Supplementary Materials

Copolymerization of Ethylene with Propylene and Higher α-Olefins Catalyzed by (Imido)vanadium(IV) Dichloride Complexes

Giorgia Zanchin,† Fabio Bertini,† Laure Vendier,‖ Giovanni Ricci,† Christian Lorber‖,#,* and Giuseppe Leone†,*

† CNR, Istituto di Scienze e Tecnologie Chimiche “Giulio Natta” (SCITEC), via A. Corti 12, I-20133 Milano, Italy.
† CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, BP44099, 31077 Toulouse, France
‖ Université de Toulouse, UPS, INPT, LCC, 31077 Toulouse, France
* Corresponding authors
E-mail address: christian.lorber@lcc-toulouse.fr (C. Lorber)
E-mail address: giuseppe.leone@ismac.cnr.it (G. Leone)

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EPR spectra

**Figure S1.** *EPR spectrum of [V(=N-Cu)Cl₂(NHMe₂)₂] (1a)*

EPR (toluene, 20°C) $g = 1.985$, $A_{iso}(^{51}V) = 93$ G.

**Figure S2.** *EPR spectrum of [V(=N-Cu)Cl₂(Py)₃] (2a)*

EPR (Toluene, 20°C) $g = 1.990$, $A_{iso}(^{51}V) = 95.7$ G.
**Figure S3.** EPR spectrum of $[V(=N-CPh_3)Cl_2(NHMe_2)_2]$ (1b)

EPR (CH$_2$Cl$_2$, 20°C) $g = 1.988$, $A_{iso}^{51V} = 93.3$ G.

![EPR spectrum of 1b](image)

**Figure S4.** EPR spectrum of $[V(=N-CPh_3)Cl_2(Py)_3]$ (2b)

EPR (CH$_2$Cl$_2$, 20°C) $g = 1.985$, $A_{iso}^{51V} = 95.7$ G.

![EPR spectrum of 2b](image)
Figure S5. EPR spectrum of $[V(=N{-}\text{Ar}^*\text{**)Cl_2(NHMe)_2}]$ (1c)

EPR (CH$_2$Cl$_2$, 20°C) $g = 1.986$, $A_{iso}^{(51V)} = 91$ G

Figure S6. EPR spectrum of $[V(=N{-}\text{Ar}^*\text{**)Cl_2(Py)_3}]$ (2c)

EPR (CH$_2$Cl$_2$, 20°C) $g = 1.985$, $A_{iso}^{(51V)} = 91$ G.
- Determination of the steric properties of the imido ligands using SambVca Web2\textsuperscript{a,b}


**Figure S7.** $[V(=N-tBu)Cl_2(NHMe_2)_2]$ (1a)
Figure S8. $[\text{V}(=\text{N-CPh}_3)\text{Cl}_2(\text{NHMe}_2)_2]$ (1b)

Figure S9. EPR spectrum of $[\text{V}(=\text{N-Ar**})\text{Cl}_2(\text{NHMe}_2)_2]$ (1c)
**Figure S10. EPR spectrum of $[V(=N-2,6'-Pr-C_6H_3)Cl_2(NHMe_2)_2]$ (1d)**
Figure S11. DSC heating scans of selected poly(ethylene)s (Table 2 in the manuscript).

entry 6
$T_m = 138.7 \, ^\circ\text{C}$, $\Delta H_m = 201.9 \, \text{J/g}$

entry 5
$T_m = 138.1 \, ^\circ\text{C}$, $\Delta H_m = 198.8 \, \text{J/g}$

entry 3
$T_m = 137.3 \, ^\circ\text{C}$, $\Delta H_m = 193.8 \, \text{J/g}$
**Figure S12.** $^{13}$C NMR spectra (in C$_2$D$_2$Cl$_4$ at 103 °C, reference to HDMS) of (a) a selected poly(ethylene-co-1-hexene) (Table 5, entry 18, HEX = 11.2 mol%) and (b) a selected poly(ethylene-co-1-octene) (Table 5, entry 15, OCT = 9.0 mol%). For $S_{\beta\gamma}$, $T_{\gamma\delta}$ refer to the inset of Figure 7.

