Supplementary Materials

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

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Table S1. Crystallographic Data, Data Collection and Refinement Parameters for **Ar**NH$_2$**, **1a−c**, and **2c**.

Compound ref.	**Ar**NH$_2$**	**1a**	**1b**	**1c**	**2c**
Chemical formula	$C_{32}H_{26}ClN$	$C_8H_{23}Cl_2N_3V$	$C_{53}H_{66}Cl_4N_6V_2$	$C_{25}H_{27}Cl_{1.50}N_{1.50}V_{0.50}$	$C_{47}H_{39}Cl_3N_4V$
Formula weight	460.02	283.13	1030.84	427.12	817.11
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	Cc	$P2_1/c$	$C2/c$	$\underline{P}$-1
a, Å	9.59870(4)	17.139 (3)	12.320(5)	13.7831(5)	9.343(3)
b, Å	11.36410(4)	9.122 (2)	23.643(5)	12.4060(5)	12.699(3)
c, Å	22.08550(6)	12.098 (2)	19.162(5)	25.9963(10)	18.845(5)
α, deg	90	90	90	90	94.699(9)
β, deg	93.217(4)	126.55 (3)	108.331(5)	96.265(1)	97.476(7)
γ, deg	90	90	90	90	94.983(8)
V, Å^3	2405.30(2)	1519.5 (7)	5298(3)	4418.6(3)	2198.6(10)
Z	4	4	4	8	2
D_{calc}, g cm^{-3}	1.270	1.238	1.29	1.284	1.234
μ (Mo-Kα), mm^{-1}	0.18	0.98	0.595	0.44	0.44
F(000)	968	596		1796	846
θ range (deg)	2 – 33	2 – 26	2 – 24	3.4 – 26.4	3 – 28
Measured reflections	85480	7615	42991	43482	51790
Unique reflections / R_{int}	9710 / 0.052	4408 / 0.041	7929 / 0.09	4516 / 0.031	8947 / 0.036
Parameters / restraints	315 / 6	136 / 32	552 / 0	267 / 0	496 / 0
Final R indices all data	R = 0.038 wR = 0.045	R = 0.045 wR = 0.125	R = 0.0466 wR = 0.0446	R = 0.027 wR = 0.075	R = 0.035 wR = 0.134
Goodness of fit	0.97	0.84	1.134	1.10	1.12
Δρmax - Δρmin	0.49 and −0.23	0.38 and −0.31	0.39 and −0.45	0.34 and −0.33	0.49 and −0.40
CCDC number	1940732	1940733	1940734	1940735	1940736

EPR spectra

Figure S1. *EPR spectrum of [V(=N-^{t}Bu)Cl$_2$(NHMe$_2$)$_2$]* (**1a**)

