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Living and block polymerization of α-olefins using a Ni(II)-α-diimine catalyst containing $OSiPh_2{}^tBu$ groups

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Abstract

A new siloxy-substituted α-diimine compound and its corresponding Ni(II) complex, {bis[*N*,*N*′-(4-*tert*-butyl-diphenylsiloxy-2,6-dimethylphenyl)imino]acenaphthene}dibromonickel (**6**), were successfully synthesized and the molecular structure of **6** characterized by X-ray crystallography. The precatalyst **6** activated by methylaluminoxane (MAO) or diethylaluminum chloride (DEAC) was tested in the polymerization of ethylene, showed to be highly active (e.g. 2.2×10^7 and 1.8×10^7 g polymer (mol Ni.h.bar)$^{-1}$, respectively) and led to a branched polyethylene (ca. 35–55 branches/1000 C). The catalyst system **6**/methylaluminoxane (MAO) catalyzes, at −11 °C, living polymerization of propylene, to a polypropylene showing a syndiotactic-rich microstructure ($P_r=0.74$). 1-Hexene was also successfully polymerized via a living process, both at −11 and +16 °C. The ^{13}C NMR spectra of the poly(1-hexene)s obtained at room temperature show a microstructure almost exclusively composed by *n*-butyl and methyl branches, the latter being present in a much higher number. Diblock polypropylene-*block*-poly(1-hexene) and triblock poly(1-hexene)-*block*-poly(propylene-*ran*-1-hexene)-*block*-poly(1-hexene) copolymers have also been synthesized and characterized by GPC/SEC, DSC and NMR.

Keywords: Block copolymerization; Living polymerization; Ni(II) α-diimine complex

1. Introduction

Living polymerization has attracted a great deal of attention due to the possibility to easily synthesize polymers with narrow molecular weight distributions, block copolymers and chain end-functionalized materials [1]. In transition-metal catalyzed polymerizations, a living system requires, among other conditions, that chain growth occurs without significant chain transfer (e.g. β-hydride elimination, β-alkyl elimination, and chain transfer to a cocatalyst) or deactivation [1b].

Several homogeneous early transition-metal catalysts have been found for living polymerization of α-olefins [2–9], most of them employing boron compounds as co-catalysts, at low temperature in order to suppress chain transfer reactions. On the other hand, living polymerization using late transition-metal catalysts has only been reported in limited cases by Brookhart and co-workers for Ni [10a] and Pd [10b,10c] catalysts.

In this paper, we report the synthesis and structure of a new chelating Ni(II) α-diimine complex, {bis[*N*,*N*′-(4-*tert*-butyl-diphenylsiloxy-2,6-dimethylphenyl)imino]acenaphthene}di-bromonickel (**6**) and its application in living polymerization. In an attempt to enrich the electron density at the metal

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center, thus inducing a different reactivity, polymer microstructures or degrees of co-monomer incorporation, we have used in this new complex a diimine framework (**5**) where the hydrogen of the traditional 2,6-dialkylaryl fragment in the *para*-position [11] has been replaced by the electron-donating $OSiPh_2{}^tBu$ group. Living homopolymerization of propylene, 1-hexene and their block copolymerizations were achieved by complex **6** in combination with methylaluminoxane (MAO) as co-catalyst.

2. Experimental

2.1. General

All operations were carried out under N_2 atmosphere using standard Schlenk techniques unless otherwise noted. Methylene chloride and *o*-dichlorobenzene were pre-dried with 4 Å molecular sieves and refluxed over CaH_2 under an atmosphere of N_2, and collected by distillation. Toluene, diethyl ether and hexane were distilled under N_2 atmosphere from sodium. $NiBr_2$, DEAC, MAO, 4-nitro-aniline, 3,5-dimethylphenol, *tert*-butyldiphenylchlorosilane and acenaphthoquinone were purchased from Aldrich and used without further purification. $NiBr_2(DME)$ was synthesized according to the literature [12].

The ^1H and ^{13}C NMR spectra of all the materials were recorded on a Varian Unity 300 Spectrometer. Elemental analyses were performed on a Fisons Instrument 1108 analyzer at the Laboratório de Análises do IST.

2.2. Preparation of 3,5-dimethyl-4-(4-nitro-phenylazo)-phenol (*1*)

4-Nitroaniline (6.9 g; 50 mmol) was dissolved in hot water (75 ml) containing hydrochloric acid (27.5 ml; 330 mmol). The solution was poured over ice (250 g) and when the temperature has fallen below 0 °C, sodium nitrite (3.65 g; 52 mmol) in water (28 ml) was added with stirring. After 15 min, the remaining ice and a small amount of yellow solid were filtered off, and the filtrate was added slowly with stirring to a cooled (ice-salt bath) solution of 3,5-dimethylphenol (6.1 g; 50 mmol) in water (150 ml) containing sodium hydroxide (2.2 g; 55 mmol). The brick red sticky mass of the coupling product was allowed to stand overnight at room temperature. The brick red solid was filtered off, washed with water thoroughly and dried at 75 °C under vacuum for 6 h. Yield: 12.85 g (95%). The product was dissolved in boiling ethanol (100 ml) and the hot solution was filtered. When cooled in a refrigerator, the filtrate deposited a brick red fibrous mass of the azo compound. ^1H NMR ($CDCl_3$): δ 2.52 (s, 6H, CH_3), 6.62 (s, 2H, phenyl ring near OH), 7.90 (d, 2H, phenyl ring near N=N), 8.33 (d, 2H, phenyl ring near NO_2). Melting point: 166–168 °C, with decomposition.

2.3. Preparation of acetic acid 3,5-dimethyl-4-(4-nitro-phenylazo)-phenyl ester (*2*)

The azo compound **1** (9.6 g; 35.4 mmol) was refluxed for 1 h with pyridine (152.5 ml) and acetic anhydride (30.5 ml; 272 mmol). The reaction mixture was poured into water (1500 ml) and, after standing for 30 min, the solid product was removed, washed thoroughly with water, and dried at 75 °C under vacuum for 6 h. Yield: 10.64 g, 96%. ^1H NMR ($CDCl_3$): δ 2.29 (s, 3H, CH_3 of acetate group), 2.45 (s, 6H, 2 CH_3 in phenyl ring), 6.89 (s, 2H, phenyl ring near CH_3COO), 7.94 (d, 2H, phenyl ring near N=N), 8.36 (d, 2H, phenyl ring near NO_2). Melting point: 130–132 °C.

