Supporting Information

for

Ethylene Copolymerization with 4-Methylcyclohexene, 1-Methylcyclopentene by Half-Titanocene Catalysts: Effect of Ligands and Microstructural Analysis of the Copolymers

Hitoshi Harakawa,[‡,a] Srisuda Patamma, [‡,a] Antonella Caterina Boccia,[b] Laura Boggioni, [b] Dino Romano Ferro,[b] Simona Losio, [b] Kotohiro Nomura,*[,a] and Incoronata Tritto*[,b]

[a]*Department of Chemistry, Tokyo Metropolitan University, 1-1 Minami Osawa, Hachioji, Tokyo 192-0397, Japan.* [b]*CNR Istituto per lo Studio delle Macromolecole (ISMAC), Via E. Bassini, 15 - 20133 Milano, Italy*

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*Corresponding Authors, tel.: +39-02-23699370, fax: +39-02-70636400, tritto@ismac.cnr.it (I.T.), tel.&fax: +81-42-677-2547, e-mail: ktnomura@tmu.ac.jp (K.N.)

‡H. Harakawa and S. Patamma: contributed equally as the first author

1. Additional copolymerization results. Time course, and effects of temperature, Al/Ti molar ratios.

Table S1-1. Copolymerization of ethylene and 4-methylcyclohexene (4-MeCHE), 1-methylcyclopentene (1-MeCPE) by (1,2,4-$Me_3C_5H_2$)$TiCl_2$(O-2,6-$^i Pr_2C_6H_3$) (**1**) — MAO catalyst system.[a]

run	**1** / μmol	comonomer (conc.[b] M)	MAO / mmol	time / min	temp / °C	yield / mg	activity[c]	M_n[d] ×10^{-4}	M_w/M_n[d]	T_m[f] / °C
S1	0.2	4-MeCHE (5.0)	3.0	5	25	93.9	5630	21.0	1.82	74
8	0.2	4-MeCHE (5.0)	3.0	10	25	187	5600	30.8	1.80	79
9	0.2	4-MeCHE (5.0)	3.0	10	25	206	6170	28.7	1.81	74
S2	0.2	4-MeCHE (5.0)	3.0	15	25	258	5160	27.0	1.89	79
S3	0.2	4-MeCHE (5.0)	3.0	10	60	252	7570	17.3	2.01	80[g]
S4	0.2	4-MeCHE (5.0)	3.0	10	60	289	8670	18.9	2.09	82[g]
31	0.5	1-MeCPE (2.5)	1.0	10	25	51.9	623	10.7	1.37	112
32	0.5	1-MeCPE (2.5)	3.0	10	25	130	1560	6.28	1.40	110
S5	0.5	1-MeCPE (2.5)	3.0	10	25	129	1540	6.29	1.49	111
S6	0.5	1-MeCPE (2.5)	5.0	10	25	98.8	1190	11.1	1.41	109

[a]Conditions: toluene+comonomer total 10 mL, ethylene 2 atm. [b]Initial comonomer concentration (mol/L). [c]Activity in kg-polymer/mol-Ti·h. [d]GPC data in *o*-dichlorobenzene *vs* polystyrene standards. [e]Comonomer content (mol%) estimated by ^{13}C NMR spectra. [f]By DSC thermograms. [g]Additional melting temperature (T_m) at ca.120 ºC was also observed in trace amount in the DSC thermogram (shown in Figure S4-14).

2. Selected ^{13}C NMR spectra for resultant copolymers including assignment of resonances and estimation of comonomer contents.

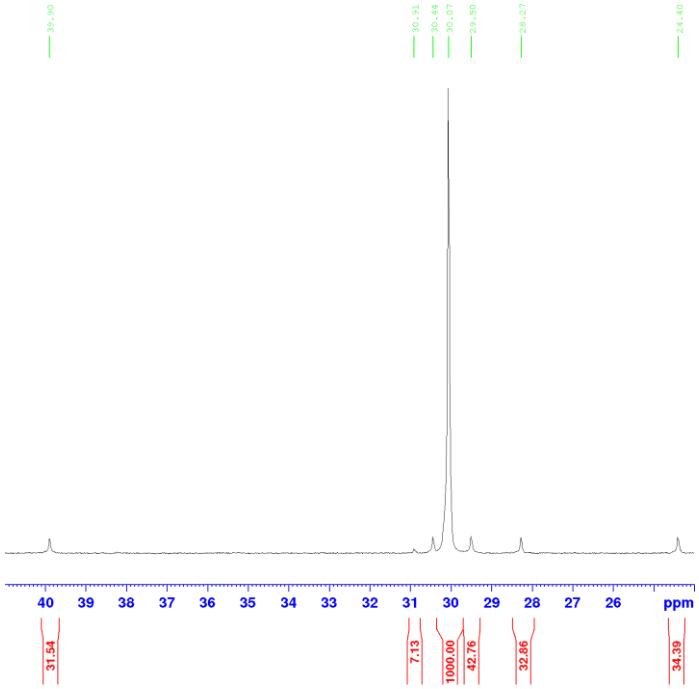


Figure S2-1. ^{13}C NMR spectrum (in 1,1,2,2- tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-CHE) prepared by (1,2,4-$Me_3C_5H_2$)$TiCl_2$(O-2,6-$^i Pr_2C_6H_3$) (**1**) - MAO catalyst system (run 1, Table 1, CHE 3.0 mol%).

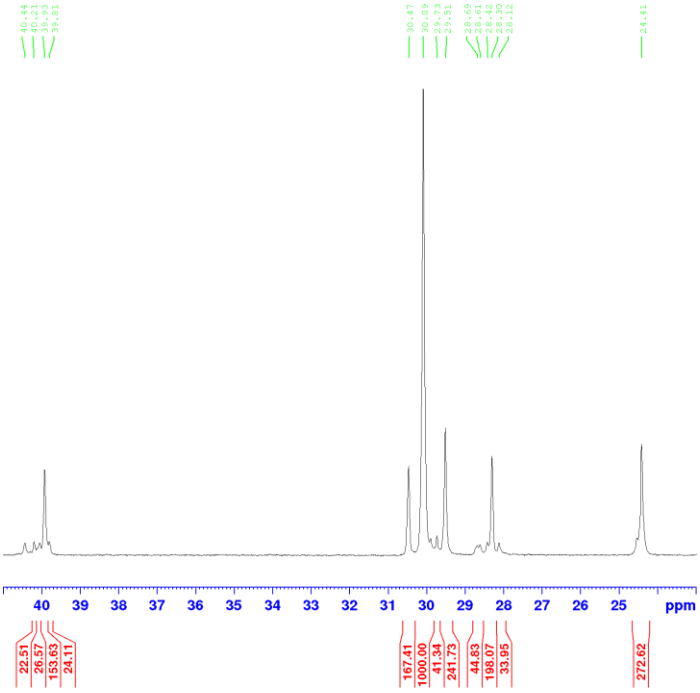


Figure S2-2. ^{13}C NMR spectrum (in 1,1,2,2- tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-CHE) prepared by (1,2,4-$Me_3C_5H_2$)$TiCl_2$(O-2,6-$^i Pr_2C_6H_3$) (**1**) - MAO catalyst system (run 3, Table 1, CHE 12.9 mol%).

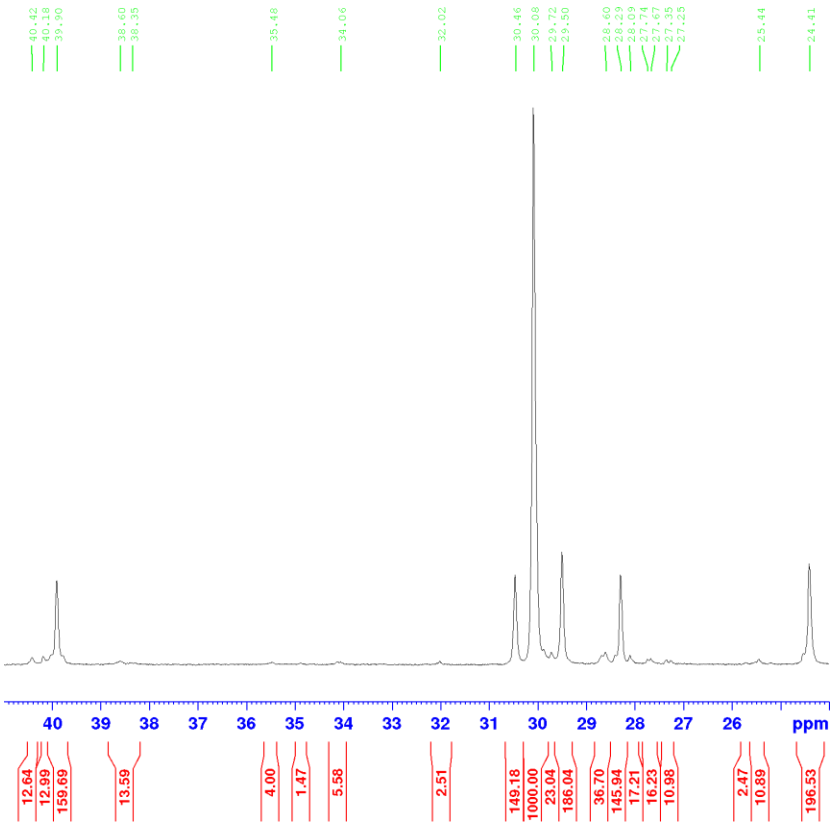
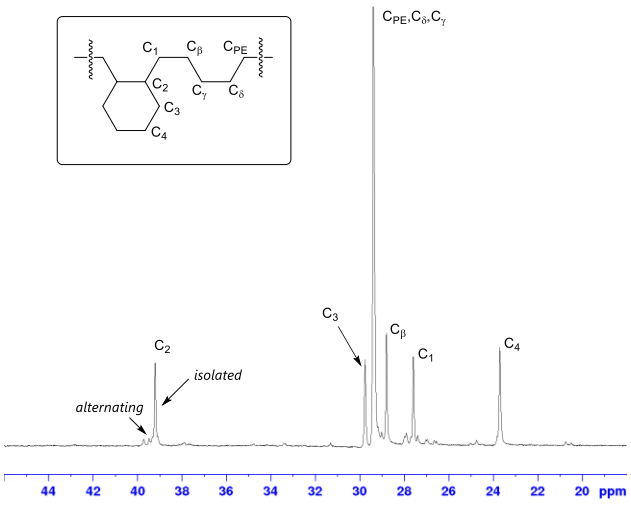


Figure S2-3. ^{13}C NMR spectrum (in 1,1,2,2- tetrachloroethane-d_2 at 110 °C) for poly(ethylene-*co*-CHE) prepared by ($^{t}BuC_5H_4$)$TiCl_2$(O-2,6-$^{i}Pr_2C_6H_3$) (**2**) - MAO catalyst system (run 12, Table 1, CHE 11.1 mol%).



(spectrum, run 3)

$$\text{CHE (mol\%)} = \frac{(C_2 + C_3 + C_4)/6}{(C_2 + C_3 + C_4)/6 + (C_1 + C_\beta + C_\gamma + C_\delta + C_{PE})/2} \times 100$$

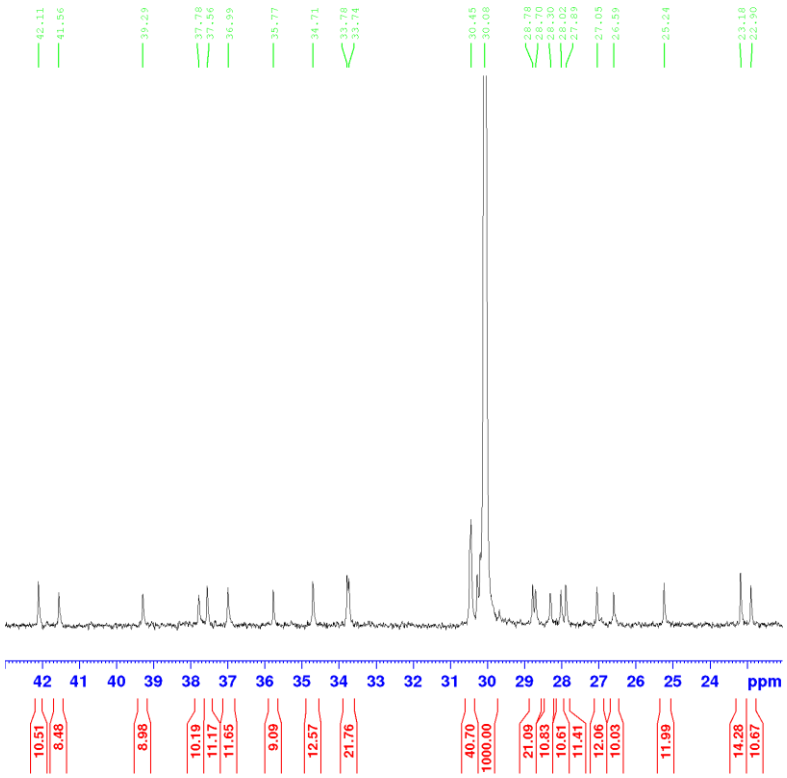


Figure S2-4. ^{13}C NMR spectrum (in 1,1,2,2- tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-4-MeCHE) prepared by (1,2,4-$Me_3C_5H_2$)$TiCl_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**) - MAO catalyst system (run 6, Table 1, 4-MeCHE 4.3 mol%).