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

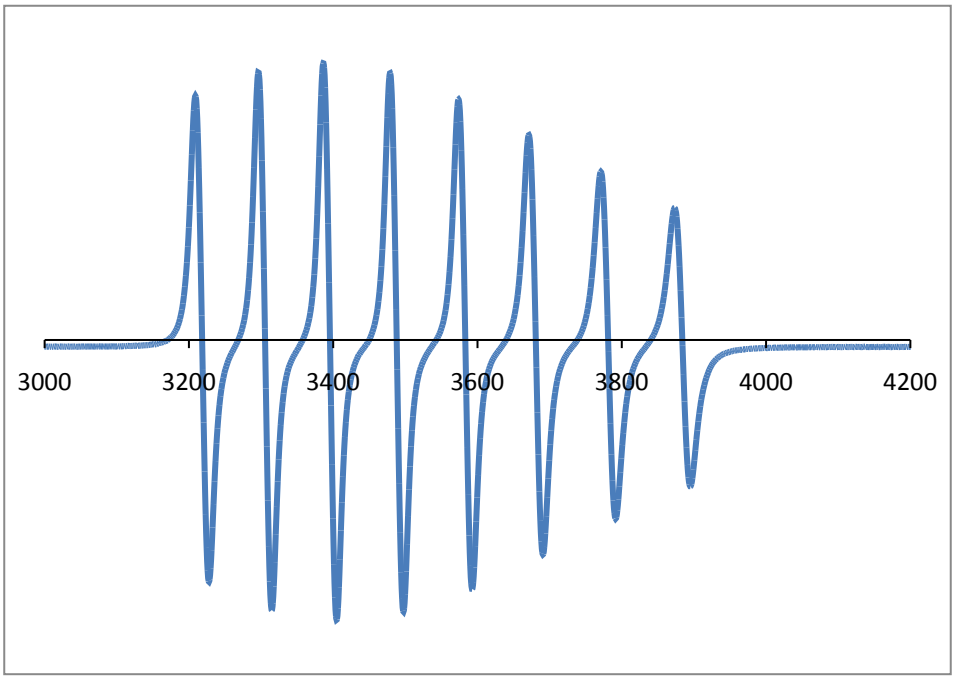


Figure S2. *EPR spectrum of [V(=N-^{t}Bu)Cl$_2$(Py)$_3$]* (**2a**)

EPR (Toluene, 20°C) g = 1.990, A_{iso}(^{51}V) = 95.7 G.

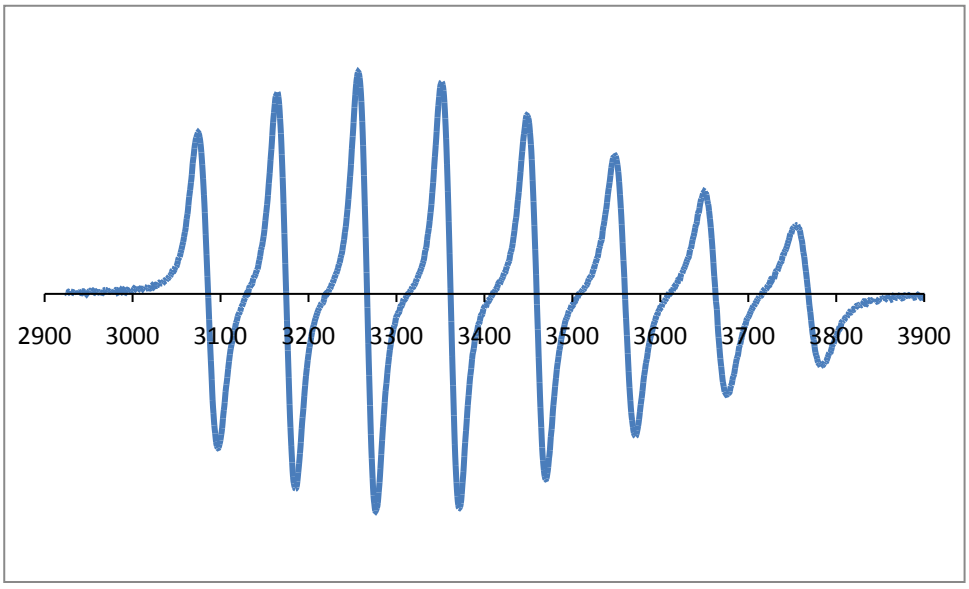


Figure S3. *EPR spectrum of [V(=N-*CPh_3*)*Cl_2*(*$NHMe_2$*)*$_2$*]* (**1b**)

EPR (CH_2Cl_2, 20°C) g = 1.988, A_{iso}(^{51}V) = 93.3 G.