2.4. Preparation of 4-amino-3,5-dimethylphenol (*3*)

Compound **2** (10.47 g; 33.4 mmol) was dissolved in boiling ethanol (108 ml) and a suspension of sodium dithionite (78 g; 448 mmol) in water (167 ml) was added slowly. When the color faded to light amber, the hot solution was filtered and the filtrate concentrated under reduced pressure until a heavy granular solid separated. The aminophenol **3** (3.13 g, 68% yield) was removed from the cooled residue. ^1H NMR (pyridine-d_5): δ 2.27 (s, 6H, CH_3), 7.00 (s, 2H, phenyl ring). $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 18.3 (CH_3), 116.3 (phenyl ring no substituent), 123.9 (phenyl ring near CH_3), 137.1 (phenyl ring near amino group), 150.3 (phenyl ring near OH). Melting point: 177–180 °C.

2.5. Preparation of 4-(tert-butyldiphenylsilanyloxy)-2,6-dimethylphenylamine (*4*)

To a mixture of 4-amino-3,5-dimethylphenol (**3**) (2.74 g; 20 mmol) and imidazole (2.72 g; 40 mmol) in DMF (10 ml), *tert*-butylchlorodiphenylsilane (8.24 g; 30 mmol) was added at room temperature. The reaction mixture was stirred for 12 h, diluted with water, and extracted with diethyl ether. The organic extracts were washed with saturated aqueous solution of NaCl and dried over $MgSO_4$. Then the solvent was removed and the residue was distilled under vacuum to give compound **4** (6.03 g, 80% yield). ^1H NMR ($CDCl_3$): δ 1.07 (s, 9H, $C(CH_3)_3$), 1.95 (s, 6H, CH_3 in aniline ring), 6.42 (s, 2H, aniline ring), 7.36 (m, 6H, phenyl ring near Si), 7.71(d, 2H, phenyl ring near Si). ^{13}C NMR ($CDCl_3$): δ 19.0 (CH_3 in aniline), 19.9), ($C(CH_3)$), 26.8 ($C(CH_3)_3$), 118.8 (CH of substituted phenyl ring), 127.8 (phenyl ring near Si), 130.0 (aniline ring near CH_3),130.6 (phenyl ring near Si), 134.0 (phenyl ring near Si), 135.8 (phenyl ring near Si), 150.5 (aniline ring near NH_2), 154.0 (aniline ring near O). Boiling point: 160 °C (0.1 mmHg).

2.6. Preparation of ligand **5**

Acenaphthoquinone (1.78 g; 9.76 mmol), 150 ml of methanol and 7.33 g (19.52 mmol) of the amine **4** were placed in a beaker and allowed to stir for 76 h in the presence of formic acid (1.5 ml; 19.7 mmol). Dichloromethane and water were added and the layers separated. The resulting organic layer was dried with $MgSO_4$ overnight, filtered and the solvent was removed to give the crude ligand as a brown solid. The impure ligand was recrystallized from diethyl ether to give orange microcrystals. Yield: 8.26 g, 94%. ^{1}H NMR ($CDCl_3$): δ 1.18 (s, 18H, $C(CH_3)_3$), 1.97(s, 12H, CH_3 in aniline ring), 6.56 (s, 4H, aniline ring), 7.42 (m, 12H, phenyl ring near Si), 7.78 (d, 8H, phenyl ring near Si), 7.64 (m, 2H, naphthyl ring), 7.82 (d, 2H, naphthyl ring), 7.91 (d, 2H, naphthyl ring). ^{13}C NMR ($CDCl_3$): δ 18.0 (CH_3, in aniline ring), 19.8 ($C(CH_3)_3$), 26.9 ($C(CH_3)_3$), 119.8 (CH of substituted phenyl ring), 122.3 (naphthyl ring), 126.0 (naphthyl ring), 127.9 (phenyl ring near Si), 128.3 (naphthyl ring), 128.9 (naphthyl ring), 130.0 (phenyl ring near Si), 131.2 (naphthyl ring), 133.7 (naphthyl ring), 136.0 (phenyl ring near Si), 143.6 (aniline ring near N), 152.0 (aniline ring near O), 161.8 (acenaphthoquinone ring near N). Anal. Calc. for $C_{60}H_{60}N_2O_2Si_2$: C, 80.31; H, 6.74; N, 3.12. Found: C, 80.13; H, 7.06; N, 3.22.

*2.7. Preparation of complex **6***

$NiBr_2$(DME) (0.664 g, 2.16 mmol), the ligand **5** (2 g, 2.2 mmol) and dichloromethane (50 ml) were mixed in a Schlenk flask and stirred at room temperature for 16 h. The resulting suspension was filtered. The solvent was removed under vacuum and the residue was washed with diethyl ether (3×16 ml), and then dried under vacuum at room temperature to give catalyst **6** (2.2 g, 96% yield). Anal. Calc. for $C_{60}H_{60}Br_2N_2Ni_2O_2Si_2\cdot 0.35CH_2Cl_2$: C, 63.25; H, 5.30; N, 2.45. Found: C, 63.30; H, 5.28; N, 2.57.

*2.8. Preparation of complex **6** (one-pot reaction)*

Acenaphthoquinone (1.00 g; 5.55 mmol) was placed in a Schlenk tube followed by 100 ml glacial acetic acid. The resulting suspension was allowed to warm up to 50 °C and then a slight excess of the amine **4** (6.03 g; 16 mmol) was introduced. The mixture was warmed to 120 °C and allowed to reflux for 4 h. $NiBr_2$ (1.24 g; 6.84 mmol) was added as a solid to the resulting mixture and the reaction was allowed to reflux overnight. The solvent was removed under vacuum and the resulting sticky solid was washed with diethyl ether (3×20 ml). The residue was extracted with dichloromethane and the resulting deep red solution was filtered via a cannula to another Schlenk tube. This process was repeated twice and the solvent was removed under vacuum to give catalyst **6**. Yield: 7.27 g, 95.6%. This procedure led to analytically impure **6**, difficult to purify by recrystallization.

2.9. X-ray crystallography

Single crystals of complex **6** suitable for an X-ray analysis were obtained at −30 °C by dissolving the nickel complex in CH_2Cl_2, following by slow layering of the subsequent solution with *n*-hexane.

X-ray diffraction data were collected at 100(2) K on a Bruker SMART APEX 3-circle diffractometer with CCD area detector at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz. Hemispheres of the reciprocal space were measured by omega scan frames with $\delta(\omega)$ 0.30°. Corrections for absorption and crystal decay were applied. The structure was solved by direct methods, completed by subsequent difference Fourier synthesis and refined on F^2 by full matrix least-squares procedures using the program SHELXTL [13]. Crystal data, data collection, and refinement parameters [14] are listed in Table 1.

