Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

SUPPLEMENTARY INFORMATION

Titanium-based phenoxy-imine catalyst for selective ethylene trimerization: effect of temperature on the activity, selectivity and properties of polymeric side product

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Evolution of the SFI system selectivity with temperature

The results of the temperature study represented in Fig. 2 are gathered in the following table.

*Table S1. Yields and selectivities according to reaction temperature for the SFI system complex **2**/MAO*

Entry	n_{Ti} (µmol)	T (°C)	t (min)	C_6 (g) (wt %)	C_{10} (g) (wt %)	C_{14} (g) (wt %)	PE (g) (wt %)
1	2.77	26	29	22.20	4.49	0.03	0.08
				82.9%	**16.7%**	**0.1%**	**0.3%**
2	3.46	32	35	49.86	8.00	0.12	0.55
				85.37%	**13.7%**	**0.2%**	**0.9%**
3	3.78	42	32	44.21	5.75	0.10	1.69
				85.4%	**11.1%**	**0.2%**	**3.3%**
4	3.4	49	31	6.80	0.59	0.01	6.07
				50.4%	**4.4%**	**0.1%**	**45.1%**
5	4.59	58	31	9.61	0.38	0.00	9.55
				49.2%	**1.9%**	**0.0%**	**48.9%**
6	3.19	68	28	2.00	0.03	0.00	4.84
				29.1%	**0.5%**	**0.0%**	**70.4%**
7	3.85	80	31	1.44	0.00	0.00	5.93
				19.6%	**0.0%**	**0.0%**	**80.4%**

Conditions: 300 mL toluene, Al/Ti = 1 000 - 1 700, MAO 30 wt % in toluene, 10 bar of ethylene

Evolution of 1-hexene content in PE-T (T = 26-80 °C)

1-hexene contents in Fig. 3 were calculated from ^{13}C NMR results. The signal corresponding to the CH_2 of the polyethylene backbone was calibrated at 30 ppm (Figure S1). The characteristic carbons are identified using the notation from Galland *et al.*[1]