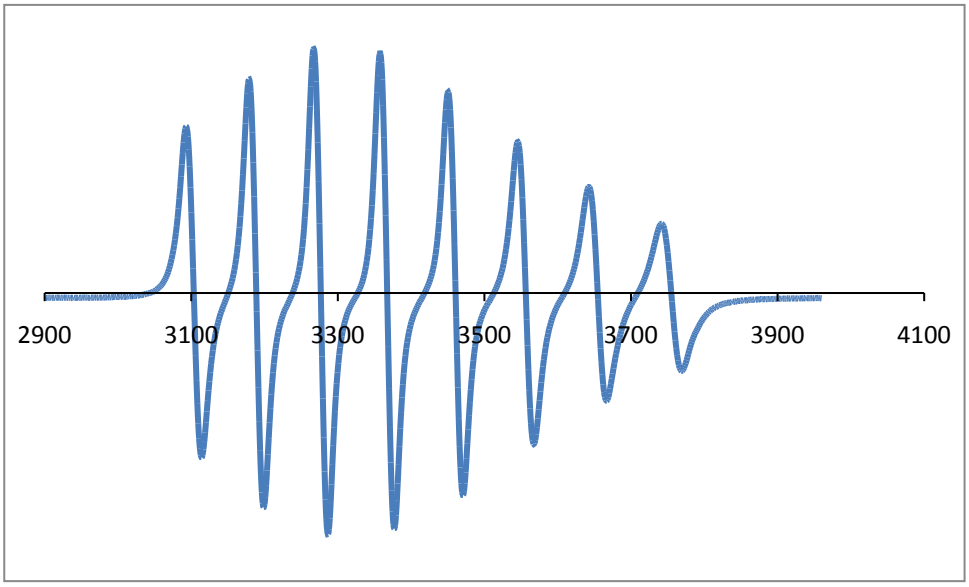


Figure S4. *EPR spectrum of [V(=N-*CPh_3*)*Cl_2*(Py)*$_3$*]* (**2b**)

EPR (CH_2Cl_2, 20°C) g = 1.985, A_{iso}(^{51}V) = 95.7 G.

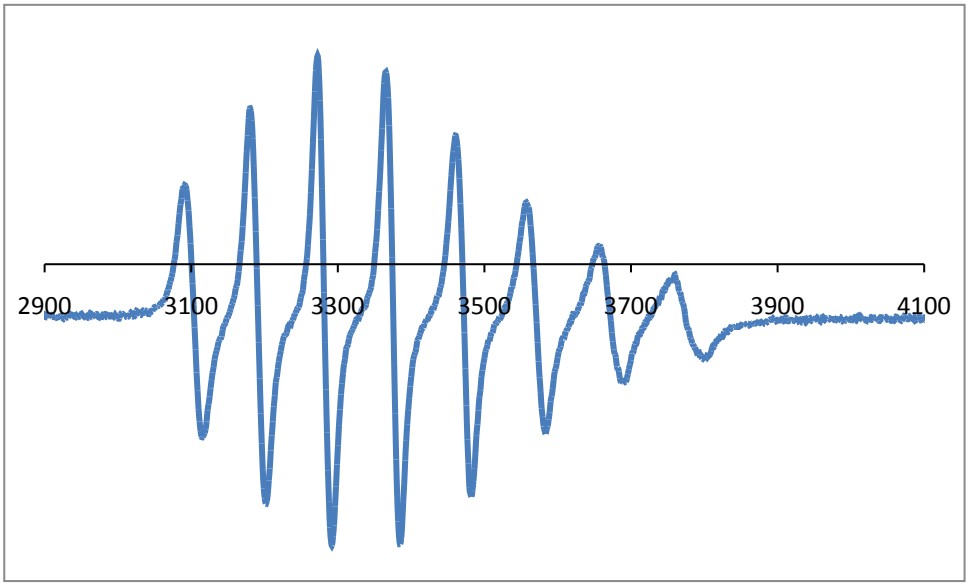


Figure S5. *EPR spectrum of [V(=N-*Ar***)$Cl_2(NHMe_2)_2$]* (**1c**)