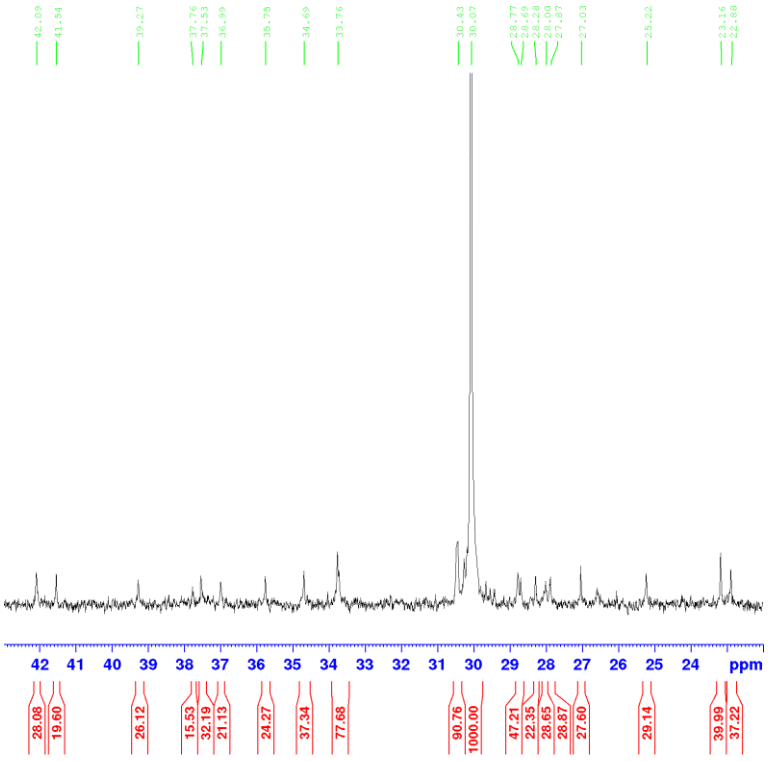


Figure S2-5. ^{13}C NMR spectrum (in 1,1,2,2- tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-4-MeCHE) prepared by (1,2,4-$Me_3C_5H_2$)$TiCl_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**) - MAO catalyst system (run 9, Table 1, 4-MeCHE 11.6 mol%).

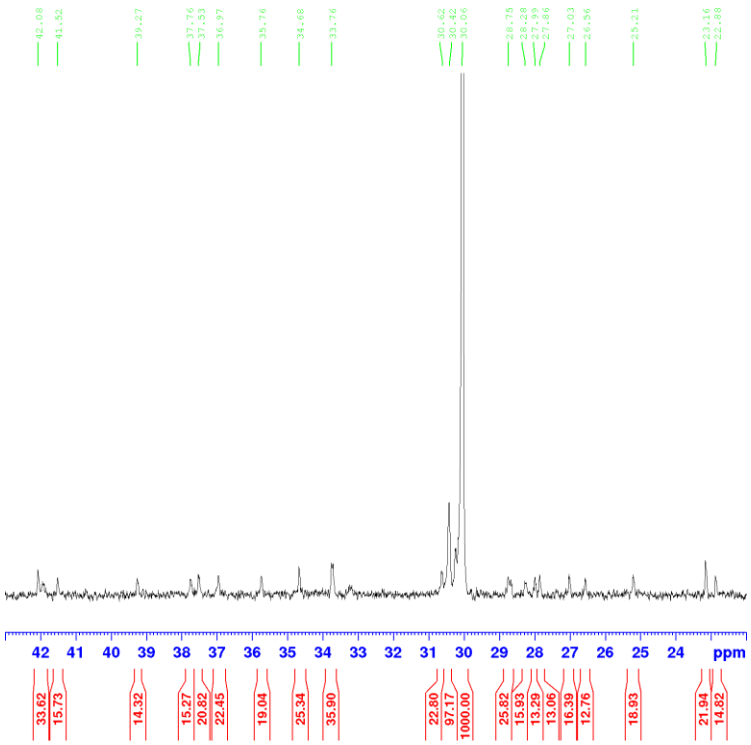


Figure S2-6. ^{13}C NMR spectrum (in 1,1,2,2- tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-4-MeCHE) prepared by (^{t}BuC$_5$H$_4$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**2**) - MAO catalyst system (run 15, Table 1, 4-MeCHE 6.3 mol%).

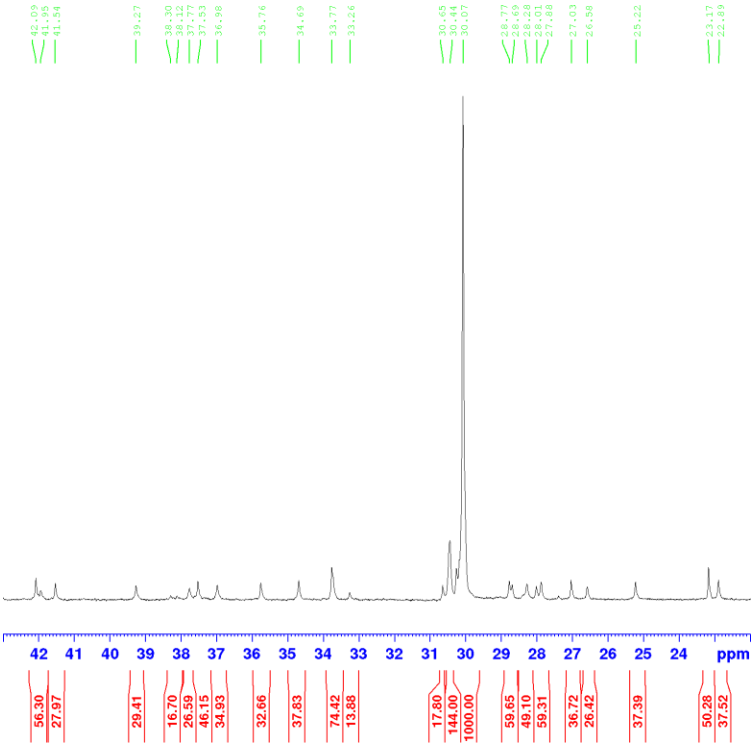


Figure S2-7. ^{13}C NMR spectrum (in 1,1,2,2- tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-4-MeCHE) prepared by (^{t}BuC$_5$H$_4$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**2**) - MAO catalyst system (run 16, Table 1, 4-MeCHE 12.3 mol%).

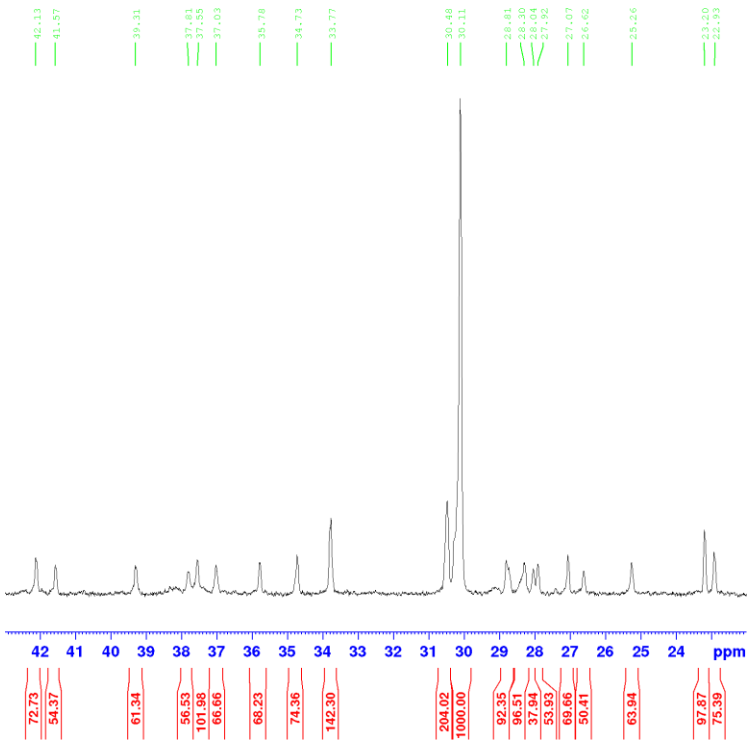
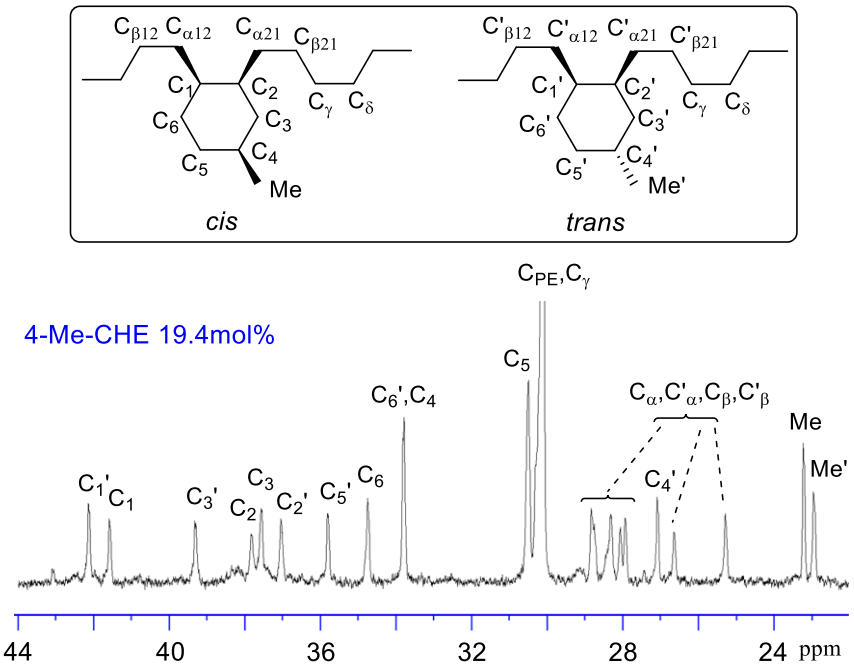


Figure S2-8. ^{13}C NMR spectrum (in 1,1,2,2- tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-4-MeCHE) prepared by ($^{t}BuC_5H_4$)$TiCl_2$(O-2,6-$^{i}Pr_2C_6H_3$) (**2**) - MAO catalyst system (run 17, Table 1, 4-MeCHE 19.4 mol%).



$$4\text{MeCHE (mol\%)} = \frac{\text{Me} + \text{Me}'}{\text{Me} + \text{Me}' + (\text{C}_\alpha + \text{C}_\beta + \text{C}_\gamma + \text{C}_{\text{PE}})/2} \times 100$$