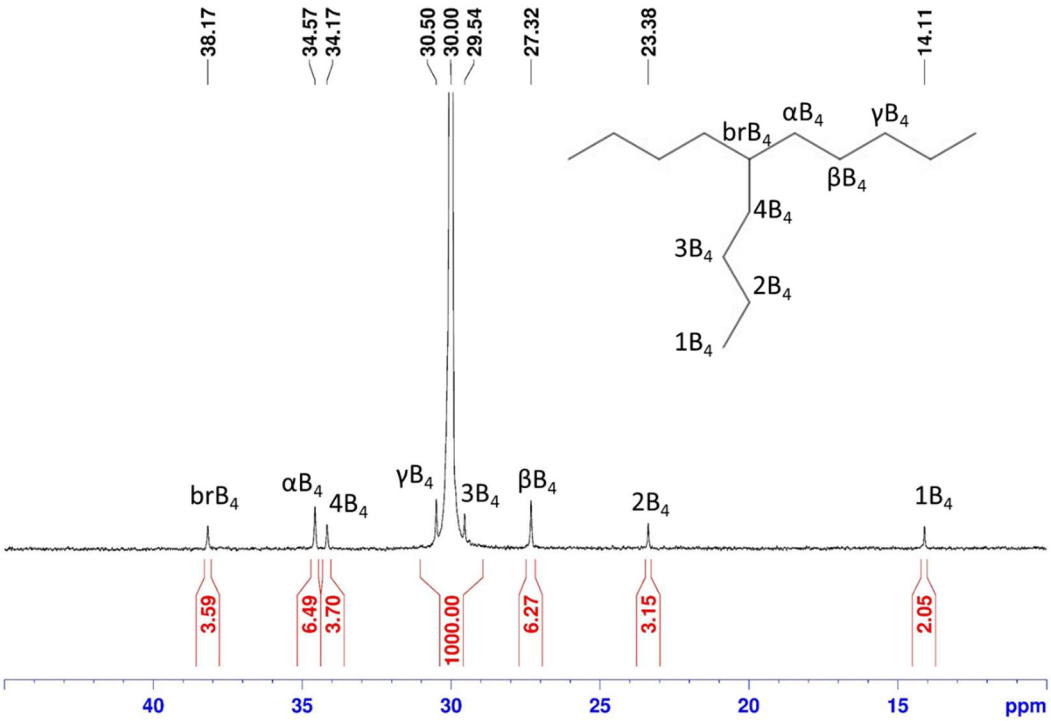


Figure S1. ^{13}C NMR of PE-42 in o-DCB-d_4/o-DCB (1/9) at 393 K

The calculation of 1-hexene content in the polymer was made based on the method reported by Cossoul *et al.*[2] They considered the integral of the polyethylene backbone I(CH_2) as well as Iα and Iβ, corresponding to αB_4 and βB_4 respectively.

The integration between 29 and 31 ppm, called I(CH_2), is calibrated at 1 000 carbons. This range is composed of signals corresponding to CH_2 from the ethylene units (E) in the polyethylene backbone excluding 1-hexene moiety as well as CH_2 in $3B_4$ position of 1-hexene (H) units. Therefore, I(CH_2) is defined as:

$$I(CH_2) = 2(E-H)$$

αB_4 and βB_4 counting for two 1-hexene molecules, their integrals (Iα at 34.5 ppm and Iβ at 27.3 ppm) were averaged to quantify the number of 1-hexene units:

$$H = (I\alpha + I\beta)/4$$

Consequently, the 1-hexene content was calculated as follow:

$$\text{mol \% 1-hexene} = H/(E+H) = (I\alpha + I\beta)/(2x(I(CH_2) + I\alpha + I\beta)$$

The melting temperature of the polymer measured by DSC and the 1-hexene content calculated from high temperature ^{13}C NMR are plotted in the following graph :

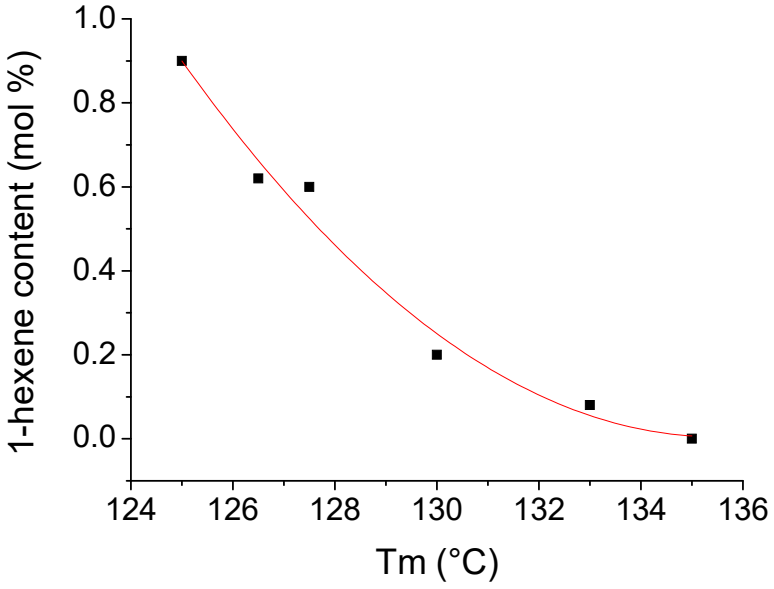


Figure S2. Relationship between 1-hexene content and melting temperature for PE-32 to PE-80

The equation of the corresponding fitting curve is:

$$\%_{C6} = 0.00799\,\mathrm{Tm}^2 - 2.168\,\mathrm{Tm} + 147.01 \text{ with } R^2 = 0.97$$

The relationship between 1-hexene content in the polymer and in the reaction medium was compared with a common metallocene (nBuCp)$_2$ZrCl$_2$/MAO[2]. It was found that the polymerization catalyst from (FI)TiCl$_3$/MAO system incorporates less 1-hexene than the metallocene, which is known for its limited ability for LAO copolymerization.