EPR (CH_2Cl_2, 20°C) g = 1.986, $A_{iso}(^{51}V)$ = 91 G

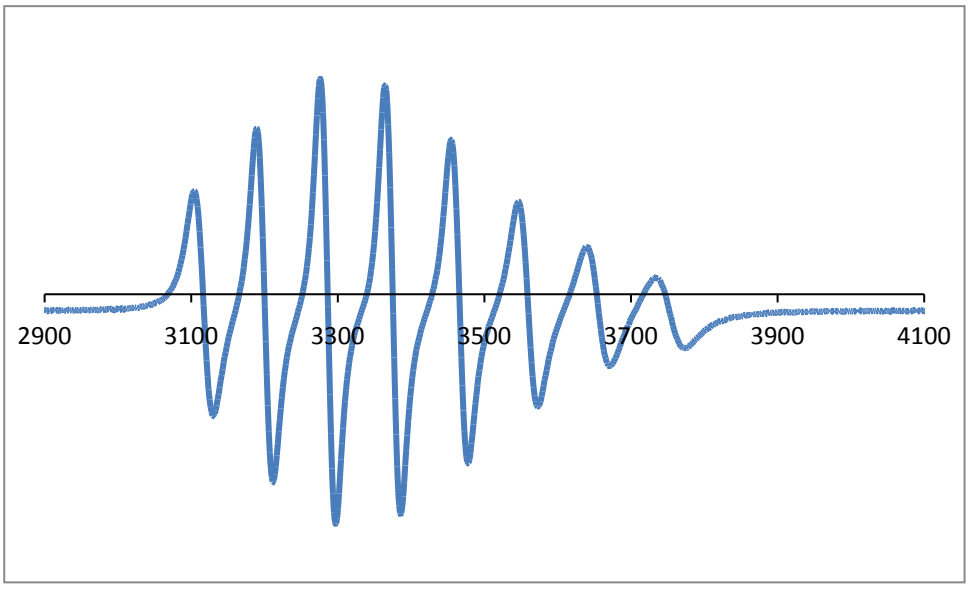
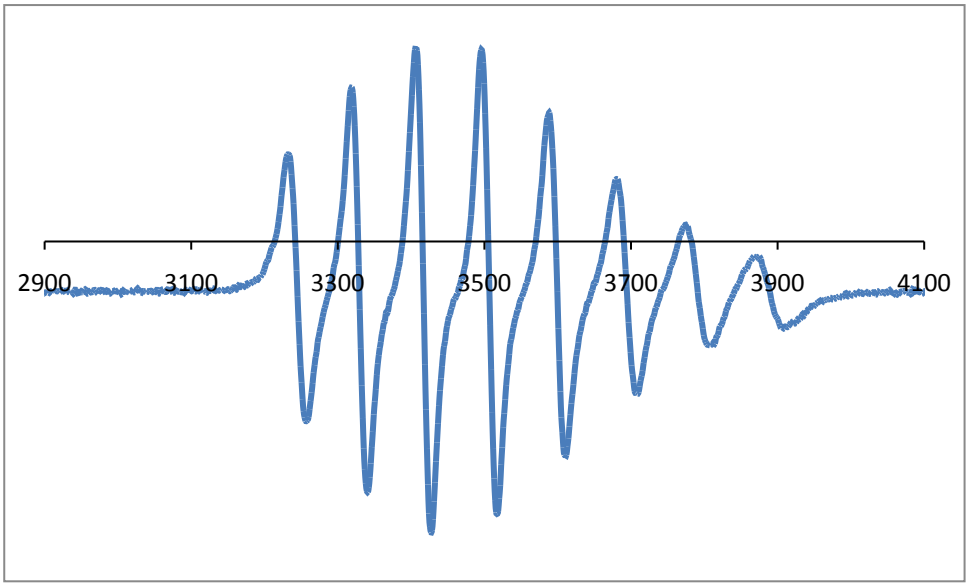


Figure S6. *EPR spectrum of [V(=N-*Ar***)$Cl_2(Py)_3$]* (**2c**)

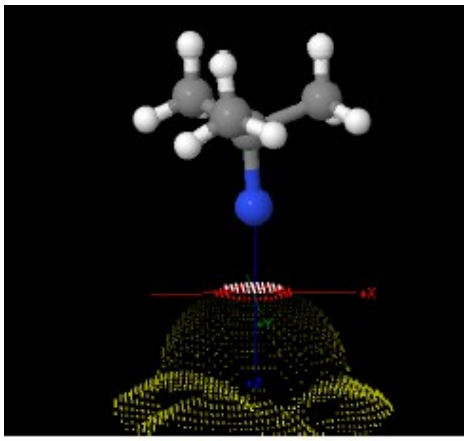
EPR (CH_2Cl_2, 20°C) g = 1.985, $A_{iso}(^{51}V)$ = 91 G.