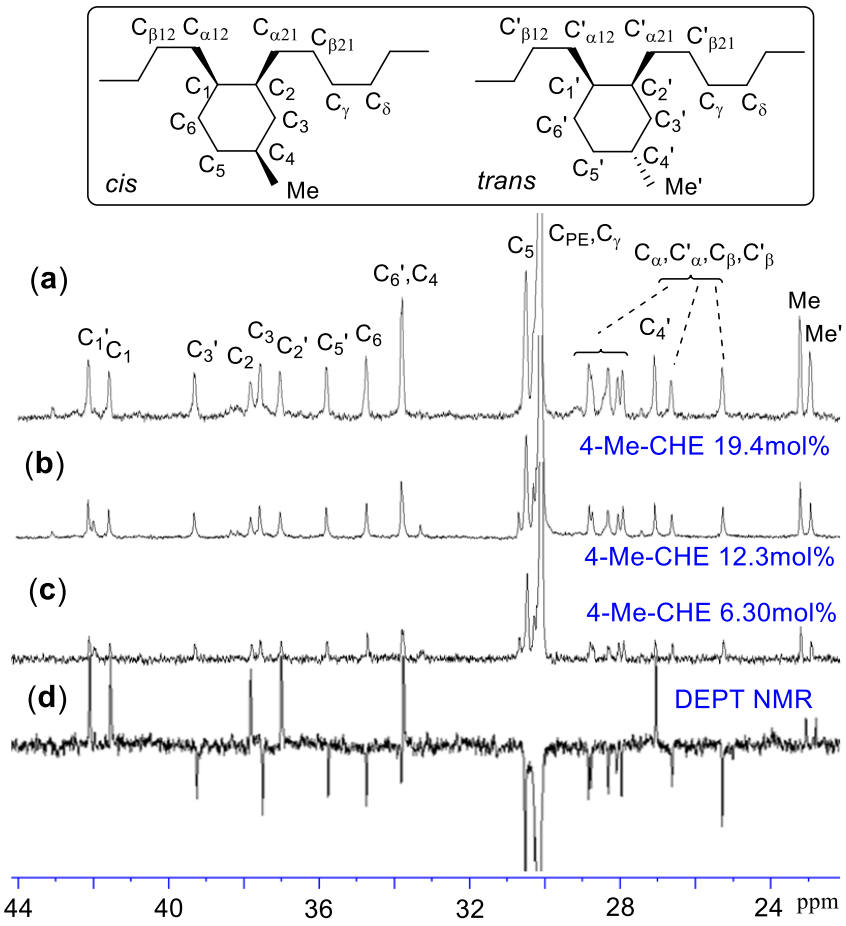


Figure S2-9. ^{13}C NMR spectra and the dept spectrum (in 1,1,2,2- tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-4-MeCHE)s prepared by ($^{t}BuC_5H_4$)$TiCl_2$(O-2,6-$^{i}Pr_2C_6H_3$) (**2**) - MAO catalyst system (runs 15-17, Table 1).

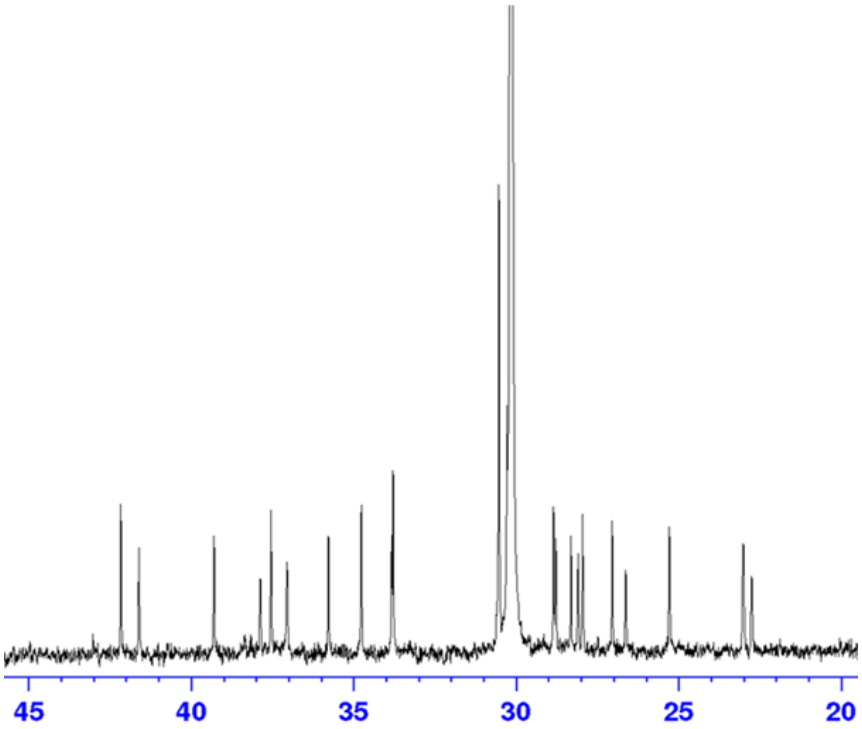


Figure S2-10. ^{13}C NMR spectrum (in 1,2,4-trichlorobenzene/C_6D_6 at 110 ºC) for poly(ethylene-*co*-4-MeCHE) prepared by ($^{t}BuC_5H_4$)$TiCl_2$(O-2,6-$^{i}Pr_2C_6H_3$) (**2**) - MAO catalyst system (runs 19, Table 1, 4-MeCHE 2.0 mol%).

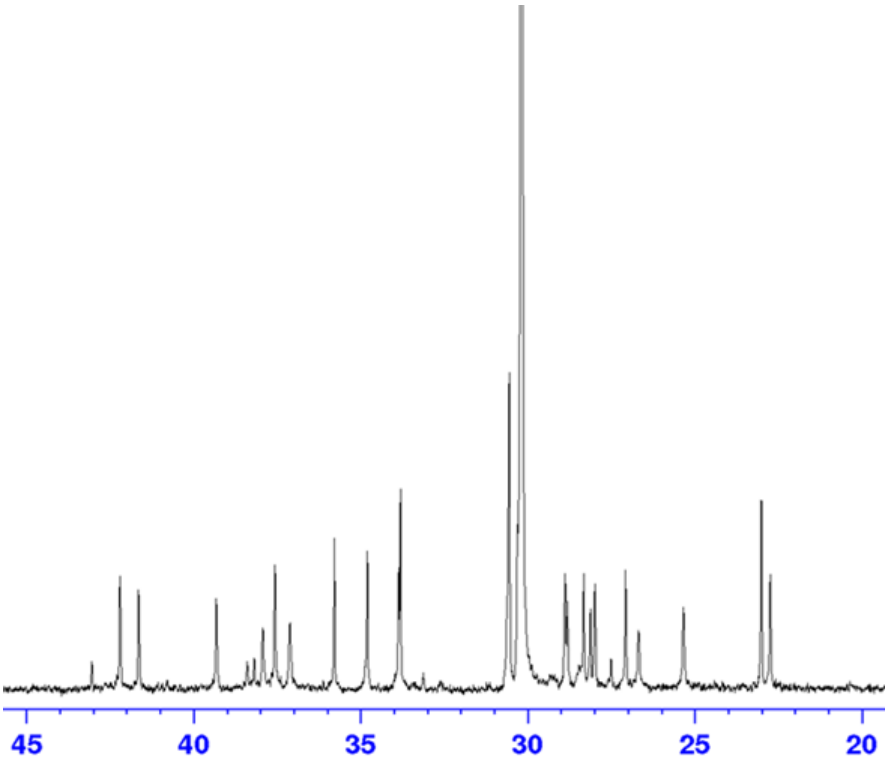


Figure S2-11. ^{13}C NMR spectrum (in 1,2,4-trichlorobenzene/C_6D_6 at 110 ºC) for poly(ethylene-*co*-4-MeCHE) prepared by ($^{t}BuC_5H_4$)$TiCl_2$(O-2,6-$^{i}Pr_2C_6H_3$) (**2**) - MAO catalyst system (runs 20, Table 1, 4-MeCHE 8.0 mol%).

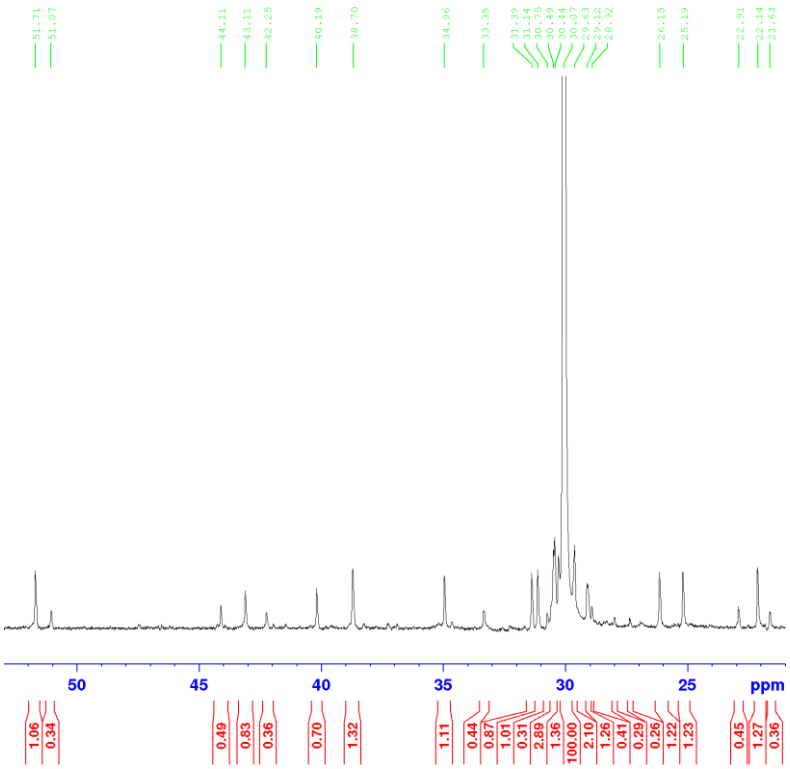


Figure S2-12. ^{13}C NMR spectrum (in 1,1,2,2- tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-1-MeCPE) prepared by (1,2,4-$Me_3C_5H_2$)$TiCl_2$(O-2,6-$^{i}Pr_2C_6H_3$) (**1**) - MAO catalyst system (runs 31, Table 2, 1-MeCPE 3.2 mol%).

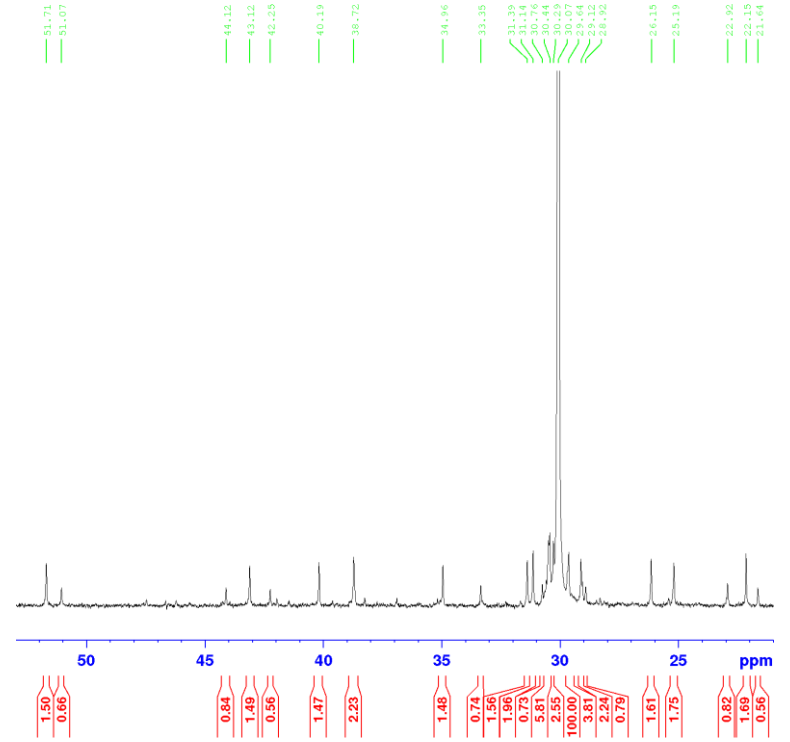


Figure S2-13. ^{13}C NMR spectrum (in 1,1,2,2- tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-1-MeCPE) prepared by (1,2,4-$Me_3C_5H_2$)$TiCl_2$(O-2,6-$^{i}Pr_2C_6H_3$) (**1**) - MAO catalyst system (runs 33, Table 2, 1-MeCPE 4.4 mol%).