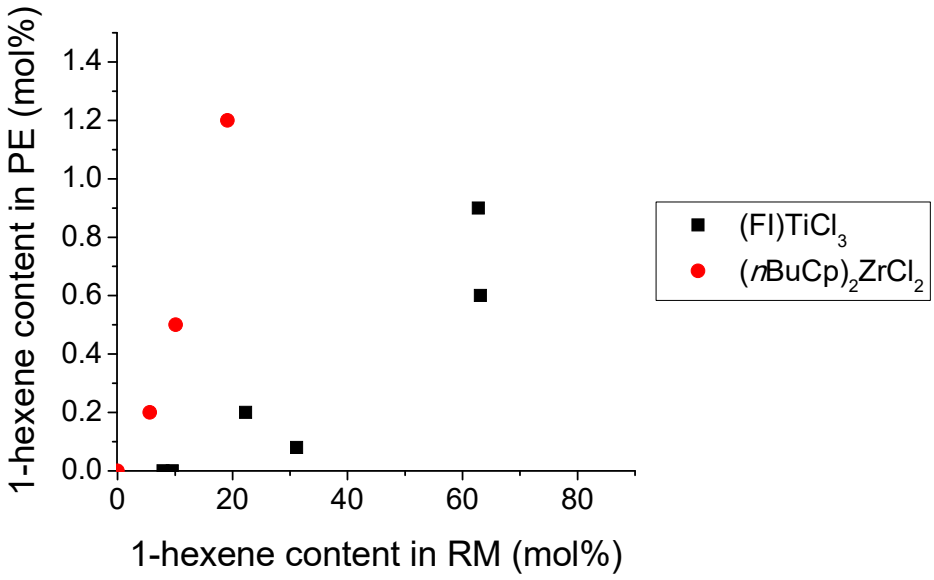


Figure S3. Comparison of 1-hexene incorporation ability between (FI)TiCl$_3$/MAO and (nBuCp)$_2$ZrCl$_2$/MAO.

Kinetic studies

Homogeneous catalysis and polymerization platform

The homogeneous catalysis and polymerization platform used for the kinetic studies provides reliable reproducibility given its automation, protected atmosphere and efficient cooling/heating system.

Complex **2** synthesis was performed using the ISYNTH® module (**Erreur ! Source du renvoi introuvable.**, right), which is able to cool/heat (-20/150 °C) and stir at ambient or reduced atmosphere. Reflux, evaporation, crystallization, filtration and drying are common steps that can be performed automatically with this device.

Catalytic tests for the kinetic studies were performed on the three 270 mL-semi batch reactors (**Erreur ! Source du renvoi introuvable.**, left) equipped with two high pressure pumps. The control of temperature is managed individually by coupling of a heating and cooling circuit.

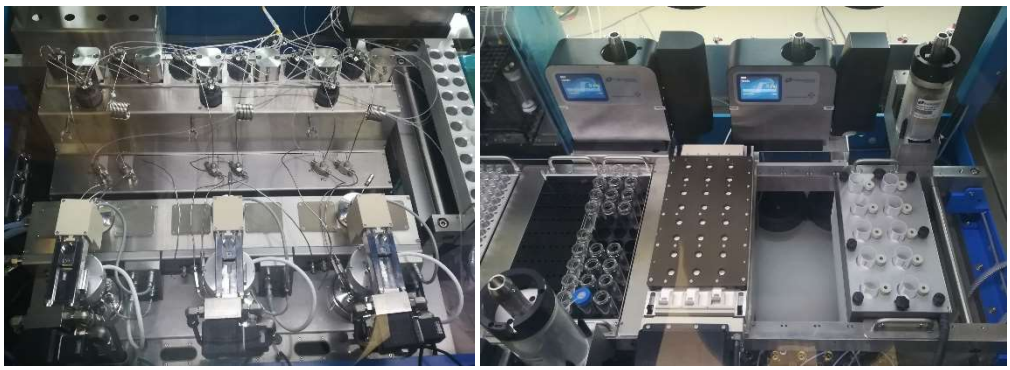


Figure S4. Automated Chemspeed platform equipped with three semi-batch reactors (left) and ISYNTH© module (right)

Reproducibility of catalytic tests with Chemspeed autoclaves

A series of experiments were carried out at 40, 60 and 80 °C by varying the time of reaction. The conditions and results are presented in the following table:

Table S2. Catalytic tests for the kinetic studies

Entry	T (°C)	t (min)	n_{Ti} (µmol)	Al/Ti
1	40	5	1.73	1 550
2	40	10	1.90	1 420
3	40	20	1.90	1 420
4	40	30	1.90	1 420
5	60	5	1.73	1 550
6	60	20	1.95	1 380
7	60	30	1.73	1 550
8	80	5	1.79	1 506
9	80	10	1.84	1 460
10	80	20	1.84	1 460
11	80	30	1.78	1 130

Conditions: complex **2**, 120 mL toluene, MAO 30 wt % in toluene, 10 bar of ethylene

The reproducibility of experiments performed at the same reaction temperature was verified by comparing temperature and ethylene consumption overtime (**Erreur ! Source du renvoi introuvable.**).