2.10. Polymerization of ethylene

Polymerization of ethylene was carried out in a flame dried 250 ml crown capped pressure bottle sealed with neoprene septa. After drying the polymerization bottle under N_2 atmosphere, 50 ml of dry toluene was added to the polymerization bottle. The resulting solvent was then saturated with 1 bar ethylene pressure. The co-catalyst (MAO or DEAC) was then added in the proper Al/Ni ratio to the polymerization bottle via a syringe. At this time, the

Table 1
Summary of crystallographic data for complex **6**

Empirical formula	$C_{60}H_{60}Br_2N_2NiO_2Si_2\cdot 0.35CH_2Cl_2$	α (deg)	90.00
Formula weight	1166.40	β (deg)	109.960(6)
Crystal color	Orange	γ (deg)	90.00
a (Å)	21.6063(16)	F_{000}	2401
b (Å)	13.7670(10)	D_{calc} (g/cm^3)	1.399
c (Å)	19.8007(15)	Z	4
Crystal size (mm)	0.30×0.24×0.02	λ (Mo-Kα) (Å)	0.71073
Crystal system	Monoclinic	μ (Mo-Kα)/mm^{-1}	1.920
V (Å^3)	5536.0(7)	no. of total reflns	7929
Space group	$P2_1/c$(No. 14)	Reflns. gt. [$I > 2(I)$]	6508
R[$I > 2(I)$]	0.0829	Refined parameters	646
R all reflns.	0.1049	Goodness of fit	1.089

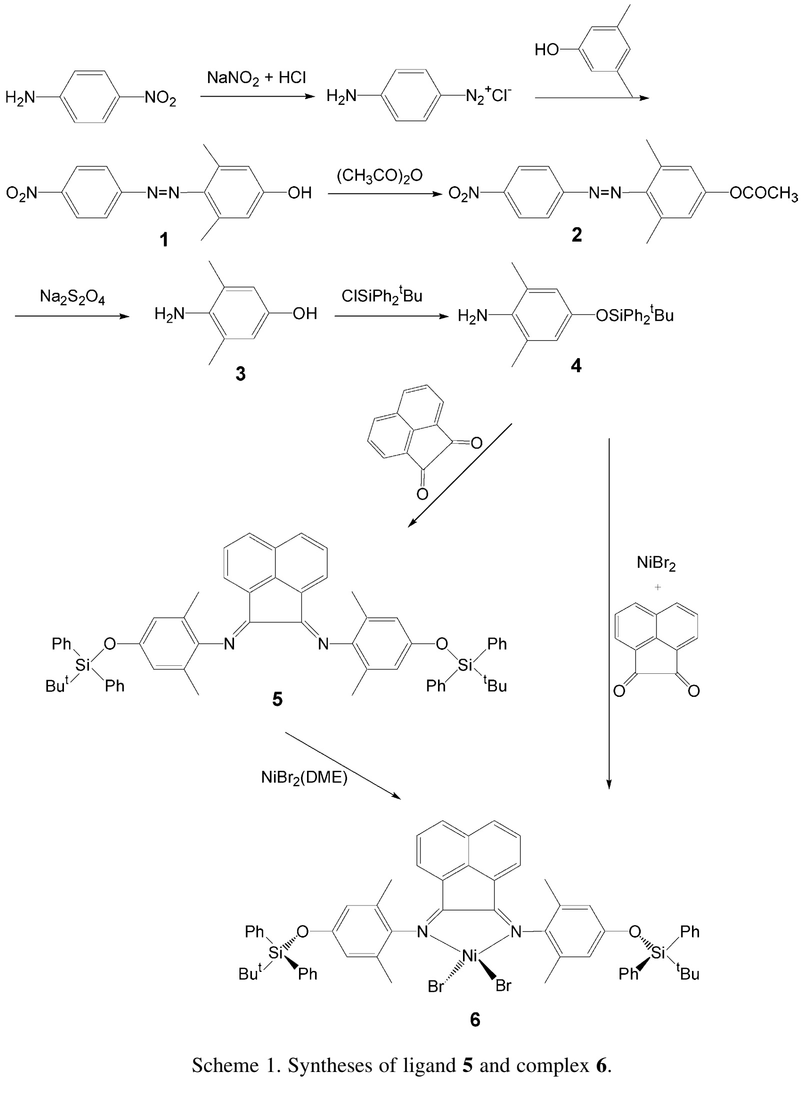
solutions were thermostated to the desired temperature and allowed to equilibrate for 15 min. Subsequently, *o*-dichlorobenzene solution of Ni catalyst was added to the polymerization reactor. The polymerization, conducted under a dynamic pressure of ethylene, was terminated by quenching the reaction mixtures with 100 ml of a 2% HCl–MeOH solution. The precipitated polymer was filtered, washed with methanol and dried under vacuum at 60 °C for 3 days.

2.11. Living polymerization of propylene

Polymerization of propylene was conducted in a 250 ml glass reactor by batchwise operation thermostated at −11 °C. Propylene (0.33 bar) was added to the cooled toluene (50 ml) and the solution equilibrated for 15 min. Then the cocatalyst MAO was added and, after 5 min, the *o*-dichlorobenzene solution of Ni catalyst was added to the polymerization reactor. The polymerization, conducted under a static pressure of propylene, was terminated by quenching the reaction mixtures with 100 ml of a 2% HCl–MeOH solution. The precipitated polymer was filtered, washed with methanol and dried under vacuum at 60 °C for 3 days.

2.12. Living polymerization of 1-hexene

Polymerization of 1-hexene was carried out in a 250 ml glass reactor by batchwise operation thermostated at −11 °C or at room temperature. 1-Hexene (2.5 ml) was added to the cooled toluene (50 ml) via a syringe. Then the co-catalyst MAO was added and, after 5 min, the *o*-dichlorobenzene solution of Ni catalyst was added to the polymerization reactor. The polymerization was terminated by quenching the reaction mixtures with 100 ml of a 2% HCl–MeOH solution. The precipitated polymer was filtered, washed with methanol and dried in vacuum at 60 °C for 3 days.



Scheme 1. Syntheses of ligand **5** and complex **6**.

2.13. Synthesis of a diblock copolymer of propylene and 1-hexene

In a 250 ml reactor thermostated at −15 °C, propylene (0.33 bar) was added to the cooled toluene (50 ml), and the solution equilibrated for 15 min. Then the co-catalyst MAO was added and, after 5 min, the *o*-dichlorobenzene solution of Ni catalyst was added to the reactor. After 20 minutes of polymerization, conducted under a static pressure of propylene, the unreacted propylene was removed in vacuum (ca. 2 min), and 1-hexene (2.5 ml) was added to the reactor, and the reaction solution allowed to react for 40 min. The polymerization was terminated by quenching the reaction mixture with 100 ml of a 2% HCl–MeOH solution. The precipitated polymer was filtered, washed with methanol and dried in vacuum at 60 °C for 3 days.