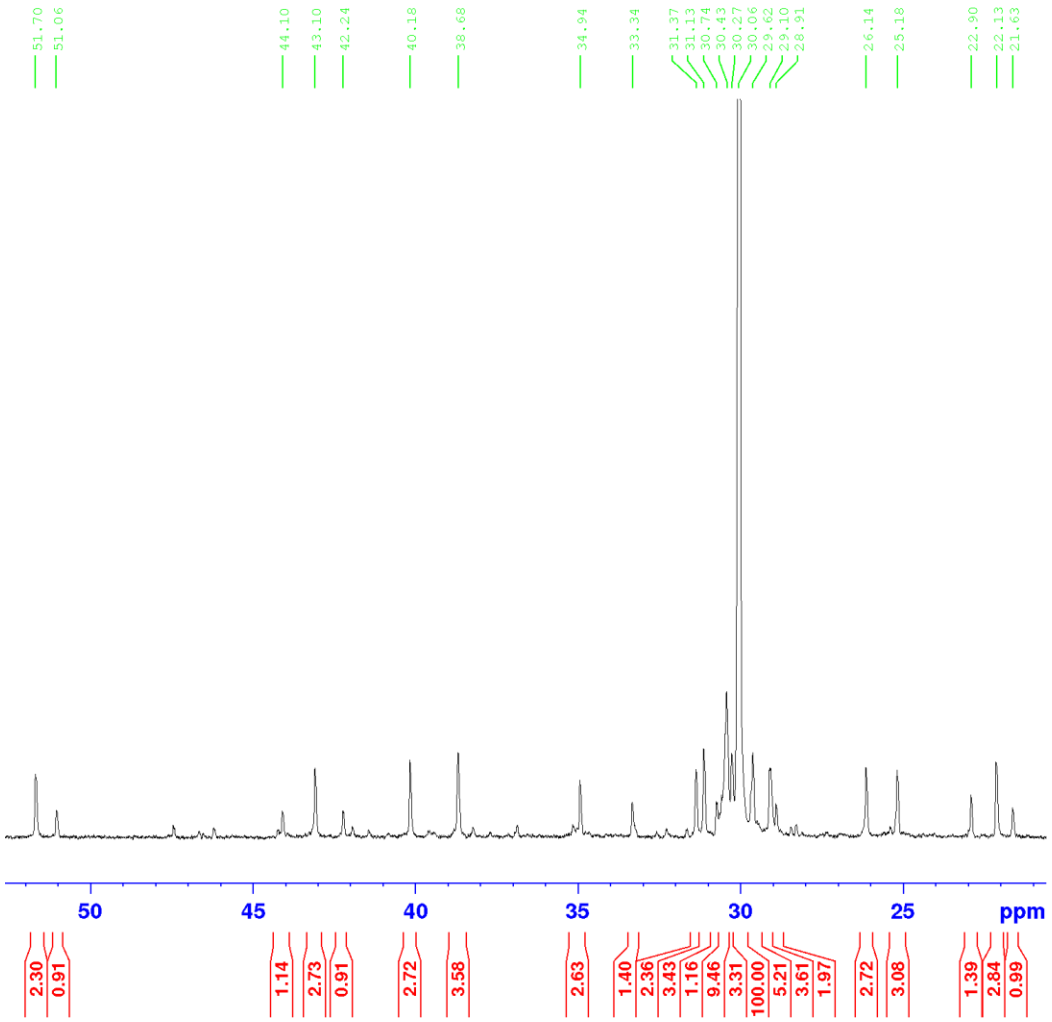


Figure S2-14. ^{13}C NMR spectrum (in 1,1,2,2- tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-1-MeCPE) prepared by (1,2,4-$Me_3C_5H_2$)$TiCl_2$(O-2,6-$^{i}Pr_2C_6H_3$) (**1**) - MAO catalyst system (runs 35, Table 2, 1-MeCPE 7.1 mol%).

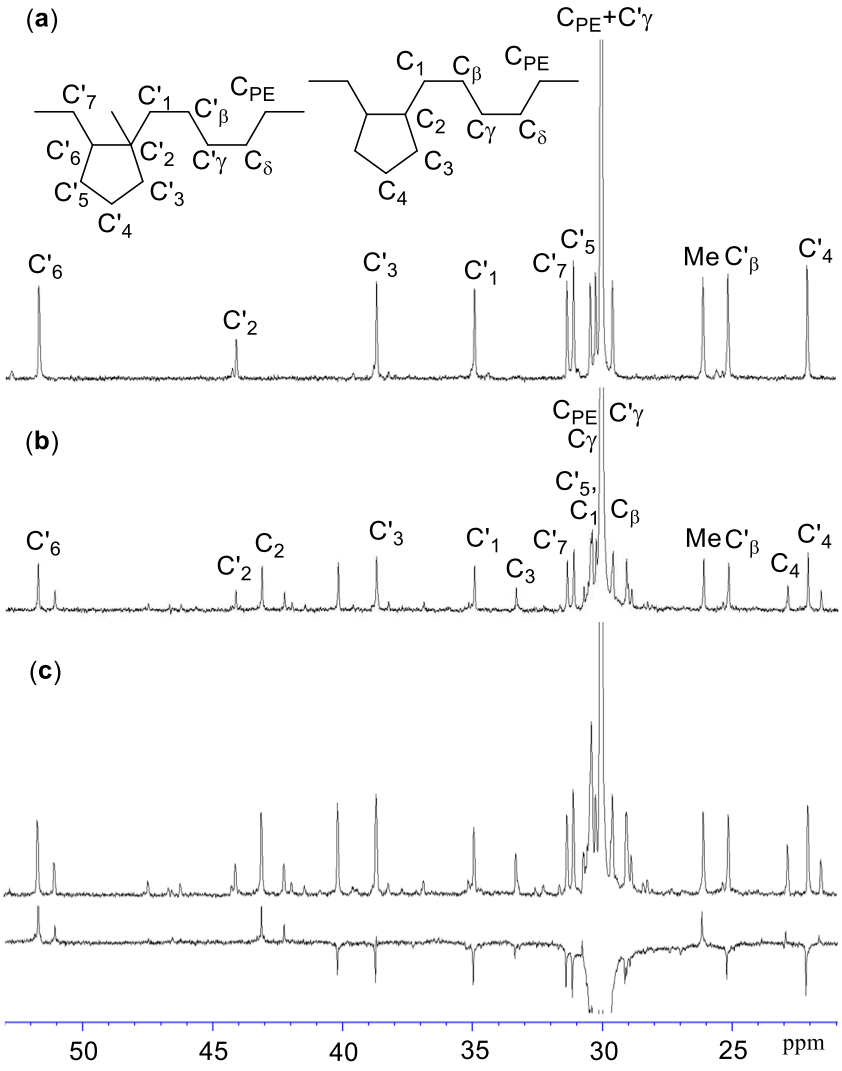


Figure S2-15. ^{13}C NMR spectra and the dept spectrum for poly(ethylene-*co*-1-MeCPE)s prepared by: (a) (^{t}BuC$_5$H$_4$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) - MAO catalyst system [**2**, run 41, Table 2 (1-MeCPE 8.2 mol%)]; (b,c) (1,2,4-Me$_3$C$_5$H$_2$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**) - MAO catalyst system [1-MeCPE content: (b) 4.4 mol% (run 33, Table 2), and (c) 7.1 mol% (run 35, Table 2)] (in 1,1,2,2- tetrachloroethane-d_2 at 110 ºC).

$$1\text{MeCPE (mol\%)} = \frac{\text{Me} + (C_4 + C_2)/3}{\text{Me} + (C_4 + C_2)/3 + (C_\beta + \text{C}'_7 + \text{C}'_\beta + \text{C}_\gamma + \text{C}_\delta + \text{C}_{\text{PE}})/2} x\ 100$$

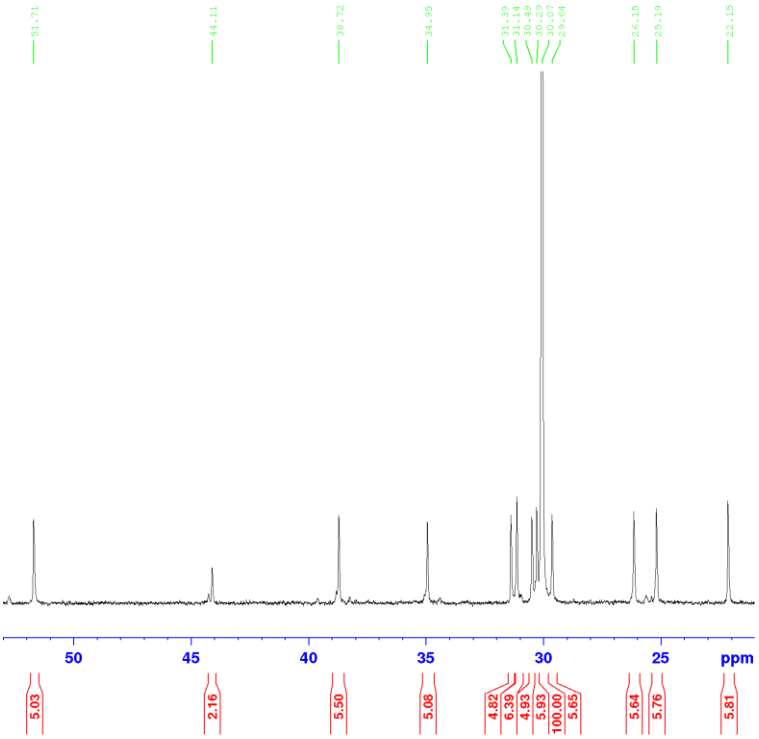


Figure S2-16. ^{13}C NMR spectrum (in 1,1,2,2- tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-1-MeCPE) prepared by ($^{t}BuC_5H_4$)$TiCl_2$(O-2,6-$^{i}Pr_2C_6H_3$) (**2**) - MAO catalyst system [runs 41, Table 2, 1-MeCPE 8.2 mol% (1-MeCPE content in the whole polymer)].

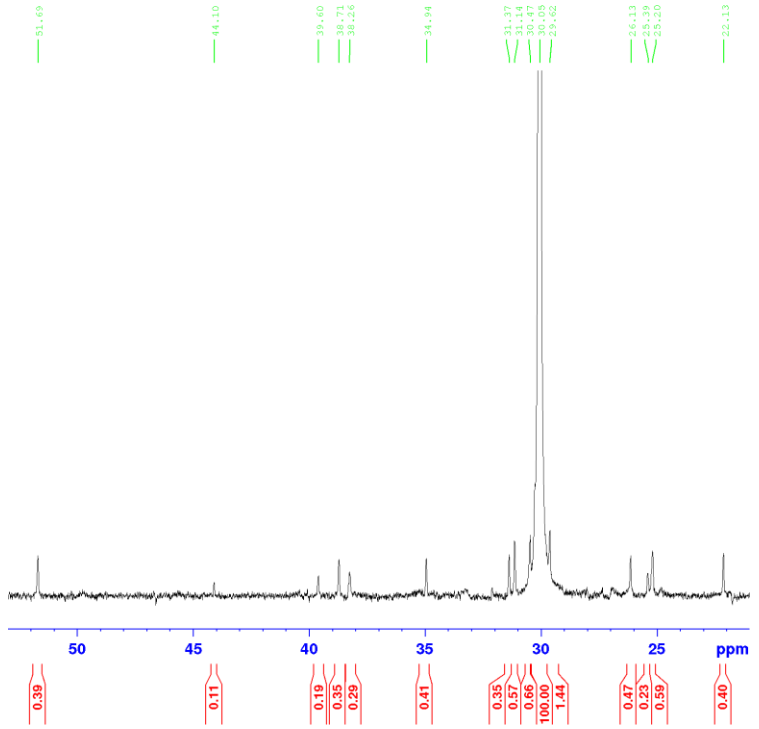


Figure S2-17. ^{13}C NMR spectrum (in 1,1,2,2- tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-1-MeCPE) prepared by Cp*$TiCl_2$(O-2,6-$^{i}Pr_2C_6H_3$) (**8**) - MAO catalyst system (runs 44, Table 2).