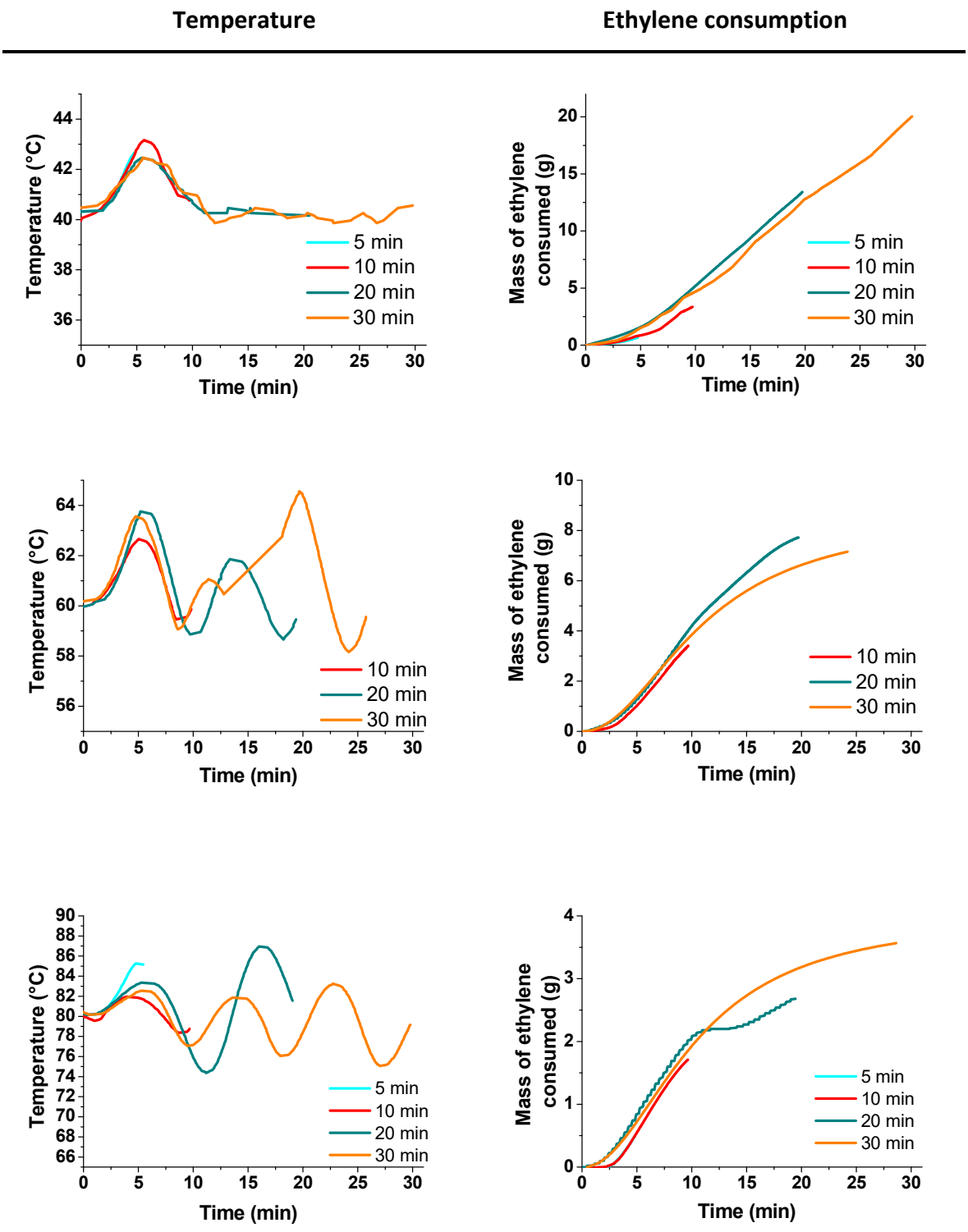


Figure S5. Comparison of temperature and ethylene consumption profiles for catalytic tests conducted for 5, 10, 20 and 30 minutes at 40, 60 and 80 °C

Kissin's model

Reaction rate profiles are extracted from ethylene consumption for experiments lasting 30 minutes (Table S3). From these profiles, the speed of reaction is calculated and fitted with Kissin's model for polymerization reaction (Table S5).