2.14. Synthesis of a triblock copolymer of propylene and 1-hexene

In a 250 ml reactor thermostated at −15 °C, 1-hexene (5 ml) was added to the cooled toluene (50 ml). Then the co-catalyst MAO was added and, after 5 min, the *o*-dichlorobenzene solution of Ni catalyst was added to the polymerization reactor. After 40 min of reaction, the propylene (1 bar, dynamic pressure) was added, and the mixture reacted for 20 min. Subsequently, the propylene was removed under vacuum and the reaction allowed to continue for an additional 40 min. The polymerization was terminated by quenching the reaction mixture with 100 ml of a 2% HCl–MeOH solution. The precipitated polymer was filtered, washed with methanol and dried in vacuum at 60 °C for 3 days.

2.15. Polymer characterization

The ^1H and ^{13}C NMR spectra of the polymers were obtained in 1,2,4-trichlorobenzene and C_6D_6 (3:1), at 110 °C, and referenced internally to the highest field solvent resonance (127.9 ppm). Molecular weights were measured by GPC/SEC on a Waters 150 CV chromatograph, using a series of three columns Ultrastyragel HR1, HR3, HR4 (10 μm; 7.8×300 mm), at 35 °C, in tetrahydrofuran and at a flow rate of 1 $cm^3\ min^{-1}$. Thermal analyses of selected samples were carried out on a modulated differential scanning calorimeter, TA Instruments 2920 MTDSC2920, connected to a liquid nitrogen cooling system and calibrated with different standards. Runs were performed at standard mode. The sample weights were around 11 mg in all the specimens. A temperature range from −100 to 150 °C has been studied and the used heating rate was 10 °C min^{-1}. The melting temperatures of polyethylene samples were determined from the second heating cycle.

3. Results and discussion

*3.1. Synthesis and characterization of the catalyst precursor **6***

The synthesis of ligand **5** used in complex **6** was obtained via a five step reaction sequence starting from 3,5-dimethylphenol and 4-nitroaniline (Scheme 1).

The amination of 3,5-dimethylphenol to 4-amino-3,5-dimethylphenol (**3**) followed by the silylation of the hydroxyl group in **3** led to the desired amine **4**. In this reaction sequence, 3,5-dimethylphenol was reacted with 4-amino-benzenediazonium chloride and the resulting coupling product 3,5-dimethyl-4-(4-nitro-phenylazo)-phenol (**1**) readily formed in 96% yield when the parent substance was heated for an hour in pyridine, in the presence of an excess of acetic anhydride. 4-Amino-dimethylphenol (**3**) was obtained in 68% yield by reductive cleavage of the azo group using sodium dithionite. Compound **3** was reacted with *tert*-butylchlorodiphenylsilane producing 4-(*tert*-butyldiphenylsilanyloxy)-2,6-dimethylphenylamine (**4**) in 80% yield.

The α-diimine ligand **5** was finally obtained by acid catalyzed condensation of the amine **4** and acenaphthoquinone, and recrystallized from diethyl ether to afford an orange microcrystalline solid in 94% yield. Compound **5** was characterized by ^1H-NMR and ^{13}C-NMR and was found elementally pure. The overall yield of this multi-step synthesis of **5** was 47%.

The reaction of equimolar amounts of $NiBr_2(DME)$ and the α-diimine ligand **5** in CH_2Cl_2 led to the displacement of

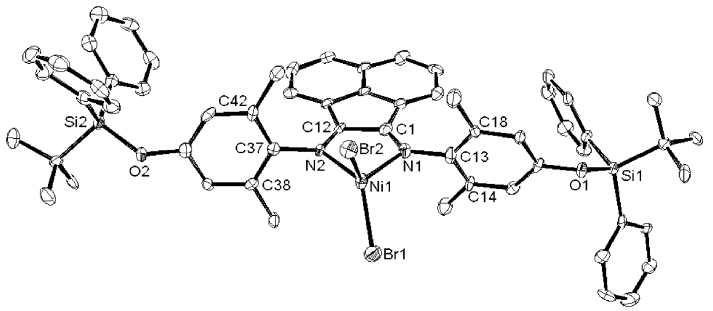


Fig. 1. Molecular structure of complex **6**, using 50% probability level ellipsoids (the hydrogens have been omitted for clarity).

1,2-dimethoxyethane and afforded the catalyst precursor **6** as a moderately air-stable deep red microcrystalline solid in almost quantitative yields (ca. 96%). Following a procedure described in the literature [15], the catalyst precursor **6** was also synthesized via the one-pot reaction of acenaphthoquinone, compound **4** and $NiBr_2$, in refluxing acetic acid, but the purity of the complex formed is lower and its purification showed to be more difficult.

Due to the geometry around the nickel atom, this α-diimine Ni(II) complex is paramagnetic and its ^{1}H-NMR is not assignable. Elemental analysis of complex **6** fits the molecular structure obtained by X-ray structural studies (see below).

Suitable crystals of **6** for X-ray diffraction were obtained by double layering a solution of the complex in CH_2Cl_2 with *n*-hexane. The molecular structure of complex **6** was determined and the corresponding diagram is shown in Fig. 1, while selected bond distances and angles are summarized in Table 2. The X-ray structure of complex **6** features a pseudo-tetrahedral geometry about the nickel atom. Complex **6** exhibits a pseudo C_{2v} symmetry due to the crystallographically inequivalent -$OSiPh_2{}^t$Bu groups. Its structure is quite similar to those reported in the literature of [bis(*N*,*N*′-2,4,6-trimethylphenylimino)acenaphthene](dibromonickel [15] and [bis(*N*,*N*′-2-pentafluorophenyl-6-methylphenylimino)acenaphthene] dibromonickel [16]. In fact, the Ni–N bond distances in complex **6** (2.017–2.018 Å) are similar to those determined for those compounds (2.021 and 2.035 Å, respectively), as well as the Ni–Br bond distances (2.3242–2.3306 Å for complex **6** vs. 2.318 and 2.323 Å, respectively) and the Br–Ni–Br angles (125.67° for complex **6** vs. 117.94 and 117.43°, respectively). The aryl rings of the α-diimine lie nearly perpendicular to the plane formed by the nickel and coordinated nitrogen atoms.