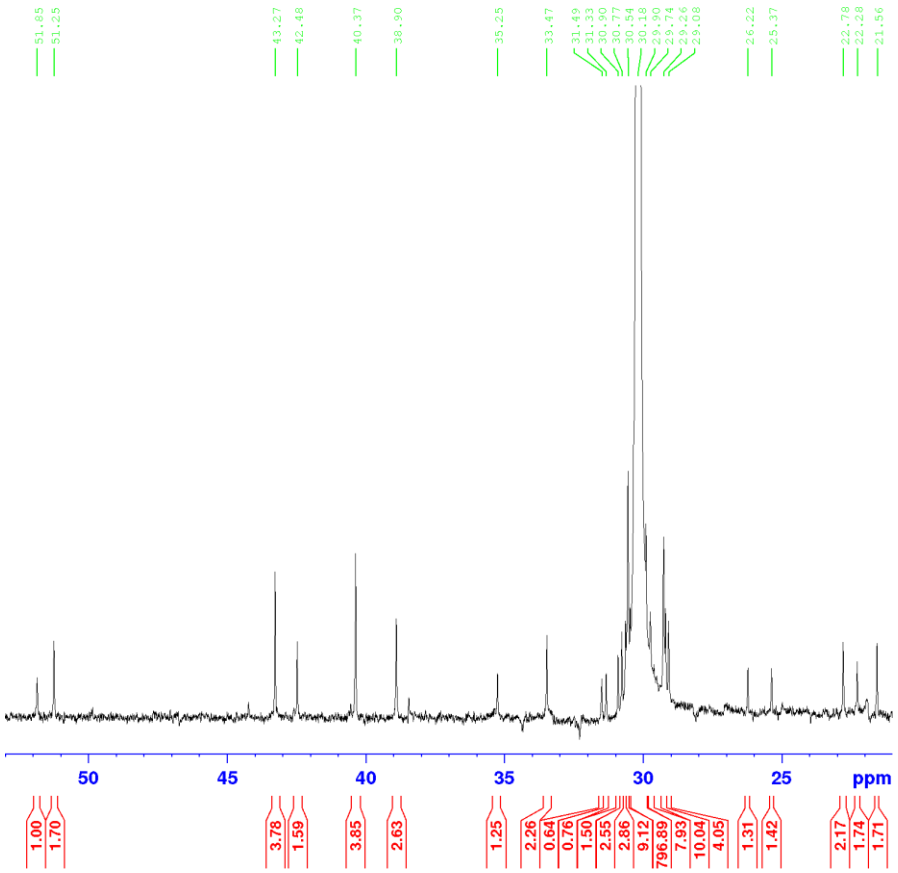


Figure S2-18. ^{13}C NMR spectrum (in 1,1,2,2- tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-1-MeCPE) prepared by ($^{t}BuC_5H_4$)$TiCl_2$(N=C$^{t}Bu_2$) (**3**) - MAO catalyst system (runs 48, Table 2).

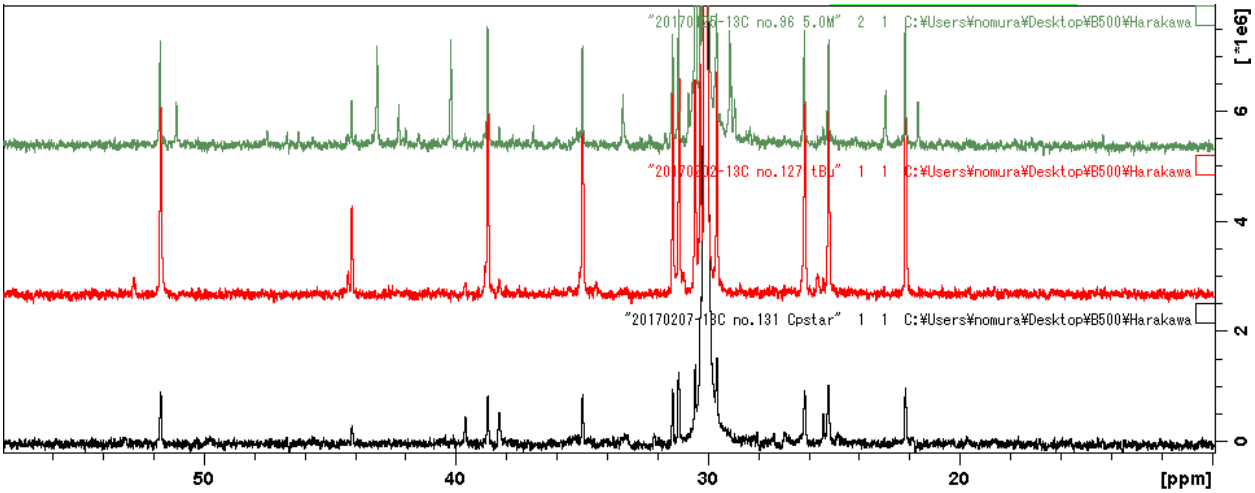


Figure S2-19. ^{13}C NMR spectra (in 1,1,2,2- tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-1-MeCPE)s prepared by (1,2,4-$Me_3C_5H_2$)$TiCl_2$(O-2,6-$^{i}Pr_2C_6H_3$) (**1**, run 33, top), ($^{t}BuC_5H_4$)$TiCl_2$(O-2,6-$^{i}Pr_2C_6H_3$) (**2**, run 41, middle), Cp*$TiCl_2$(O-2,6-$^{i}Pr_2C_6H_3$) (**8**, run 44, bottom)- - MAO catalyst systems (Table 2).

3. Assignment of resonances in poly(ethylene-*co*-4-MeCHE) and poly(ethylene-*co*-1-MeCPE) in ^{13}C NMR spectra.

3-1. Assignment of resonances in poly(ethylene-*co*-4-MeCHE).

In order to elucidate the microstructure of poly(ethylene-*co*-4-methylcyclohexene)s we have performed 2D NMR experiments such as HSQC (Heteronuclear Single Quantum Coherence) and HMBC (Heteronuclear Multiple Bond Correlation) (run 16, Table 1).

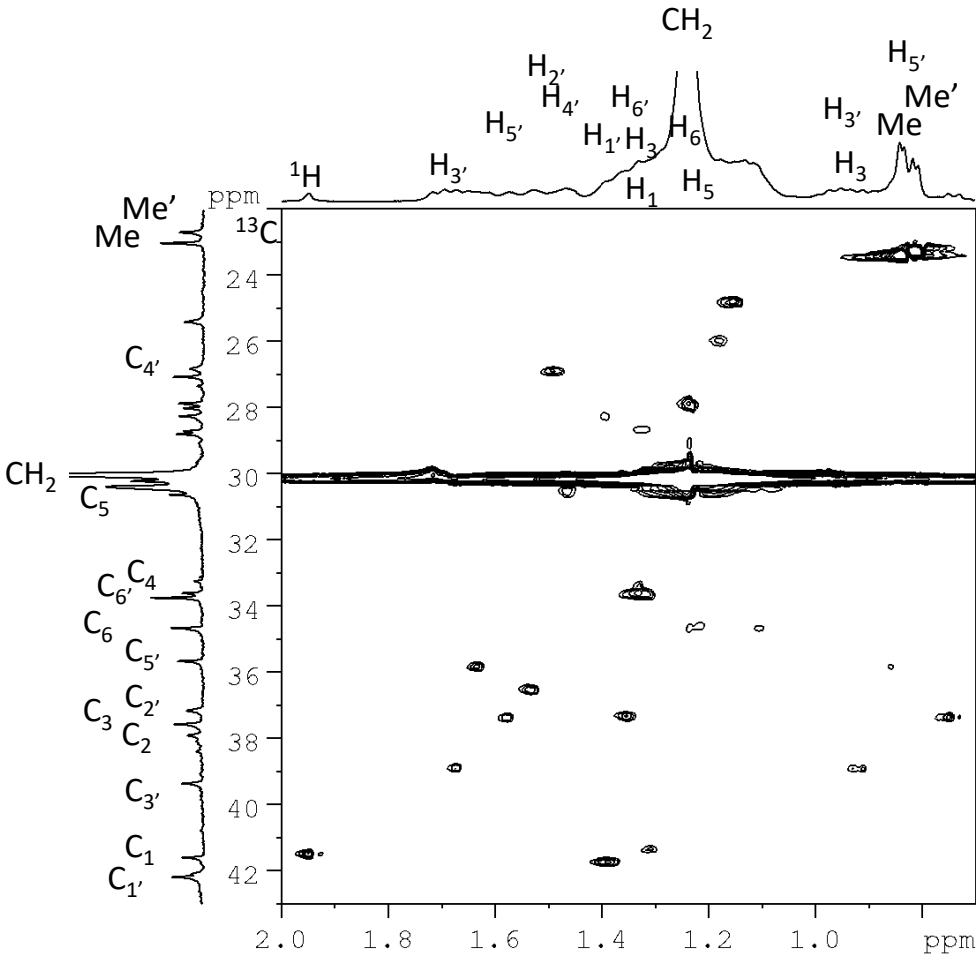


Figure S3-1. 2D ^{1}H-^{13}C HSQC spectrum of poly(ethylene-*co*-4MeCHE) (run 16 of Table 1) in 1,1,2,2-tetracholoroethane-d_2, recorded at 60 °C, on a 600 MHz spectrometer.

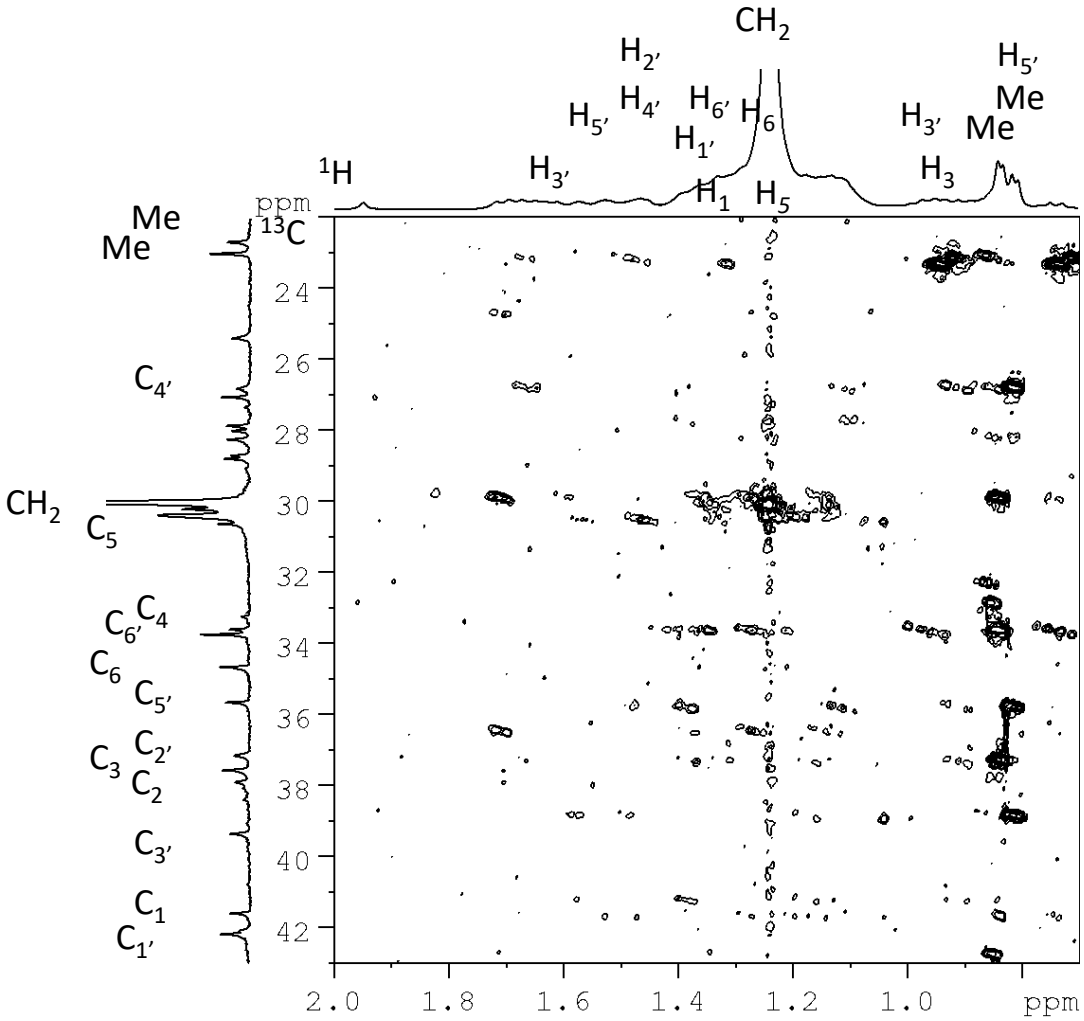


Figure S3-2. 2D ^{1}H-^{13}C HMBC spectrum of poly(ethylene-*co*-4MeCHE) (run 16 of Table 1) in 1,1,2,2-tetracholoroethane- d_2, recorded at 60 °C, on a 600 MHz spectrometer.