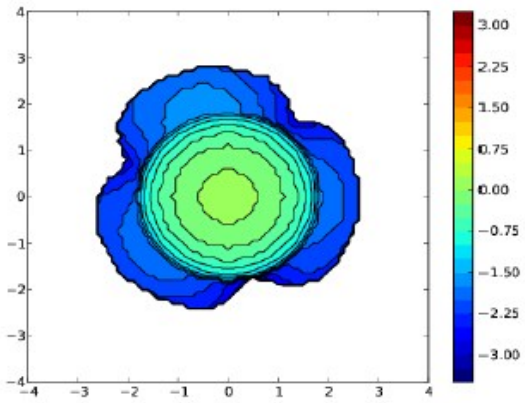


- Determination of the steric properties of the imido ligands using SambVca Web2[a,b]

(a) Falivene, L.; Credendino, R.; Poater, A.; Petta, A.; Serra, L.; Oliva, R.; Scarano, V.; Cavallo, L. SambVca 2. A Web Tool for Analyzing Catalytic Pockets with Topographic Steric Maps. *Organometallics* **2016**, *35*, 2286–2293. (b) SambVca 2.0: a web application for analyzing catalytic pockets https://www.molnac.unisa.it/OMtools/sambvca2.0/.

Figure S7. *[V(=N-^{t}Bu)$Cl_2(NHMe_2)_2$]* (**1a**)



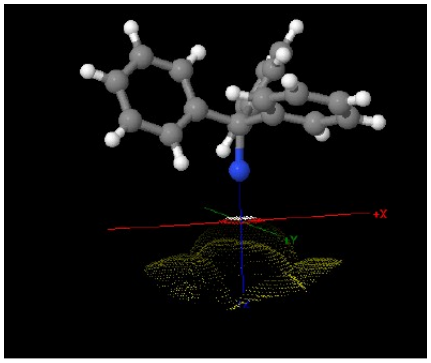


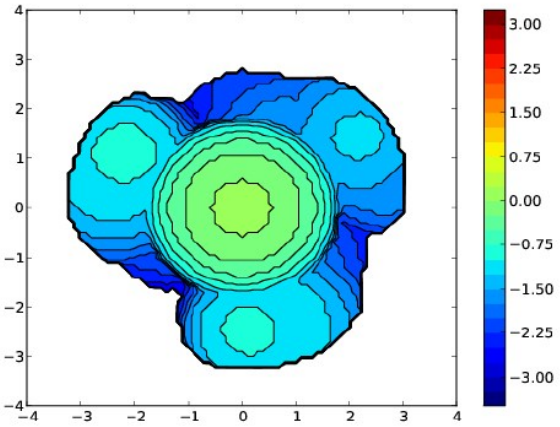
V Free	V Buried	V Total	V Exact
143.7	35.8	179.5	179.6

%V_Free	%V_Bur	% Tot/Ex
80.1	19.9	100.0

Quadrant	V_f	V_b	V_t	%V_f	%V_b
SW	35.8	9.1	44.9	79.8	20.2
NW	35.4	9.5	44.9	78.8	21.2
NE	36.0	8.9	44.8	80.2	19.8
SE	36.5	8.3	44.9	81.4	18.6

Figure S8. *[V(=N-*CPh_3*)$Cl_2(NHMe_2)_2$*]* (**1b**)