3.2. Polymerization studies

Complex **6**, activated by methylaluminoxane (MAO) or diethylaluminum chloride (DEAC), was first tested in the polymerization of ethylene at room temperature and −11 °C in order to assess the influence of the siloxyl group in its reactivity. The polymerization activities obtained in this work (2.2×10^7 g polymer (mol Ni.h.bar)$^{-1}$ when activated by MAO, and 1.8×10^7 g polymer (mol Ni h bar)$^{-1}$ when activated by DEAC—cf. Supplementary Data) showed to be higher than those observed with similar catalyst precursors such as [bis(*N*,*N*′-2,6-dimethylphenylimino)acenaphthene]dibromonickel, which activity reported by Brookhart et al. is ca. 10^5 g polymer (mol Ni.bar.h)$^{-1}$, although the experimental conditions are not exactly the same [11]. The activities obtained with [bis(*N*,*N*′-dimesitylimino)acenaphthene]dibromonickel (mesityl = 2,4,6-trimethylphenyl), now under similar experimental conditions (8.3×10^6 g polymer (mol Ni.bar.h)$^{-1}$ in the case of MAO, and 4.9×10^6 g polymer (mol Ni.bar.h)$^{-1}$ in the case of DEAC) [17] are also lower than those observed with the new complex **6**. The activities of **6** towards ethylene are higher even when compared to catalysts containing diimine ligands with bulkier 2,6-substituents. In fact, for [bis(*N*,*N*′-2,6-diisopropylphenylimino)acenaphthene]dibromonickel the activities reported either by Brookhart (5×10^6 g polymer (mol Ni.bar.h)$^{-1}$) [16] or those observed in our laboratory (4×10^6 g polymer (mol Ni.bar.h)$^{-1}$) [18] are about an order of magnitude lower. The activity increase observed for **6** may, therefore, be attributed to the electron donor effect of the $OSiPh_2{}^t$Bu group. Similar trends have been observed for group 4 metallocenes [19] where, in a series of cyclopentadienyl or indenyl substituted complexes, the activities observed generally increase with the electron donor capacity of the substituent ($SiR_3 > Me > H$) [20,21].

Table 2
Selected bond distances (Å) and angles (°) for complex **6**

Bond distances (Å)			
Ni1–Br1	2.3242(14)	Ni1–Br2	2.3306(14)
Ni1–N1	2.018(6)	Ni1–N2	2.017(6)
N1–C1	1.278(10)	N1–C13	1.451(10)
N2–C12	1.274(9)	N2–C37	1.450(9)
Bond angles (°)			
N2–Ni1–N1	83.0(2)	N2–Ni1–Br1	117.35(19)
N1–Ni1–Br1	104.45(19)	N2–Ni1–Br2	103.12(18)
N1–Ni1–Br2	115.53(19)	Br1–Ni1–Br2	125.67(5)
Torsion angles (°)			
Ni1–N1–C13–C14	95.78(8)	Ni1–N2–C37–C42	99.0(7)
Ni1–N1–C13–C18	−83.5(8)	Ni1–N1–C37–C38	−76.7(9)

The polyethylenes obtained in the present work showed branched microstructures (ca. 35–55 branches/1000 carbons) that seem to be independent of the co-catalyst used (cf. Supplementary Data).

Noteworthy, either in the polymerization of ethylene or in the subsequently described polymerizations of propylene and 1-hexene, are the blank experiments carried out with MAO alone, under similar conditions, showing its inability to polymerize these monomers on its own.

3.2.1. Living polymerization of propylene

Propylene polymerizations in the presence of complex **6**, using methylaluminoxane (MAO) as co-catalyst, were carried out at −11 °C. The results are collected in Table 3 and suggest that chain transfer reactions are very reduced in the polymerization system. Furthermore, the polypropylene

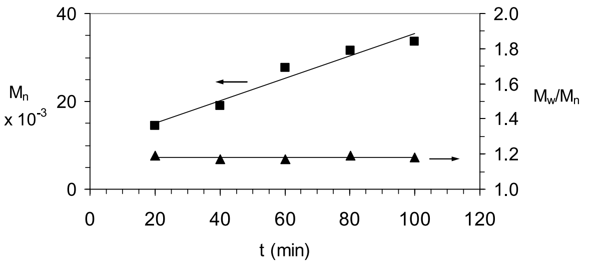


Fig. 2. Plot of M_n (squares) and M_w/M_n (triangles) as a function of reaction time for propylene polymerization catalyzed by **6**/MAO at −11 °C.

Table 3
Living polymerization of propylene with complex **6**/MAO catalyst system at −11 °C

Entry	Time (min)	Yield (g)	Activity[a] ($\times 10^{-4}$)	TOF[b] ($h^{-1}.bar^{-1}$)	M_n[c] ($\times 10^{-4}$)	M_w/M_n[c]
1	20	0.083	4.2	998	1.45	1.19
2	40	0.169	4.3	1016	1.90	1.17
3	60	0.194	3.3	778	2.76	1.17
4	80	0.268	3.4	806	3.16	1.19
5	100	0.375	3.8	902	3.35	1.18

Polymerization conditions: 18 μmol of Ni complex in 50 ml of toluene; Al/Ni = 180; propylene relative pressure = 0.33 bar; $[\text{Propylene}]_o = 0.68$ M.

[a] Activity in g PP $(\text{mol Ni.bar.h})^{-1}$.

[b] Turnover frequency = mol Propylene/(mol Ni.pressure.time).

[c] Determined by GPC.

obtained shows very narrow monomodal molecular weight distributions ($M_w/M_n = 1.17$–1.19). The plots in Fig. 2 show a linear increase in the polypropylene molecular weight with time accompanied by a very narrow polydispersity. Therefore, living polymerization of propylene can be achieved with **6**/MAO at −11 °C. This system seems to be less active than those originally reported by Brookhart and co-workers (e.g. $[\text{NiBr}_2(\text{IPPBIAN})]$/MAO) and leads to lower molecular weight polypropylenes [10a]. These variations may be attributed either to different 2,6-aryl substituents used (bulkier isopropyl groups in Brookhart's system and methyl groups in complex **6**) or to different reaction conditions, namely a lower propylene pressure in the present case.

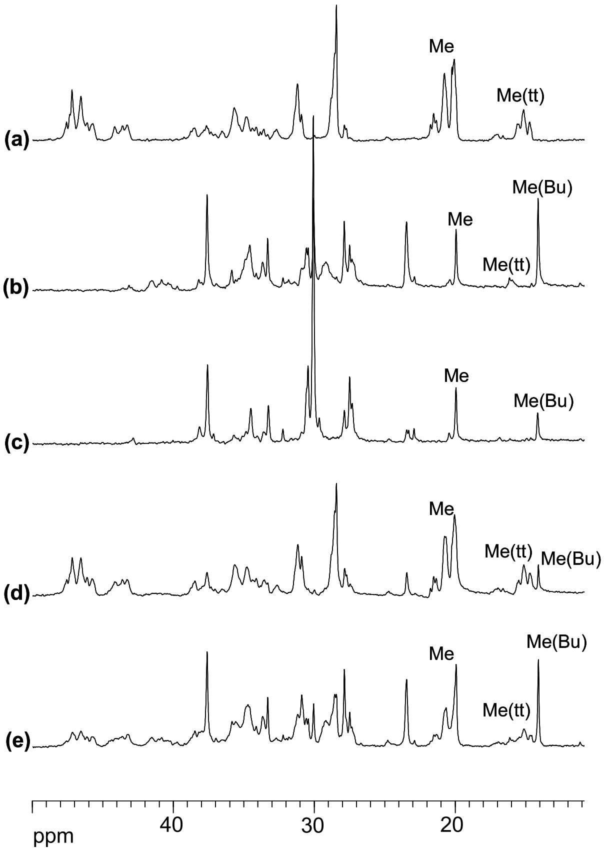


Fig. 3. ^{13}C NMR spectra (300 MHz, TCB/C_6D_6, 110 °C) of the (a) polypropylene obtained at −11 °C (entry 4), (b) poly(1-hexene) obtained at −11 °C (entry 7), (c) poly(1-hexene) obtained at +16 °C (entry 23), (d) polypropylene-*block*-poly(1-hexene), obtained at −15 °C (entry 24), and (e) poly(1-hexene)-*block*-poly(propylene-*ran*-1-hexene)-*block*-poly(1-hexene) (entry 25). Me = normal methyl branches, Me(tt) = adjacent tail-to-tail methyl branches, Me(Bu) = methyl groups of butyl branches.