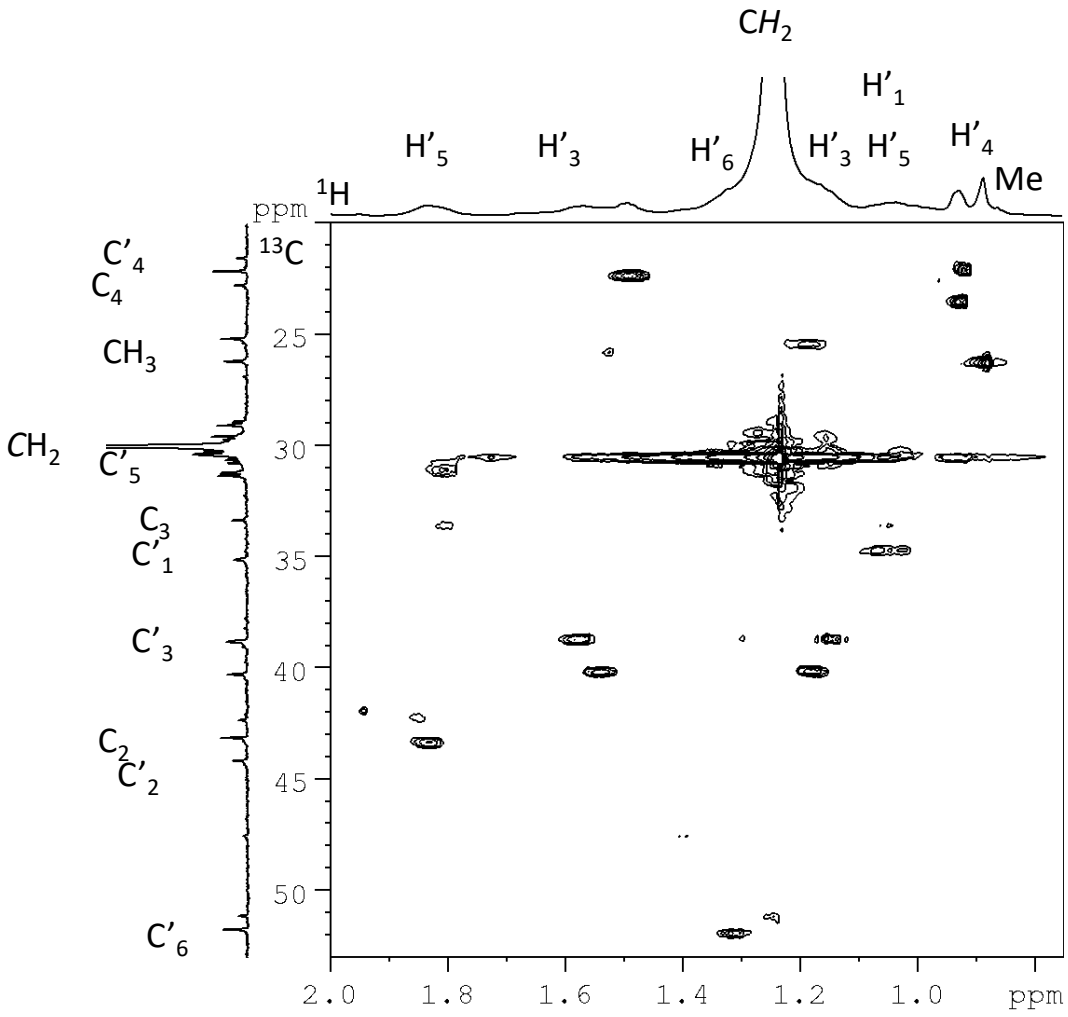


Figure S3-3. HSQC spectrum of poly(ethylene-*co*-1MeCPE) (run 33 of Table 2) in 1,1,2,2-tetracholoroethane-d_2, recorded at 60 °C, on a 600 MHz spectrometer.

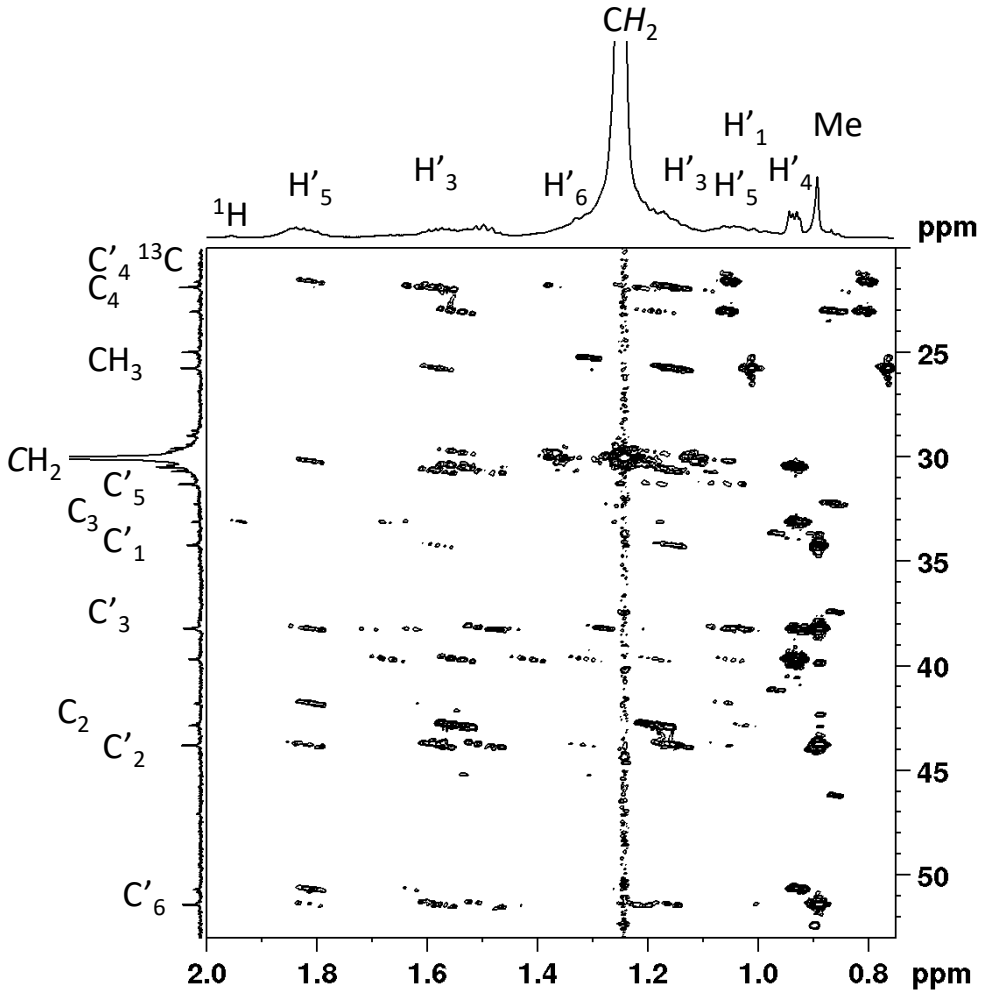
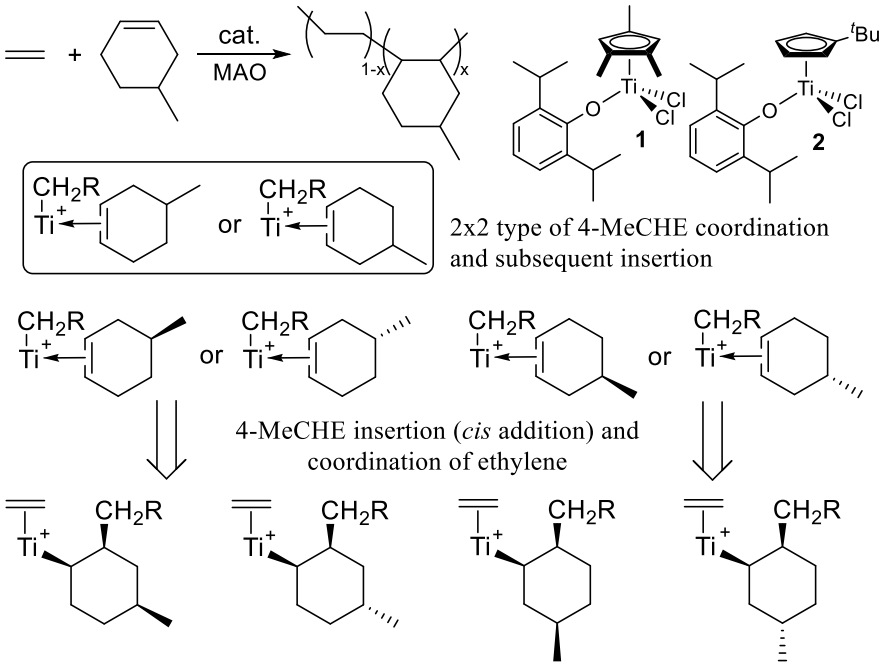


Figure S3-4. HMBC spectrum of poly(ethylene-*co*-1MeCPE) (run 33 of Table 2) in 1,1,2,2-tetracholoroethane-d_2, recorded at 60 °C, on a 600 MHz spectrometer.

In order to assign the spectra of Figure 1, it is necessary to take into account that, after insertion of one or more 4-MeCHE units, the presence of the methyl in position 4 of CHE may cause different stereoisomers. Thus, most of resonances could be assigned on the basis of the dept spectrum, 2D ^{1}H-^{13}C HSQC (Heteronuclear Single Quantum Coherence) and HMBC (Heteronuclear Multiple Bond Correlation) spectra, 2D ^{1}H-^{1}H COSY and TOCSY (Totally Correlated), on the basis of comparison with the ^{13}C NMR spectra of poly(ethylene-*co*-CHE)s (Wang, W.; Fujiki, M.; Nomura, K. *J. Am. Chem. Soc.* **2005**, *127* (13), 4582-4583.), and considering possible stereo-chemical shifts, originated from the conformational characteristics of the copolymer chain.

As shown in Scheme 5 (in text, also shown below), there are 4 insertion patterns for incorporation of 4-MeCHE: *cis* 1,2 or *cis*-2,1 insertions with methyl position *cis*/*trans* to Ti-alkyls.



Possible *cis* (1,2- and 2,1-) insertion modes in copolymerization of ethylene with 4-methylcyclohexene.

In a copolymer with a low content of 4-MeCHE, as those obtained from the synthesis, the four possible 4-MeCHE additions will give rise to two possible stereoisomers of the sequence EE(4-MeCHE)EE, that we call *cis* or *trans* depending on whether Me in 4 is *cis* or *trans* with respect to the first CH_2 of the polymer chain (see Figure S3-5, shown below). Such a difference can have big effect on the chemical shifts of the carbons.

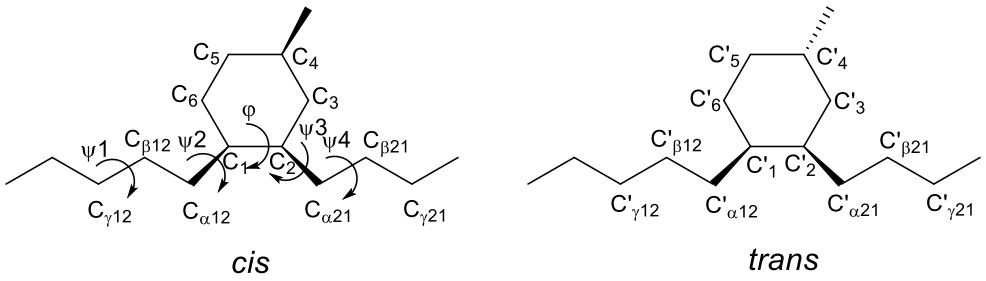


Figure S3-5

Conformations

In order to understand if there are differences in the ^{13}C NMR spectrum, depending on *cis* or *trans* configurations, the most stable conformations of the cyclohexane ring of the stereoisomers (the chair forms) have been considered in a simple and qualitative way (Figure S3-6). For each stereoisomer, there are two chair conformations and the stability of the conformer and thus the average properties of each isomer depend on the axial or equatorial positions assumed by the Me, $CH_{2(12)}$, and $CH_{2(21)}$ substituents and on their interactions in each conformer. The ^{13}C chemical shifts are influenced by γ-gauche effects in the allowed conformations and by the populations of the different conformers (Figure S3-7). In Table S3-1 the possible conformers of the *trans* and *cis* isomers are described.