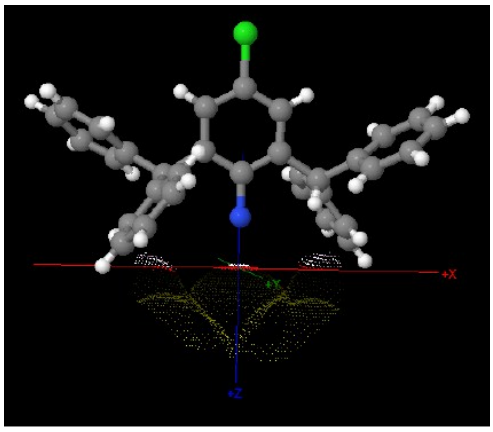


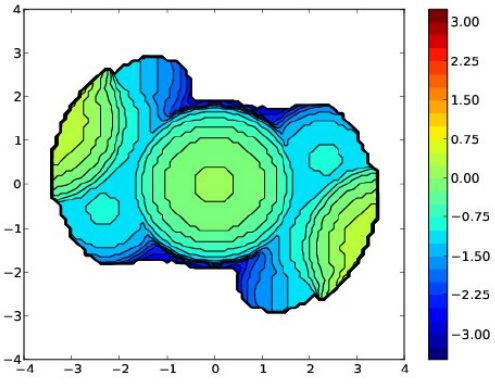
V Free	V Buried	V Total	V Exact
133.0	46.5	179.5	179.6

%V_Free	%V_Bur	% Tot/Ex
74.1	**25.9**	100.0

Quadrant	V_f	V_b	V_t	%V_f	%V_b
SW	34.1	10.7	44.9	76.1	**23.9**
NW	32.8	12.1	44.9	73.1	**26.9**
NE	33.1	11.8	44.8	73.8	**26.2**
SE	33.0	11.9	44.9	73.5	**26.5**

Figure S9. *EPR spectrum of [V(=N-*Ar**$)Cl_2(NHMe_2)_2$*]* (**1c**)



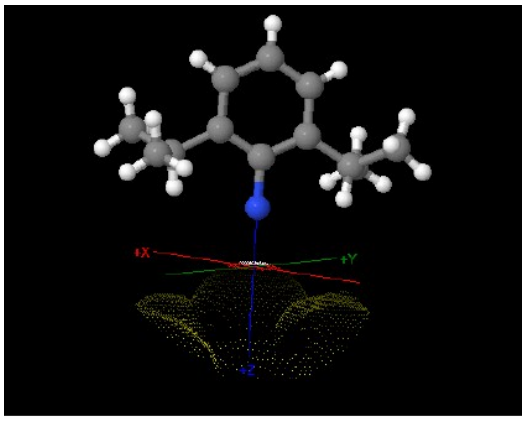


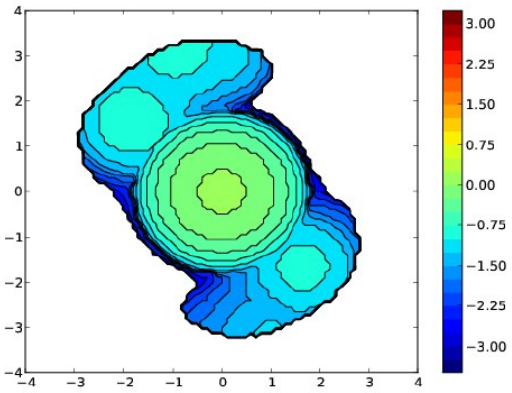
V Free	V Buried	V Total	V Exact
127.5	52.0	179.5	179.6

%V_Free	%V_Bur	% Tot/Ex
71.1	**28.9**	100.0

Quadrant	V_f	V_b	V_t	%V_f	%V_b
SW	34.1	10.8	44.9	76.0	**24.0**
NW	29.7	15.2	44.9	66.1	**33.9**
NE	34.1	10.8	44.8	76.0	**24.0**
SE	29.7	15.2	44.9	66.1	**33.9**

Figure S10. *EPR spectrum of [V(=N-2,6-^{i}Pr-C_6H_3)$Cl_2(NHMe_2)_2$]* (**1d**)





V Free	V Buried	V Total	V Exact
136.9	42.7	179.5	179.6

%V_Free	**%V_Bur**	% Tot/Ex
76.2	**23.8**	100.0

Quadrant	V_f	V_b	V_t	%V_f	**%V_b**
SW	37.1	7.8	44.9	82.6	**17.4**
NW	31.0	13.9	44.9	69.1	**30.9**
NE	36.5	8.3	44.8	81.4	**18.6**
SE	32.2	12.6	44.9	71.8	**28.2**

Figure S11. DSC heating scans of selected poly(ethylene)s (Table 2 in the manuscript).

