Polymers of propylene and higher 1-alkenes produced with post-metallocene complexes containing a saligenin-type ligand

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ABSTRACT

Polymerization reactions of propylene and three higher linear 1-alkenes, 1-hexene, 1-octene and 1-decene, were carried out with post-metallocene catalysts derived from Ti complexes **I** and **II** with a bidentate phenol-alcohol (saligenin-type) ligand derived from 2,4-di-*tert*-butyl-6-(1,1,1,3,3,3-hexafluoro-2-hydroxy-propan-2-yl)phenol, in the presence of two cocatalysts, MAO and a combination of AlEt$_2$Cl and MgBu$_2$. All catalyst systems contain a large variety of active centers and produce both amorphous atactic polymers and partially crystalline isotactic material. The AlEt$_2$Cl-MgBu$_2$ cocatalyst produces significantly more active catalyst systems. Analysis of ^{13}C NMR data for the propylene polymers shows that the mechanism of isotactic chain growth is principally different for the active centers formed in the presence of the two cocatalysts.

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1. Introduction

Soluble post-metallocene catalysts for alkene polymerization usually contain a transition metal complex with one or two multidentate ligands and an activator (a cocatalyst) such as methylalumoxane (MAO) [1–3]. All these catalyst systems exhibit very high activity in ethylene polymerization reactions, some of them can also polymerize propylene to a partially or a nearly perfectly isotactic material [4–6]. Earlier we demonstrated that titanium complexes with bidentate dioxalan-dicarboxylate, binol and phenoxyimine ligands afford the formation of partially isotactic polypropylene (PP) with depressed melting points, 150–157 °C, and with mechanical properties characteristic of elastic polymers [6–9].

Although each such post-metallocene catalyst is formed from a single well characterized transition metal complex with a multidentate ligand, interactions of the complex with different co-catalysts can produce either single-center or multi-center catalysts and, respectively, can lead either to the formation of polymers with a narrow molecular weight distribution (the M_w/M_n ratio of ∼2) or polymers with a broad molecular weight distribution, with M_w/M_n >10 [1–3,5,8,9].

The subject of this paper is the study of homopolymerization reactions of propylene and three higher linear 1-alkenes, 1-hexene, 1-octene and 1-decene, with new post-metallocene catalysts derived from two Ti complexes containing a strongly asymmetric bidentate saligenin-type ligand **L**: complex **I** − LTi(iso-PrOH)$_2$Cl$_2$, {2-[α,α-(CF$_3$)$_2$-methanolato]-4,6-tert-Bu$_2$-phenolato}TiCl$_2$·(iso-PrOH)$_2$, complex **II** − **L**TiCl$_2$··MgCl$_2$, {2-[α,α−(CF$_3$)$_2$−methanolato]-4,6-*tert*-Bu$_2$-phenolato}TiCl$_2$··MgCl$_2$.
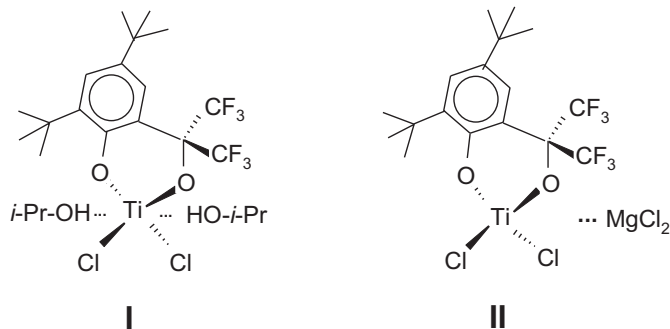
2. Experimental

2.1. Materials

The source of the bidentate ligand **L** in both complexes, the oxyphenol 2,4-*tert*-Bu$_2$-6-(1,1,1,3,3,3-F$_6$-hydroxy-propan-2-yl) phenol, was prepared from hexafluoroacetone and 2,4-di-*tert*-butylphenol as described in Ref. [10].

Complex **I** A two-necked flask equipped with a magnetic stirrer was loaded with toluene (10 ml) and the oxyphenol (0.38 g, 1.0 mmol) under argon flow. Solution of Ti(O-iso-Pr)$_2$Cl$_2$ (0.28 g, 1.0 mmol) in 10 ml of toluene was added to the flask under stirring. The slurry of black precipitate was formed; it was heated until dissolved in toluene and then the solution was slowly cooled to 20 °C to yield a mat of dark-brown crystals, which were filtered and washed with toluene. The yield of **I** is 0.4 g (59%).

For C$_{23}$H$_{36}$Cl$_2$F$_6$O$_4$Ti, calculated (%): C 45.49; H 5.64; Cl 11.68; F 18.77; Ti 7.89.

Found (%): C 45.33; H 5.62; Cl 11.25; F 18.55.

^{1}H NMR (CDCl$_3$): ppm: 7.59 (s, 1H), 7.43 (d, J = 2.2 Hz, 2H), 4.95–4.78 (m, 2H), 3.80 (s, 2H), 1.47 (s, 12H), 1.44 (s, 9H), 1.31 (s, 9H).

^{19}F NMR (CDCl$_3$): 4.15 ppm (s).

Complex **II** A two-necked flask equipped with a magnetic stirrer was loaded with toluene (10 ml) and the oxyphenol (0.19 g, 0.50 mmol) under argon flow and the solution was cooled to −78 °C. MgBu$_2$ (1 M solution in *n*-heptane, 1 ml) was added drop-wise and the mixture was slowly heated to 20 °C and kept at 20 °C for 4 h under stirring. Then the temperature was again decreased to −78 °C, neat TiCl$_4$ (0.055 ml, 0.50 mmol) was added to the mixture and its temperature was increased to 20 °C. The complex **II** was repeatedly crystallized from toluene dried under vacuum at 30 °C.