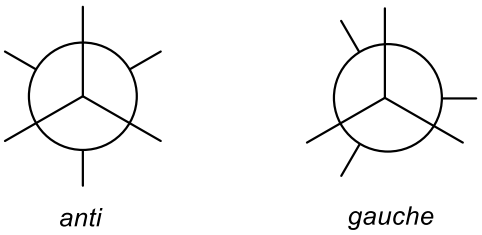


Figure S3-6

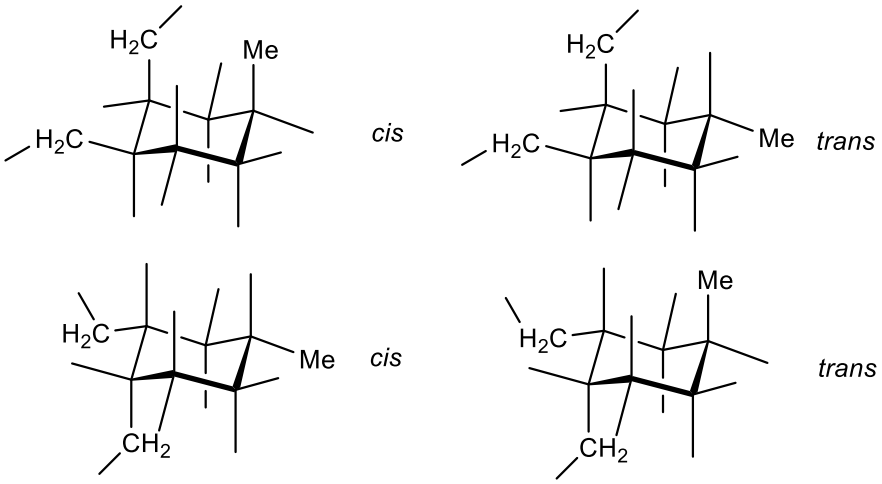


Figure S3-7

Table S3-1.

isomer	φ	Me	E_{12}	E_{21}	ΔE	ψ1ψ2	ψ3ψ4
cis	G'	Eq	Ax	Eq	E = 0	tt(0), g't(Eg)	tt(0), gt(Eg), g't(0), g'g'(Eg)
~~*cis*~~	~~G~~	~~Ax~~	~~Eq~~	~~Ax~~	~~E ω~~	tt(0), g't(Eg), tg(0), gg(Eg)	tt(0), gt(Eg)
trans	G	Eq	Eq	Ax	E = 0	tt(0), g't(Eg), tg(0), gg(Eg)	tt(0), gt(Eg)
trans	G'	Ax	Ax	Eq	E_{ax}	tt(0), g't(Eg)	tt(0), gt(Eg), g't(0), g'g'(Eg)

In each stereoisomer the two CH_2 of ethylene units adjacent to cyclohexane ring are one axial and one equatorial (named $C_{\alpha 21}$ and $C_{\alpha 12}$ in Figure 2, in text). The methyl in 4 position causes strong interactions when in the axial position. When the methyl of the *cis* isomer is axial, it has a strong interaction with the axial CH_2, thus this conformer can be ignored. Vice versa, when the methyl of the *trans* isomer is axial, it only shows gauche interactions with the ring, hence is less stable than the other *trans* conformer with the methyl in equatorial position, thus it should not be omitted.

In Figure 1 where the ^{13}C NMR spectrum of run 15, containing only 6.3 mol% of 4 MeCHE is reported, two signals, at 22.69 and 23.01 ppm assigned from dept to two methyls , are observed. On the basis of conformational effects, the methyl at high field should be assigned to *trans* stereoisomer. From 2D ^{1}H-^{13}C HSQC the protons of two methyls at 22.69 and 23.01 ppm resonate at about 0.8 ppm. In the HMBC spectrum, which gives direct correlations, the two methyls at 22.69 and 23.01 ppm correlate well with 6 signals.

The methyl at 22.69 ppm correlates with the signals at 39.34, 26.77, and 35.65 ppm and the methyl at 23.01 ppm with 37.56, 33.59, and 30.36 ppm, which have to be assigned at the closest carbons C_3, C_4 and C_5. From dept the signals at 26.77 and at 33.59 ppm are tertiary carbons and thus they were assigned to C_4 carbons in *trans* and *cis* stereoisomers, respectively. The other four signals belong to CH_2 carbons from dept. Since C_3 has in β position both the CH_2 of the polymer chain and the methyl, the signal at 39.34 and at 37.56 ppm should be assigned to C_3. According to conformational characteristics the signal at 39.34 ppm should be assigned to *trans* stereoisomer and the signal at 37.56 ppm to the *cis* stereoisomer. Thus, the other couple of CH_2 signals at 35.65 and 30.36 ppm corresponds to C_5 carbons of *trans* and *cis* stereoisomers, respectively.

Next, there are 4 tertiary carbons at 42.18, 41.58, 37.14, and 37.89 ppm that have to be assigned to C_1, C_2 or to C_1', C_2' according to this nomenclature. According to the conformational effects the signals at 42.18 and 41.58 ppm are assigned to C_1'and C_1 of *trans* and *cis* stereoisomers, respectively, and the signals at 37.14 and 37.89 ppm to C_2'and C_2 of *trans* and *cis* stereoisomers, respectively. The other two CH_2 signals left to be assigned at 33.73 and at 34.64 ppm should correspond to C_6 of *trans* and *cis* stereoisomers, respectively.

The CH_2 of the polymer chain will be also influenced, and we expect that in the isolated sequence EE(4MeCHE)EE there will be couples of signals $C_{\alpha 21}$, $C_{\alpha 12}$, $C'_{\alpha 21}$, and $C'_{\alpha 12}$ for *cis* and *trans* isomers.

Table S3-2 Assignment of resonances for poly(ethylene-*co*-4-MeCHE) in ^{13}C NMR and ^{1}H NMR spectra.

^{13}C NMR HMDS δ = 0 ppm, PE 27.8 ppm	Assignment	DEPT	^{13}C NMR PE δ = 30 ppm	^{1}H NMR
20.50	Me *trans*	+	22.69	0.82
20.82	Me *cis*	+	23.01	0.84
23.17	E CH_2	-	25.37	1.18
24.57	E CH_2	-	26.77	
24.59	C4 *trans*	+	27.05	1.49
25.66	E CH_2	-	27.84	1.23
25.80	E CH_2	-	27.99	1.23
26.06	E CH_2	-	28.25	1.39
26.50	E CH_2	-	28.68	1.32
28.17	C5 m	-	30.36	
31.41	C4 m	+	33.59	1.33
31.55	C6 trans	-	33.73	1.33
32.46	C6 cis	-	34.64	
33.47	C5 *trans*	-	35.65	1.63, 0.86
34.92	C2 trans	+	37.14	1.35
35.37	C3 *cis*	-	37.56	1.57, 0.75
35.67	C2 cis	+	37.89	
37.15	C3 *trans*	-	39.34	1.68, 0.92
39.39	C1 *cis*	+	41.58	1.31
39.98	C1 *trans*	+	42.18	1.39

3-2. Assignment of resonances in poly(ethylene-*co*-1-MeCPE).

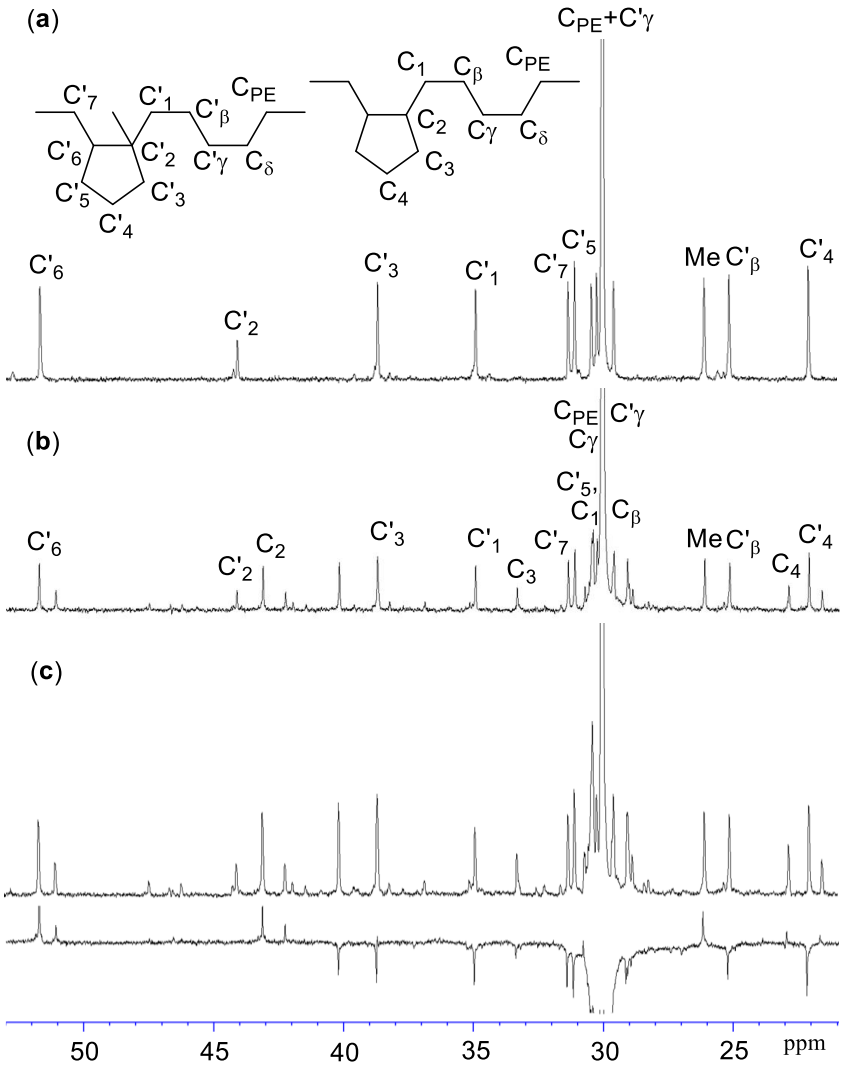


Figure S3-8. ^{13}C NMR spectra and the dept spectrum for poly(ethylene-*co*-1-MeCPE)s prepared by: (a) (^{t}BuC$_5$H$_4$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) - MAO catalyst system [**2**, run 41 (1-MeCPE 8.2 mol%)]; (b,c) (1,2,4-Me$_3$C$_5$H$_2$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**) - MAO catalyst system [1-MeCPE content: (b) 4.4 mol% (run 33), and (c) 7.1 mol% (run 35)] (in 1,1,2,2- tetrachloroethane-d_2 at 110 ºC).

Table S3-3. Assignment of resonances for poly(ethylene-*co*-1-MeCPE) in ^{13}C NMR and ^{1}H NMR spectra

Poly(E-co-1MeCPE)	Naga [a]	DEPT	^{13}C PE δ = 30 ppm	^{1}H
C_6'		+	51.42	1.30
C_2'			43.77	
C_3'		-	38.17	1.17, 1.53
C_1'		-	34.18	1.046
C_7'		-	31.3	
C_5'		-	30.7	1.80
Me		+	25.72	0.87
C'_β		-	25.0	
C_4'		-	21.84	0.91
C_2	≈ 43.3	+	42.82	1.83
C_3	≈31.2	-	33.08	1.05
C_1	≈30.5	-	30.5	
$C\gamma$	≈ 30.5			
$C\beta$	≈29.0	.	29.3-29.8.	
C_4	≈22.22	-	23.02	0.92

[a] Naga, N.; Imanishi, Y. *Macromol. Chem. Phys.* **2002**, *203* (1), 159-165.

4. DSC thermograms for resultant (co)polymers.

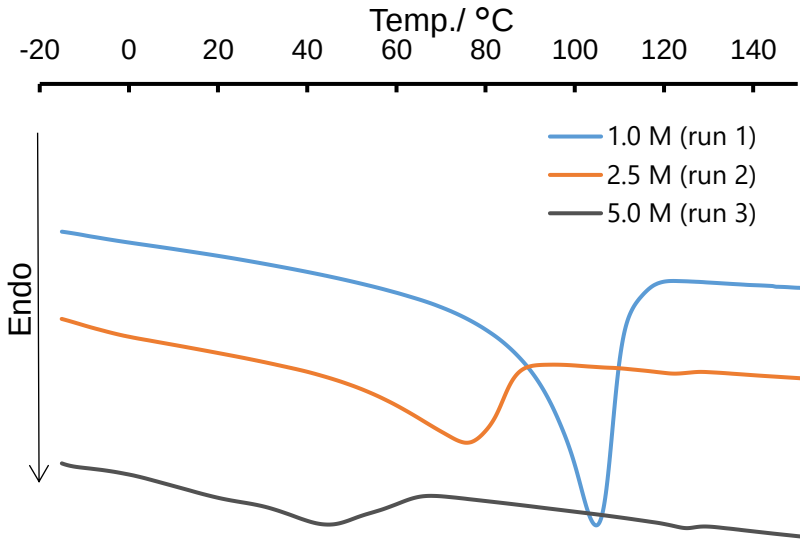


Figure S4-1. DSC thermograms of poly(ethylene-*co*-CHE)s by (1,2,4-$Me_3C_5H_2$)$TiCl_2$(O-2,6-$^i Pr_2C_6H_3$) (**1**) – MAO catalyst system. Detailed results are shown in Table 1 (runs 1-3).