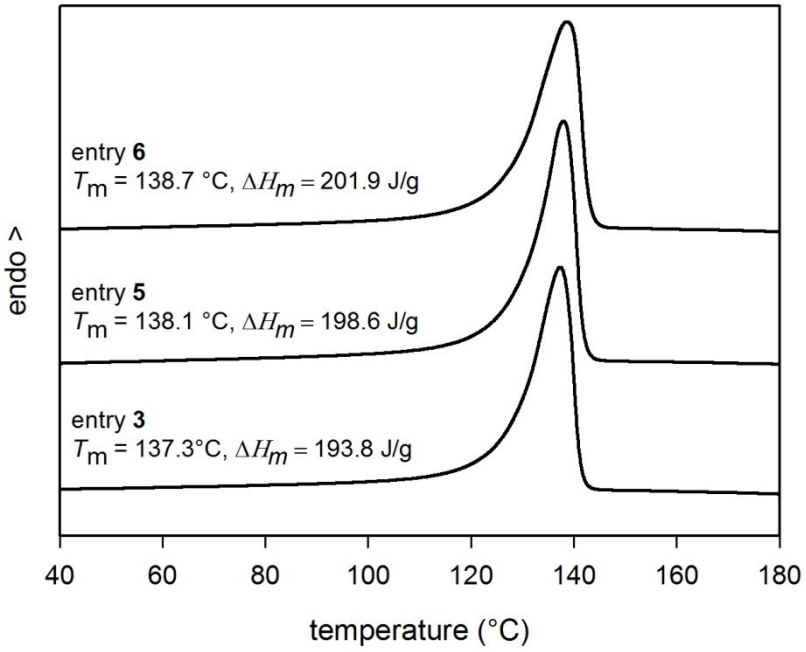


Figure S12. ^{13}C NMR spectra (in $C_2D_2Cl_4$ at 103 °C, reference to HDMS) of (a) a selected poly(ethylene-*co*-1-hexene) (Table 5, entry **18**, HEX = 11.2 mol%) and (b) a selected poly(ethylene-*co*-1-octene) (Table 5, entry **15**, OCT = 9.0 mol%). For $S_{\beta\gamma}$, $T_{\gamma\delta}$ refer to the inset of Figure 7.