Figure S12a shows the $^{13}$C NMR spectrum of sample 18 (HEX = 11.2 mol%). The copolymer mainly contains isolated butyl branches ([EYE] where Y is the comonomer and assigned as $T_{\delta\delta}$ at 35.8 ppm), but also alternated sequences ([YEY] assigned as $S_{\beta\beta}$ at 22.2 ppm). Moreover, resonances clearly ascribed to two consecutive inserted 1-hexene units ([EYY] assigned as $T_{\beta\delta}$ at 33.4 ppm), and tiny ones due to the blocky 1-hexene repeating units are present in the $^{13}$C NMR spectrum (assigned as $S_{\alpha\alpha}$ at 39.4 ppm). Finally, resonances at 25.4 and 36.2 ppm assigned to $S_{\beta\gamma}$ and $T_{\gamma\delta}$, respectively, are also visible in the spectrum: these peaks can be ascribed to 2,1-insertion of 1-hexene, leading to four uninterrupted methylene sequences ($x_{n,4}$).

Figure S12b shows the $^{13}$C NMR spectrum of a selected E/OCT copolymer (entry 15, OCT = 9.0 mol%). Similarly to the E/HEX copolymer, 1-octene is randomly distributed. The copolymer mainly contains the sequences EEE, EYE, and YEE, which are characteristic of comonomer units existing as isolated sequences. In addition, the tiny resonance assigned to the $\beta\beta$ methylene carbon at 22.2 ppm, due to the alternating YEY sequence, as well as all the other microstructural features already found in the E/HEX copolymer, were detected.
Figure S13. ¹H NMR spectrum (in C₂D₂Cl₄ at 103 °C, reference to HDMS) of a selected poly(ethylene-co-4-methyl-1-pentene) (entry 19, 4M1P = 4.7 mol%, Table 5 in the manuscript).
• Calculation of lamellar thickness \((l)\), methylene sequence length \((MSL)\), and relative polydispersities \((D)\) from final SSA thermograms.

The lamellar thickness \((l)\) was obtained by Thomson-Gibbs equation [72]:

\[
l = \frac{2\sigma_e T_m^0}{\Delta H_0 \left( T_m^0 - T_m \right)}
\]

where \(\sigma_e\) is the surface free energy equal to 0.087 J m\(^{-2}\) and \(\Delta H_0\) is the melting enthalpy of PE crystal equal to 290 \(\times\) 10\(^6\) J m\(^{-3}\), \(T_m^0\) is the equilibrium melting temperature of poly(ethylene) \((T_m^0 = 418.7\) K\), and \(T_m\) is the measured melting temperature of each melting peak. The thermodynamic melting temperature for infinitely thick lamellae in a random copolymer \((T_{cm}^0)\) was calculated by Flory’s theory [72]:

\[
\frac{1}{T_m} = \frac{1}{T_m^0} - \frac{R \ln x}{\Delta H_u}
\]

where \(R\) is the gas constant, \(T_m^0\) is the equilibrium melting temperature of polyethylene \((T_m^0 = 418.7\) K\), \(\Delta H_u\) is the molar heat of fusion of repeat units in the crystal \((\Delta H_u = 8.284\) KJ mol\(^{-1}\)\), and \(x\) is the molar fraction of the ethylene in the copolymer.

The methylene sequence length \((MSL)\) was calculated from the CH\(_2\) molar fraction \((X)\) according to [73]:

\[
\ln X = 0.331 - \left( \frac{135.5}{T_m} \right)
\]

where \(T_m\) (in unit of K) is the measured melting temperature of each melting peak.

The values of \(X\) can be converted to \(MSL\) by [74]:

\[
MSL = \frac{2X}{1 - X}
\]

As proposed by Keating,[73] the mathematical terms, \(i.e.\) arithmetic mean, weighted mean and broadness index, were employed in evaluating the heterogeneity of \(l\) and \(MSL\) distribution along the macromolecule chains. The general equations are:
\[ Z_n = \frac{n_1Z_1 + n_2Z_2 + \ldots + n_iZ_i}{n_1 + n_2 + \ldots + n_i} \]

(6)

\[ Z_w = \frac{n_1Z_1^2 + n_2Z_2^2 + \ldots + n_iZ_i^2}{n_1Z_1 + n_2Z_2 + \ldots + n_iZ_i} \]

(7)

\[ D = \frac{Z_w}{Z_n} \]

where \( n_i \) is the normalized partial area, and \( Z_i \) could be alternatively \( l \) or MSL of the fraction \( i \) in the final SSA melting curve. Taking into account the temperature dependence of specific heat of fusion, the \( n_i \) value was corrected using the ratio of \( \Delta H_0 \) to the fusion of each fraction \([ \Delta H_m(T) ] \) as the correction factor.[75]

references


75. F. Zhang, Q. Fu, T. Lu, H. Huang, T. He, Improved thermal fractionation technique for chain structure analysis of ethylene/\( \alpha \)-olefin copolymers, Polymer 2002, 43, 1031–1034.