Importantly, the lack of olefinic resonances in both ^{1}H NMR and ^{13}C NMR spectra of the polypropylene also reinforces the living character of this polymerization process that is devoid of termination via β-hydride or β-methyl elimination. Fig. 3(a) shows the ^{13}C NMR spectrum of the living polypropylene obtained in the reaction of entry 4. In this spectrum, the resonances ranging from 45 to 48 ppm are assigned to the backbone CH_2 groups, at 28.4 ppm to the backbone CH groups ($T_{\beta\beta}$), and in the range 20–22 ppm to the side chain CH_3 groups [22,23]. The other small resonances can also be assigned as follows: at 14.5–17.5 ppm the adjacent methyl groups in a tail-to-tail regioirregular sequence of propylene adjacent units; at 33–36 ppm two adjacent CH_2 s in a head-to-head sequence of propylene units which are flanked by methyl branches; from 43 to 45 ppm the CH_2 of a $–CH(CH_3)\mathit{C}H_2CH(CH_3)CH(CH_3)–$ sequence; at 31.2 ppm the $T_{\beta\delta+}$ CH groups, and at 36–39 ppm the $S_{\alpha\gamma+}$ CH_2 groups ($–CH(CH_3)\mathit{C}H_2CH_2CH_2CH(CH_3)–$), probably arising from 'chain straightening' [23]. This spectrum also indicates that 1,3-insertion is not very significant, since the total number of methyl branches (316 branches/1000 C—see below in Table 7) is quite close to the theoretical number of branches expected for a perfect polypropylene (333 branches/1000 C) [8,23]. From the relative intensities of the CH_3 region, tactic triads can be estimated as $(mm) = 0.12$, $(mr) = 0.34$, $(rr) = 0.54$ ($P_r = 0.74$). Therefore, the living polymer obtained at −11 °C

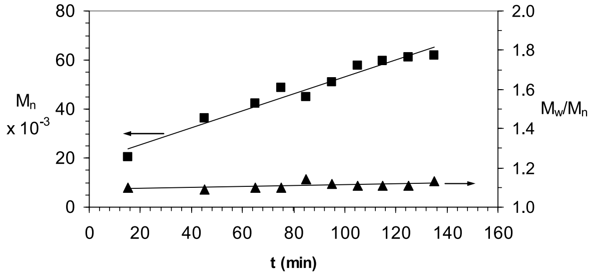


Fig. 4. Plot of M_n (squares) and M_w/M_n (triangles) as a function of reaction time for 1-hexene polymerization catalyzed by **6**/MAO at −11 °C.

Table 4
Living polymerization of 1-hexene with complex **6**/MAO catalytic system at −11 °C

Entry	Time (min)	Yield (g)	Activity[a] ($\times 10^{-4}$)	TOF[b] (h^{-1})	M_n[c] ($\times 10^{-4}$)	M_w/M_n[c]
6	15	0.102	5.7	270	2.20	1.10
7	45	0.330	6.9	291	3.61	1.09
8	65	0.359	4.5	219	4.22	1.10
9	85	0.448	4.4	209	4.49	1.14
10	95	0.570	5.0	238	5.09	1.12
11	75	0.568	6.3	301	4.86	1.10
12	105	0.712	5.6	269	5.76	1.11
13	115	0.728	5.2	251	5.96	1.11
14	125	0.862	5.7	274	6.10	1.11
15	135	0.758	4.7	223	6.20	1.13

Polymerization conditions: 18 μmol of Ni complex in 50 ml of toluene; Al/Ni = 180; [1-Hexene] = 0.40 M.

[a] Activity in g polymer (mol Ni.[1-Hexene].h)$^{-1}$.

[b] Turnover frequency = mol Hexene/(mol Ni time).

[c] Determined by GPC.

is a syndiotactic rich (74%) polypropylene which polymerization proceeds via chain end control [8,23].

3.2.2. Living polymerization of 1-hexene

Polymerization of 1-hexene was also carried out with **6**/MAO catalyst at −11 °C, and the results are summarized in Table 4. The poly(1-hexene)s obtained have monomodal and extremely narrow ($M_w/M_n = 1.09$–1.14) molecular weight distributions, consistent with a single polymerization site and little or no chain termination or transfer reactions during 135 min, at −11 °C. These results show that the polymerization of 1-hexene catalyzed by **6**/MAO system also proceeds in a living fashion. The M_n and polydispersity indexes of the poly(1-hexene) could be monitored as a function of time and results are shown graphically in Fig. 4. The M_n grows linearly with time and the polydispersitiy remains very low throughout the 135 min of reaction.

Generally, an increase in the polymerization temperature causes chain transfer, resulting in the loss of the living character of the polymerization. In particular, this behavior is reported by Brookhart when using [NiBr$_2$(IPPBIAN)]/MAO as catalyst system for the living polymerization of propylene and 1-hexene [10a]. Surprisingly, as presented in Table 5, the complex **6**/MAO catalyst system produced poly(1-hexene)s having low polydispersities ($M_w/M_n = 1.12$–1.21, monomodal) even at room temperature (+16 °C), for 80 min. Fig. 5 also shows that the molecular weight of poly(1-hexene) increases linearly with time up to 40 min, but afterward this increase becomes much slower possibly due to the rising of chain transfer processes, although the polydispersity remains low during the 80 min of reaction.