For C$_{17}$H$_{20}$Cl$_2$F$_6$O$_2$Ti Calculated (%): C 41.75; H 4.12; Cl 14.50; Ti 9.79.

Found (%): C 41.69; H 5.09; Cl 14.65; Ti 9.67.

^{1}H NMR (toluene-d$_8$), ppm: 7.89 (s, 1 H); 7.52 (d, 1 H, J = 2.2 Hz); 1.46 (s, 9 H); 1.27 (s, 9 H).

In the current research, complex **II** was used in polymerization reactions as suspension in toluene without separating it from MgCl$_2$.

Cocatalysts MAO was purchased from Witco as 10% solution in toluene. AlEt$_2$Cl and MgBu$_2$ were purchased from Acros as 0.8 M and 0.5 M solutions in heptane, respectively.

2.2. Polymerization reactions

Propylene homopolymerization reactions were carried out in liquid propylene at 30 and 50 °C; reaction conditions are given in Table 1. Details of the polymerization reactions were described earlier [7,8]. Catalyst activity is presented as a polymer yield with respect to 1 mol of Ti (kg mol$_{Ti}^{-1}$); the effective rate constant k_{eff} was calculated as $R \cdot (C_{Pr} C_{Ti})^{-1}$ (1 mol$_{Ti}^{-1}$ min^{-1}) where R is the reaction rate (M min^{-1}), and C_{Pr} and C_{Ti} are the concentrations of propylene and a Ti complex (M). All the polymers were fractionated with boiling *n*-heptane into two fractions, an insoluble, partially crystalline fraction and a soluble amorphous fraction.

Homopolymerization reactions of 1-hexene, 1-octene and 1-decene were carried out in liquid monomer media in sealed glass ampoules at 2 °C. The polymers were washed from the catalyst residue with 10% HCl solution in ethanol and dried under vacuum to a constant weight. Catalyst activity was estimated based on monomer conversion.

2.3. Polymer characterization

GPC analysis of the polymer samples was carried out with a Waters GPCV-2000 chromatograph equipped with two columns (PL-gel, 5 μ И Mixed-C, 300 × 7.5 mm) and a refractometer. GPC analysis of PP was performed at 135 °C using 1,2,4-trichlorobenzene as a solvent, the elution rate was 1 ml min^{-1}. GPC analysis of higher polyolefins was performed at 35 °C using THF as a solvent at the same elution rate. Average molecular weights of PP products were determined using the universal calibration dependence relative to polystyrene standards with a narrow MWD (for PS K$_\eta$ = 2.88 × 10^{-4}, α = 0.64; for PP K$_\eta$ = 0.74 × 10^{-4}, α = 0.83). The separation procedure of GPC curves into GPC curves of individual polymer components (Flory components, the material produced by a single type of active center) was described earlier [11].

Characteristic viscosity [η] of higher polyolefins was measured in THF solutions at 25 °C. The viscosity-average molecular weight M_η was calculated with the Mark-Houwink equation, [η] = K$_\eta$ M_η^α, where K$_\eta$ and α are the constants depending on the polymer type, solvent and temperature [12]. The chosen parameters, K$_\eta$ = 5.19 × 10^{-3} ml·g^{-1}, α = 0.77, give the best fit between the calculated M_η values and the M_w values from the GPC data for polyolefins of a medium−high molecular weight.

^{13}C NMR spectra of PP (∼5 wt% solutions in *o*-dichlorobenzene) were recorded at 100 °C on a Bruker Avance-400 spectrometer (10.613 MHz). The relaxation delay was 15 s, the number of scans varied from 500 to 2000. The signal assignment in the CH$_3$ range was based on the literature data [13,14]. Complex profiles of CH$_3$ signals in the 19−22 ppm range were resolved into the signals of stereo-components, pentads *mmmm*, *mmmr*, *rmmr*, *mmrr*, *mmrm* + *rrmr*, *mrmr*, *rrrr*, and heptads *mrrrr*, *mrrrrm*, *rmrrmr*, *mmrrmr*, and *mmrrmm*. The resolution was carried out with the Scientist Version 2.02 (MicroMath) program using the Lorentz curve shape for the representation of each signal. ^{13}C NMR spectra of higher polyolefins (10% solutions in mixtures of 1,2,4-trichlorobenzene and deuterated chloroform) were recorded at 25 °C. The [*mmmm*] content was calculated from the area under the α-CH$_2$ signal of the side group [15].

IR spectra of the polymers were recorded on a Perkin−Elmer FTIR spectrometer. Absorbance ratios A$_{998}$/A$_{973}$ and A$_{841}$/A$_{973}$ were

Table 1
Propylene homopolymerization reactions with complexes **I** and **II**.

Experiment	Catalyst	Temp, °C	Time, min	[Ti] × 10^5, mol	[Al] × 10^3, mol	[Mg] × 10^3, mol	[Al]:[Ti], mol:mol	Yield, Kg·mol$_{Ti}^{-1}$
1	**I**[a]	50	60	4.28	3.3	1.05	77	70
2	**II**[a]	50	60	2.45	2.3	0.88	92	350
3	**II**[a]	50	13	2.07	3.2	0.85	154	3500
4	**II**[a]	50	15	2.32	3.0	0.50	128	3300
5	**II**[a]	50	60	2.38	3.1	0.32	130	55
6	**II**[a]	30	60	1.99	3.3	0.97	165	700
7	**II**[a]	40	20	1.99	3.3	0.94	167	3300
8	**II**[b]	50	60	1.84	4.4	−	219	309

[a] Cocatalyst AlEt$_2$Cl-MgBu$_2$.
[b] Cocatalyst MAO.