Table S3. Kissin's model scheme and proposed analogy with the trimerization system

C('): precatalyst; C('): Catalyst; P_x: -$C_{2x}H_{4x}$; D('): dead species*

Step		Kissin model for polymerization	Analogy to trimerization reaction
Formation	k_f	C → C*	C' + C_2 → C'*
Initiation	k_i	C* + C_2H_4 → C-P_1	C'* + 2 C_2 → C'*-C_4
Propagation	k_p	C*-P_n + C_2H_4 → C*-P_{n+1}	C'*-C_4 + C_2 → C'*-C_6
Transfer	k_t	C*-P_m → C* + P_m	C'*-C_6 → C'* + C_6
Deactivation	k_d	C* → D	C'* → D'

Kissin's equation for reaction rate is:

$$\mathrm{Rp} = \mathrm{k_p[Ti][C_2]}\frac{\mathrm{k_i}}{\mathrm{k_d - k_i}}\left(\mathrm{e^{-k_i t}} - \mathrm{e^{-k_d t}}\right)$$

Ethylene concentration were calculated from Kissin's equation and applied to our conditions (P_{C_2}=10 bar)[3]:

$$[\mathrm{C_2}] = 1.74 \times 10^{-3}\, \mathrm{P_{C_2}} \mathrm{e}^{1284/\mathrm{T}}$$

P_{C_2}: ethylene pressure (bar)

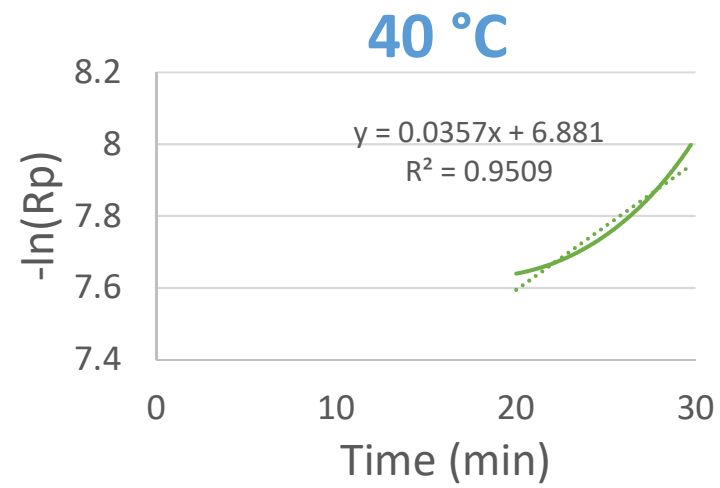
T: temperature (Kelvin)

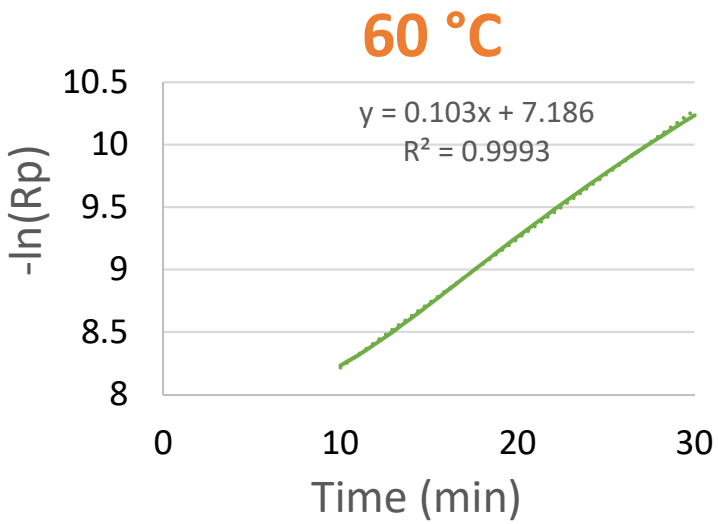
Table S4. Ethylene concentration according to reaction temperature

Temperature (°C)	[ethylene] (mol L^{-1})
40	1.052
60	0.822
80	0.661

Conditions: 120 mL toluene, 10 bar ethylene

The trimerization/polymerization reaction were found to be first-order with respect to ethylene concentration as is the logarithm of the rate of reaction is a linear function of time (**Erreur ! Source du renvoi introuvable.**).