The ^{13}C NMR of the poly(1-hexene)s obtained in living polymerization fashion at −11 °C (entry 7) and at +16 °C (entry 23) are shown in Fig. 3(b) and (c), respectively. The resonances assigned to CH_3 branches appear at 19.9 and 16.1 ppm (the latter minor resonance corresponding to adjacent methyl bonds), whereas that at 14.1 ppm is assigned to the *n*-butyl branches [23,24]. The number of branches can be calculated from the ^{13}C spectra [10c,24] (see below in Table 7) showing that the great majority of branches correspond to methyl (64 and 61 branches/1000 C, respectively at −11 and +16 °C) and *n*-butyl groups (68 and 22 branches/1000 C, respectively at −11 and +16 °C). The *n*-butyl branches obviously arise either from 'normal' 1,2- or 2,1-insertion of 1-hexene into the Ni-chain bond, whereas the CH_3 branches are produced by a sequence of 1,2-insertion followed by 2,6-enchainment of the 1-hexene units [24,25] (Scheme 2). However, when the reaction

Table 5
Living polymerization of 1-hexene with complex **6**/MAO catalytic system at +16 °C

Entry	Time (min)	Yield (g)	Activity[a] ($\times 10^{-4}$)	TOF[b] (h^{-1})	M_n[c] ($\times 10^{-4}$)	M_w/M_n[c]
16	10	0.102	21.3	406	2.27	1.12
17	20	0.150	15.6	297	2.80	1.15
18	30	0.254	17.6	335	3.40	1.15
19	40	0.313	16.3	311	3.51	1.17
20	50	0.352	14.7	279	3.71	1.17
21	60	0.384	13.3	254	3.64	1.19
22	70	0.425	12.6	241	3.78	1.18
23	80	0.471	12.3	233	3.77	1.21

Polymerization conditions: 18 μmol of Ni complex in 50 ml of toluene; Al/Ni = 180; [1-Hexene] = 0.16 M.

[a] Activity in g polymer (mol Ni.[1-Hexene].h)$^{-1}$.

[b] Turnover frequency = mol Hexene/(mol Ni.time).

[c] Determined by GPC.

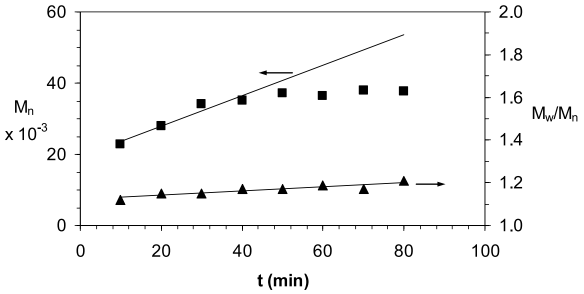


Fig. 5. Plot of M_n (squares) and M_w/M_n (triangles) as a function of reaction time for 1-hexene polymerization catalyzed by **6**/MAO at +16 °C.

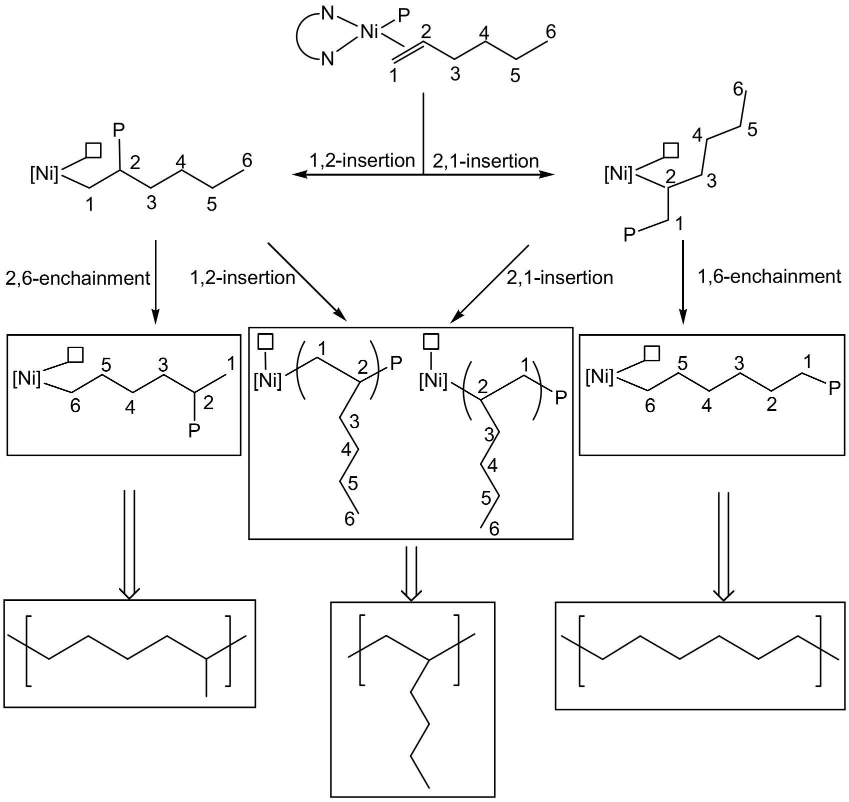
temperature increases from −11 to +16 °C, the number of *n*-butyl branches decreases considerably. The observation that the total number of branches significantly decreases from −11 to +16 °C (132 vs. 83 branches/1000 C) means that, at room temperature, 2,1-insertion followed by 1,6-enchainment increases in relation to 1,2-insertion/2,6-enchainment of 1-hexene units or normal 1,2- or 2,1-insertions.

3.2.3. Block copolymerization of propylene and 1-hexene

In view of the living nature of the systems described above, and in the light of the work by Brookhart et al. [10], we have also tested the catalyst **6**/MAO in the block copolymerization of propylene and 1-hexene.

When the catalyst precursor **6** was added to the solution of MAO and propylene, in 50 ml toluene at −15 °C, syndiotactic-rich polypropylene was formed after 20 min. Removal of the unreacted propylene under vacuum, and addition of 1-hexene to the reactor produced, for 40 min, a fairly high molecular weight polymer with a narrow monomodal molecular weight distribution ($M_n = 4.64 \times 10^4$, $M_w/M_n = 1.18$) (Table 6), indicating that a true copolymer and not a mixture of homopolymers was formed. This sample was further analyzed by thermal analysis (DSC) and showed a single transition with a $T_g = -24.5$ °C, which lies in between the values found for the homopolymers synthesized at low temperature ($T_g = -16.7$ °C for polypropylene of entry 4; $T_g = -53.5$ °C for poly(1-hexene) of entry 7) (Table 7, and Fig. 6(d)). This material, a polypropylene-*block*-poly(1-hexene) diblock copolymer, has NMR features common to both polypropylene and poly(1-hexene) homopolymers (Tables 6 and 7, and Fig. 3(d)), being evident that a shorter poly(1-hexene) block is present due to the lower reactivity of this monomer compared to propylene. The synthesis of such type of diblock copolymers had been reported previously by Brookhart et al. using [NiBr$_2$(IPPBIAN)]/MAO as catalyst system [10a].

When complex **6** was added to a solution of MAO and 1-hexene, in 50 ml toluene at −15 °C, a poly(1-hexene) block was formed during 40 min. Propylene was subsequently added to the reaction mixture, this time still in the presence of unreacted 1-hexene monomer, and the reaction proceeded



Scheme 2. Rationale for the formation of the major types of branches (*n*-butyl and methyl) in the poly(1-hexene)s obtained in this work.

