_4$ catalyzed irreversible reaction to obtain new unsymmetrical α-diimine ligands **2b-d**. The synthesis of the α-diimine ligands was confirmed by ^{1}H NMR spectra, ^{13}C NMR spectra, and elemental analysis. ^{1}H NMR spectra of the α-diimine ligands are shown in Figure 1.

(α-Diimine)nickel(II) catalysts **3a-d** were obtained by reacting the α-diimine ligands with (DME)$NiBr_2$ at ambient temperature. The structure and symmetry of the (α-diimine) nickel(II) catalysts are summarized in Table I.

Polymerization of propylene was carried out with the (α-diimine)nickel(II) catalysts activated by MAO in toluene at -45 °C. The polymerization results are summarized in Table II. Methyl region of the ^{13}C NMR spectra of the polypropylenes produced by the catalysts **3a**, **3b**, **3c**, and **3d** are shown in Figure 2.

Under the above polymerization conditions, catalyst **3a** afforded a syndiotactic polypropylene with a rr triad content of 73%, which is similar to the reported value.[9] Catalyst **3b** also afforded a syndiotactic polypropylene, but with a decreased syndiotacticity (rr triad content=66%). It was expected that catalyst **3b** would show higher syndiospecificity than catalyst **3a** because C_s symmetry of catalyst **3b** might induce a syndiospecific site control in addition to the syndiospecific chain end control of the (α-diimine)nickel(II) catalysts. Among early transition metal catalysts, C_s symmetric metallocene catalysts have been reported to afford highly syndiotactic polypropylenes.[16,17] However, C_s symmetric catalyst **3b** produced a polypropylene with a lower

Table I. Structure and Symmetry of (α-Diimine)nickel(II) Catalysts

Catalyst	Structure	Symmetry
3a		C_{2V}
3b		C_S
3c		C_1
3d		C_1

syndiotacticity than that produced by C_{2v} symmetric catalyst **3a**. It seems that the syndiospecific chain end control overwhelmed the syndiospecific site control in this catalyst sys-

Table II. Propylene Polymerization Results[a]

Run	Catalyst	Polymer Yield (g)	M_w $\times 10^{-3}$	M_w/M_n	% Triad Composition[b] mm	mr	rr	Adjacent Methyl[c]	$\frac{[CH_3]}{[CH_2]}$[d]	1,3 Inserted Monomer Units[e] (%)	T_g[f] (°C)
1	**3a**	1.2	75	2.34	1	26	73	7	0.93	2.4	-9
2	**3b**	0.2	69	1.22	5	29	66	9	0.95	1.7	-11
3	**3c**	0.6	74	1.14	16	37	47	14	0.99	0.5	-9
4	**3d**	0.3	45	2.00	35	43	22	22	0.84	5.8	-25

[a]Polymerization conditions : toluene = 30 mL, (α-diimine)nickel(II) = 30 μmol, MAO = 6 mmol, polymerization temperature = -45 °C, liquid propylene = 10 mL, time = 5 h. [b]Evaluated by ^{13}C NMR. [c]Evaluated by ^{13}C NMR.[8c] [d]Evaluated by ^{1}H NMR. [e]Calculated from $[CH_3]/[CH_2]$ (1,3-inserted monomer units = 100(1-b)/(1+2b), where b = $[CH_3]/[CH_2]$).[8c] [f]Evaluated by DSC.

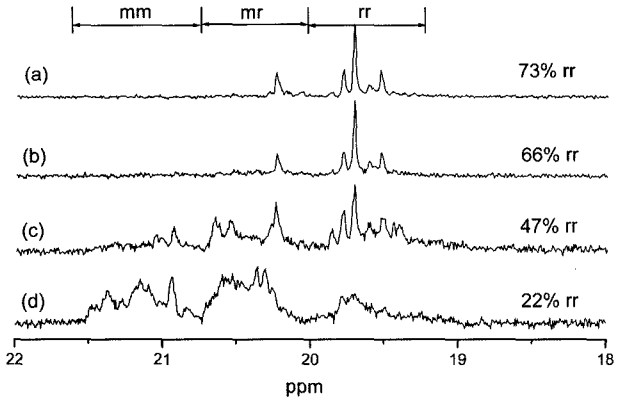


Figure 2. Methyl region of the ^{13}C NMR spectra of polypropylenes produced by catalyst (a) **3a**, (b) **3b**, (c) **3c**, and (d) **3d**.

tem. Theoretical calculations have shown that preference for the syndiospecific propagation is affected by the size of the ortho substituents on aromatic rings of the (α-diimine) nickel(II) catalyst.[9] The lower syndiospecificity of catalyst **3b** compared to the catalyst **3a** would be a result of the smaller size of the ortho substituents on aromatic rings of catalyst **3b**.

Catalyst **3c** afforded a less stereoregular polypropylene (rr triad content=47%) than catalyst **3b**. The steric crowdness of catalyst **3c** lies between catalyst **3a** and **3b**. But the rr triad content of the polypropylene produced by **3c** was much lower than that of the polypropylene produced by **3a** or **3b**. The peculiar behavior of **3c** may stem from its C_1 symmetry. Stereoselectivity of C_1 symmetric metallocene complexes is unpredictable and has been reported to produce polymer architectures ranging from highly isotactic to atactic, including isotactic-atactic stereoblock and hemiisotactic.[16] Analogous to C_1 symmetric metallocene catalysts, the C_1 symmetry of catalyst **3c** affords a weak isospecific site control. Therefore, rr triad content of the polypropylene produced by C_1 symmetric catalyst **3c** decreased due to overlap of the isospecific site control and the syndiospecific chain end control.

Another C_1 symmetric catalyst **3d** also produced a much less stereoregular polypropylene, which have a higher content of mm triad rather than rr triad (35 vs 22%). The polypropylene produced by catalyst **3d** contained a rather high fraction of 1,3 inserted monomer units (6%), due to the increased rate of "chain-walking" compared to the rate of monomer insertion that was diminished by the bulky *tert*-butyl substituent.

These results are in stark contrast to the results obtained with iron catalysts bearing tridentate pyridine-bis(imine) ligand, in which isospecific chain end control was shown to operate preferentially regardless of the steric and symmetry modifications.[18]

All of the polypropylenes produced by catalysts **3a-d** showed unimodal and narrow molecular weight distributions, confirming the single-site nature of these catalysts system. Interestingly the molecular weight distribution of the polypropylenes produced by catalyst **3b** and **3c** were quite narrow (1.22 and 1.14 respectively). Thermal property of the polypropylenes were analyzed by DSC. All the polypropylenes showed no melting transition, but glass transitions due to the low stereoregularity of the polypropylenes.

Conclusions

In conclusion, new unsymmetrical (α-diimine)nickel(II) catalysts having different ortho substituents on each aromatic ring were synthesized successfully. Variations of the ortho substituents affected the polypropylene microstructure. The (α-diimine)nickel(II) catalysts bearing mirror plane (C_{2v} or C_s symmetry) produced polypropylenes with high rr triad contents (>60%) through the syndiospecific chain end control. The rr triad contents increased as the steric bulkiness of the ortho substituents increases. The catalysts without a mirror plane (C_1 symmetry) produced polypropylenes with lower syndiotacticity because of collision of the isospecific site control and the syndiospecific chain end control.

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