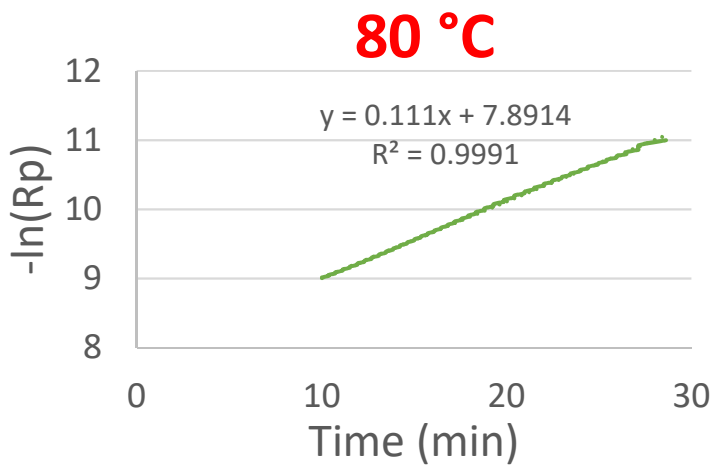


Figure S6. Evidences of first-order reaction rate at 40, 60 and 80 °C

Fitting with experimental data emphasizes the 1st order with respect to ethylene concentration. The rate constants were determined by ordinary differential equations solver with EXCEL.

Table S5. Kinetic constants obtained after data fitting

T	k_i (s^{-1})	k_p (L mol^{-1} s^{-1})	k_d (s^{-1})
40 °C	5.965×10^{-4}	146.1	1.735×10^{-3}
60 °C	2.604×10^{-3}	57.19	2.640×10^{-3}
80 °C	2.902×10^{-3}	39.98	2.901×10^{-3}

Evolution of polymer properties with temperature and time

The 1-hexene content was determined from the melting temperature of the polymers applying the equation found for PE-26 to PE-80 (**Erreur ! Source du renvoi introuvable.**).

Table S6. Melting temperature and corresponding 1-hexene content for polymers obtained in the kinetic studies

Entry	T (°C)	t (min)	T_m (°C)	1-hexene content (mol %)
1	40	5	127.6	0.51
2	40	10	128.1	0.45
3	40	20	124.8	0.93
4	40	30	125	0.90
5	60	5	129.5	0.30
6	60	20	129.6	0.29
7	60	30	128.8	0.37
8	80	5	135	0.00
9	80	10	134.6	0.01
10	80	20	134	0.02

Data presented in Fig. 6 are gathered hereafter.

Table S7. 1-hexene content in the polymer and reaction medium for each catalytic tests of the kinetic study

Entry	T (°C)	t (min)	$\%_{C6\ PE}$ (mol %)	$\%_{C6\ RM}$ (mol %)
1	40	5	0.51	29.7
2	40	10	0.45	34.4
3	40	20	0.93	51.0
4	40	30	0.90	52.2
5	60	5	0.30	28.0
6	60	20	0.29	33.6
7	60	30	0.37	34.2
8	80	5	0.00	5.2
9	80	10	0.01	5.2
10	80	30	0.02	5.6

The curve in Fig. 6 follows the equation:

$$\%_{C6\ PE} = -0.00735\ \%_{C6\ RM}{}^{2} + 83.959\ \%_{C6\ RM} + 3239.11 \text{ with } R^2=0.95$$

$\%_{C6\ RM}$ is the 1-hexene content in the reaction at the end of reaction relative to the amount of titanium (in mmol)

It was calculated based on the amount of 1-hexene dosed by GC analysis and the concentration of ethylene calculated in the conditions of catalytic tests (Table S4).

References

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