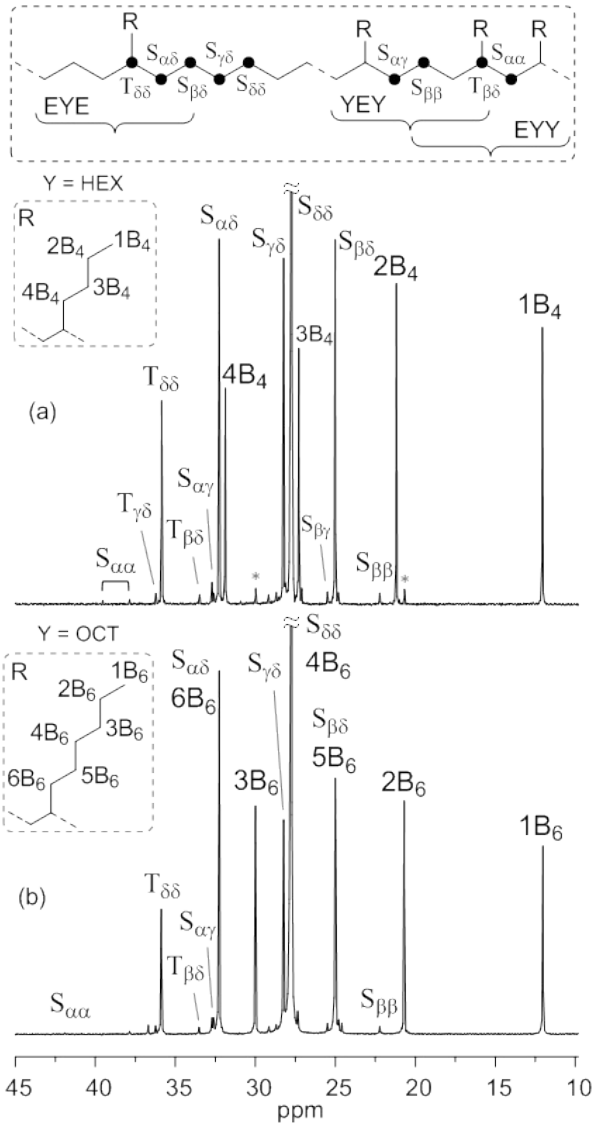
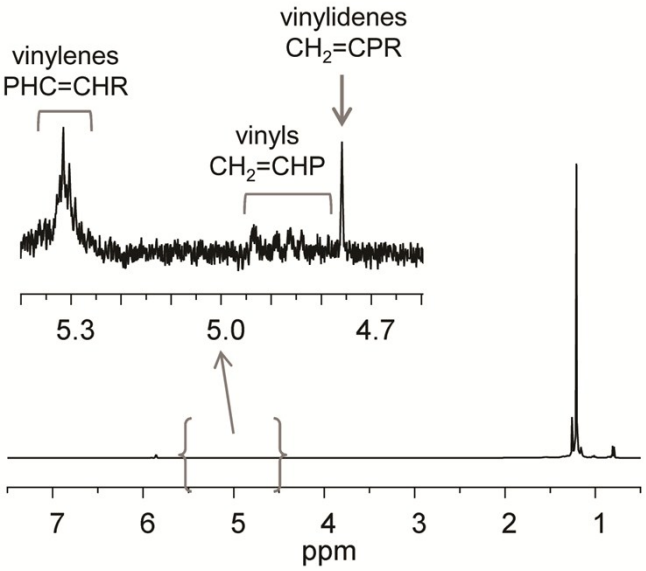


Figure S12a shows the ^{13}C NMR spectrum of sample **18** (HEX = 11.2 mol%). The copolymer mainly contains isolated butyl branches ([EYE] where Y is the comonomer and assigned as $T_{\delta\delta}$ at 35.8 ppm), but also alternated sequences ([YEY] assigned as $S_{\beta\beta}$ at 22.2 ppm). Moreover, 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 ββ 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. ^{1}H NMR spectrum (in $C_2D_2Cl_4$ 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 σ_e is the surface free energy equal to 0.087 J m^{-2} and ΔH_0 is the melting enthalpy of PE crystal equal to 290 x 10^6 J m^{-3}, T^0_m is the equilibrium melting temperature of poly(ethylene) (T^0_m = 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^c_m) was calculated by Flory's theory [72]:

$$\frac{1}{T_m^c} = \frac{1}{T_m^0} - \frac{R \ln x}{\Delta H_u}$$

where R is the gas constant, T^0_m is the equilibrium melting temperature of polyethylene (T^0_m = 418.7 K), ΔH_u is the molar heat of fusion of repeat units in the crystal (ΔH_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:

$$Z_n = \frac{n_1 Z_1 + n_2 Z_2 + \ldots\ldots\ldots\ldots + n_i Z_i}{n_1 + n_2 + \ldots\ldots\ldots\ldots + n_i}$$

(6)

$$Z_w = \frac{n_1 Z_1^2 + n_2 Z_2^2 + \ldots\ldots\ldots\ldots + n_i Z_i^2}{n_1 Z_1 + n_2 Z_2 + \ldots\ldots\ldots\ldots + n_i Z_i}$$

(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 ΔH_0 to the fusion of each fraction [$\Delta H_m(T)$] as the correction factor.[75]

references

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73. M. Keating, I.H. Lee, C.S. Wong, Thermal fractionation of ethylene polymers in packaging applications, Thermochim. Acta 284 (1996) 47–56.

74. Kong, X. Fan, Y. Xie, W. Qiao, Study on molecular chain heterogeneity of linear low density polyethylene by cross-fractionation of temperature rising elution fractionation and successive self-nucleation/annealing thermal fractionation, J. Appl. Polym. Sci. 94 (2004) 1710–1718.

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