Table 6
Synthesis of α-olefin block copolymers

Entry	Monomer	Time (min)	Yield (g)	M_n[a] ($\times 10^{-4}$)	M_w/M_n[a]
24	P/H[b]	20/40	0.149	4.64	1.18
25	H/(P-H)/H[c]	40/20/40	1.948	3.11	1.25

[a] Determined by GPC.

[b] Polymerization conditions: 3 μmol of Ni complex in 50 ml of toluene; Al/Ni = 180; [1-Hexene] = 0.40 M; [Propylene] = 0.48 M; temperature = −15 °C.

[c] Polymerization conditions: 18 μmol of Ni complex in 50 ml of toluene; Al/Ni = 180; [1-Hexene] = 0.8 M; [Propylene] = 1.54 M; temperature = −15 °C.

Table 7
Number of branches per 1000 C[a] and thermal analyses[b] of selected homopolymer and block copolymer samples

Entry	Monomer	T (°C)	Methyl branches /1000C	Adjacent methyl branches /1000C	*n*-Butyl branches /1000C	T_g (°C)
4	P	−11	252	64	–	−16.7
7	H	−11	49	15	68	−53.5
23	H	+16	54	7	22	−54.2
24	P/H	−15	226	72	10	−24.5
25	H/(P-H)/H	−15	157	41	54	−37.1

[a] Estimated by ^{13}C NMR [10c].

[b] Performed by DSC.

for a period of 20 min, after which the unreacted propylene was removed under vacuum. The reaction was allowed to continue for an additional 40 min, resulting in the synthesis of a monomodal ABA triblock copolymer, poly(1-hexene)-*block*-poly(propylene-*ran*-1-hexene)-*block*-poly(1-hexene), which was characterized by GPC ($M_n = 3.11 \times 10^4$, $M_w/M_n = 1.25$), DSC ($T_g = -37.1$ °C) and NMR (Tables 6 and 7, and Figs. 3(e) and 6(e)). The thermal analysis showed a single glass transition temperature sitting midway the corresponding homopolymer values. As the second block was synthesized in the presence of unreacted 1-hexene, the regiostructure of the middle block is likely to be that of a random copolymer of propylene and 1-hexene. The reaction conditions used, such as higher initial concentrations of 1-hexene and propylene in relation to the corresponding homopolymerizations, and the initiation of the second block in the presence of unreacted 1-hexene monomer, may have favored chain transfer processes and the slight broadening of the molecular weight distribution. The corresponding ^{13}C{^{1}H} NMR (Fig. 3(e)) shows a higher content of 1-hexene units compared to the diblock copolymer described above, but it also contains features characteristic

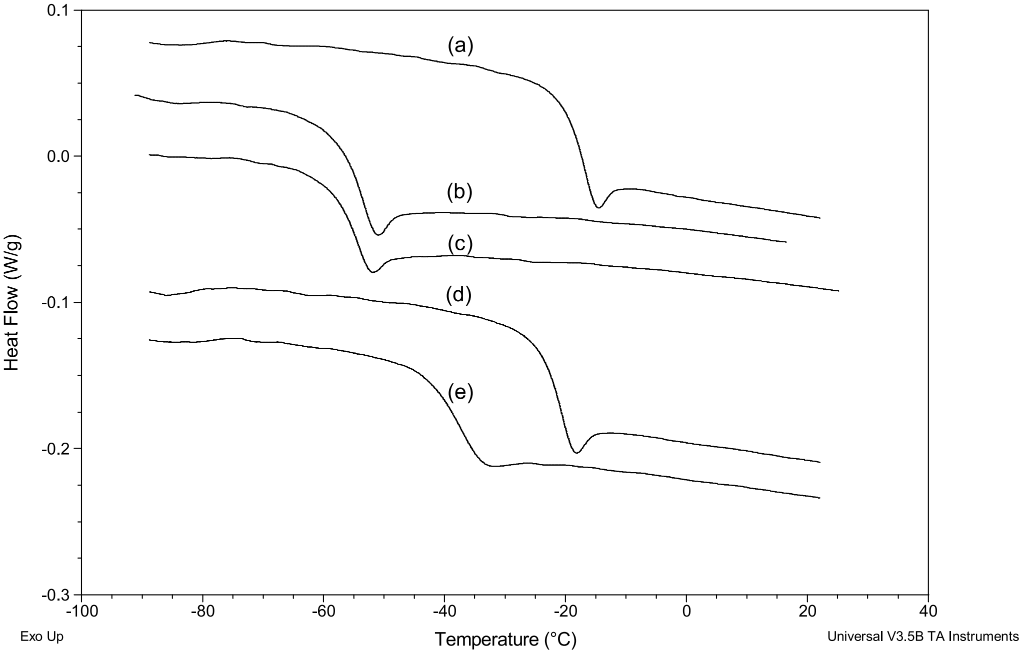


Fig. 6. DSC thermograms of (a) polypropylene obtained at −11 °C (entry 4), (b) poly(1-hexene) obtained at −11 °C (entry 7), (c) poly(1-hexene) obtained at +16 °C (entry 23), (d) polypropylene-*block*-poly(1-hexene), obtained at −15 °C (entry 24), (e) poly(1-hexene)-*block*-poly(propylene-*ran*-1-hexene)-*block*-poly(1-hexene) (entry 25).

of polypropylene blocks. This is due to the reactions conditions employed where the first block to be polymerized was that of 1-hexene.

4. Conclusions

A new α-diimine compound containing two bulky electron-donating siloxyl substituents, and its corresponding Ni(II) complex, bis{[*N*,*N*′-(4-tert-butyl-diphenylsiloxy-2,6-dimethylphenyl)imino]acenaphthene}dibromonickel (**6**), were successfully synthesized and the molecular structure of **6** determined by X-ray crystallography. The precatalyst **6** was tested in the insertion polymerization of ethylene, with methylaluminoxane (MAO) or diethylaluminum chloride (DEAC) as co-catalysts. The system **6**/MAO has shown a higher activity and can be considered as one of the most active Brookhart type catalysts. Complex **6**/MAO catalyst system was successfully employed in the living polymerization of propylene and 1-hexene at −11 °C. Very interestingly, *quasi*-living polymerization of 1-hexene at room temperature has been achieved during 40 min.

The ^{13}C NMR spectra of the polypropylenes indicate that the living system produced syndiotactic-rich polymers. The poly(1-hexene) microstructures are composed almost exclusively by methyl and *n*-butyl branches, and, at room temperature, the majority of branches are methyl groups, which were produced from 1,2-insertion followed by 2,6-enchainment.

We also have successfully synthesized polypropylene-*block*-poly(1-hexene) AB diblock copolymer and poly(1-hexene)-*block*-poly(propylene-*ran*-1-hexene)-*block*-poly(1-hexene) ABA triblock copolymer.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2005.01.011.

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