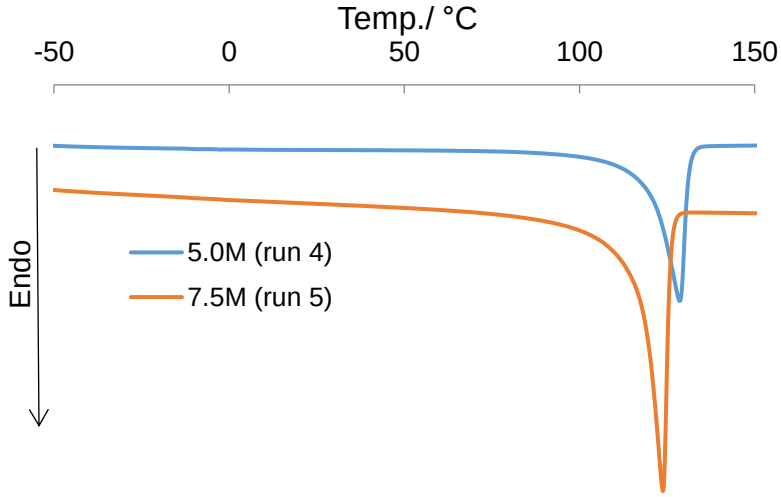


Figure S4-2. DSC thermograms of polymers prepared by (1,2,4-$Me_3C_5H_2$)$TiCl_2$(O-2,6-$^i Pr_2C_6H_3$) (**1**) – MAO catalyst system. in the ethylene polymerization in the presence of 1-MeCHE, poly(ethylene-*co*-1-MeCHE)s (with negligible 1-MeCHE incorporation). Detailed results are shown in Table 1 (runs 4,5).

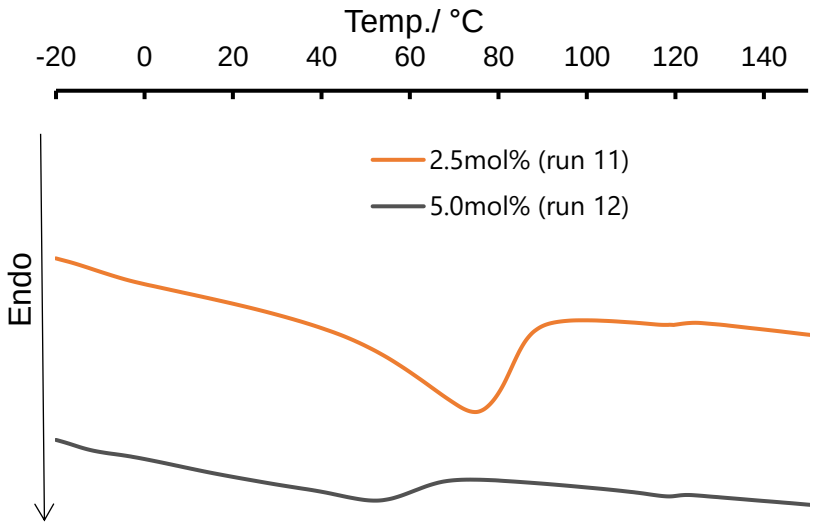


Figure S4-3. DSC thermograms of poly(ethylene-*co*-4-MeCHE)s by (^{t}BuC$_5$H$_4$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**2**) - MAO catalyst system. Detailed results are shown in Table 1 (runs 11,12).

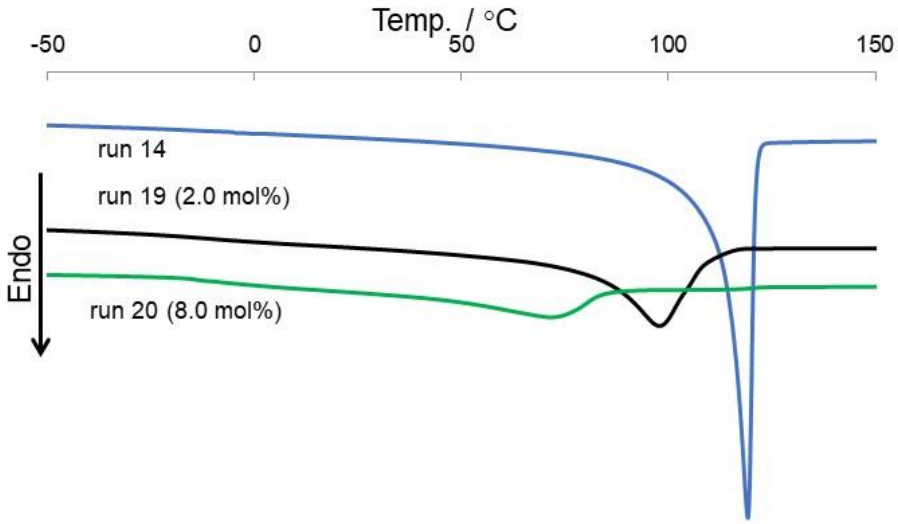


Figure S4-4. DSC thermograms of poly(ethylene-*co*-4-MeCHE)s or poly(ethylene-*co*-1-MeCHE)s (with negligible 1-MeCHE incorporation) by (^{t}BuC$_5$H$_4$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**2**) - MAO catalyst system. Detailed results are shown in Table 1 (runs 14,19,20).

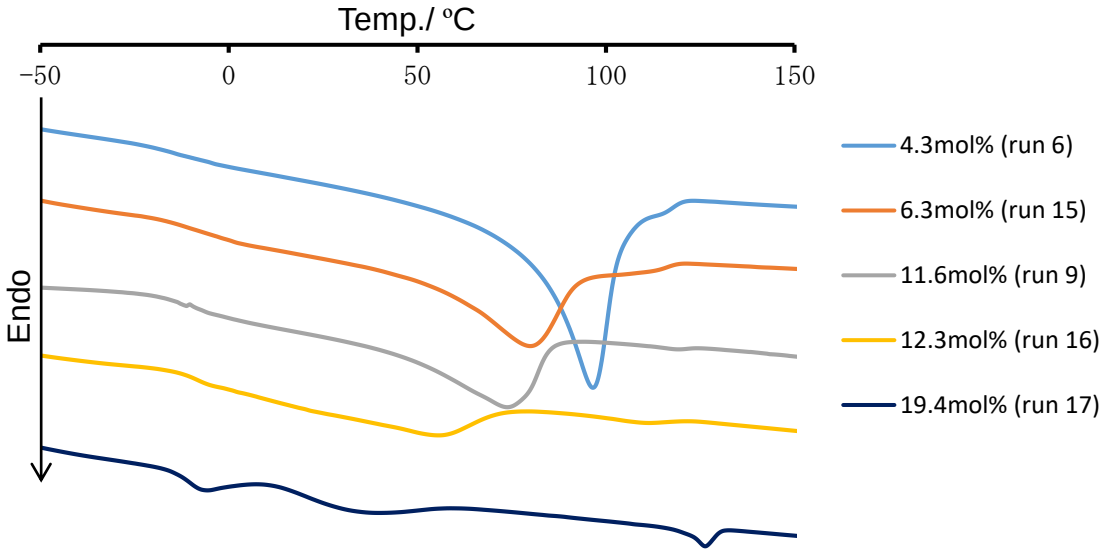


Figure S4-5. DSC thermograms of poly(ethylene-*co*-4-MeCHE)s by (1,2,4-$Me_3C_5H_2$)$TiCl_2$(O-2,6-$^i Pr_2C_6H_3$) (**1**) , ($^t BuC_5H_4$)$TiCl_2$(O-2,6-$^i Pr_2C_6H_3$) (**2**) - MAO catalyst systems. Detailed results are shown in Table 1.

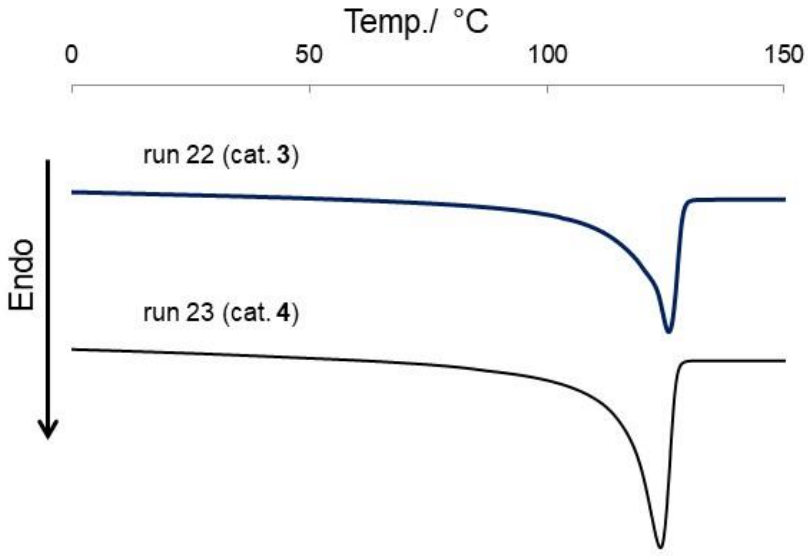


Figure S4-6. DSC thermograms of polymers prepared by ($^t BuC_5H_4$)$TiCl_2$(N=C$^t Bu_2$) (**3**), $CpTiCl_2$(N=C$^t Bu_2$) (**4**) - MAO catalyst systems in the ethylene polymerization in the presence of 4-MeCHE. Detailed results are shown in Table 1 (runs 22,23).

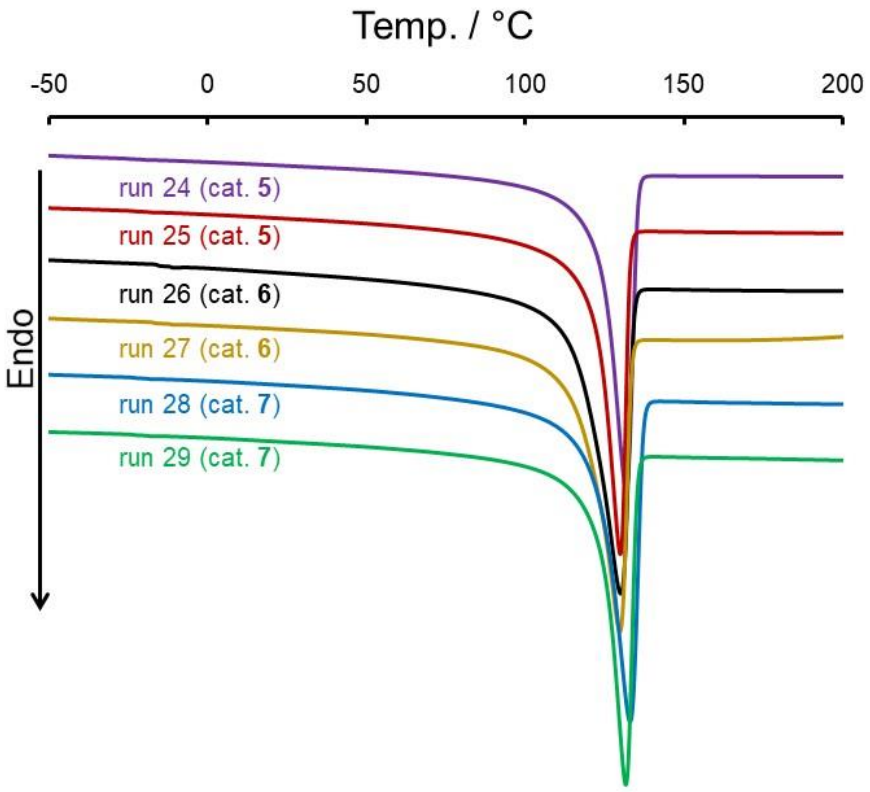


Figure S4-7. DSC thermograms of polymers prepared by various catalysts (**5**-**7**) - MAO catalyst systems in the ethylene polymerization in the presence of 4-MeCHE or 1-MeCHE. Detailed results are shown in Table 1 (runs 24-29).

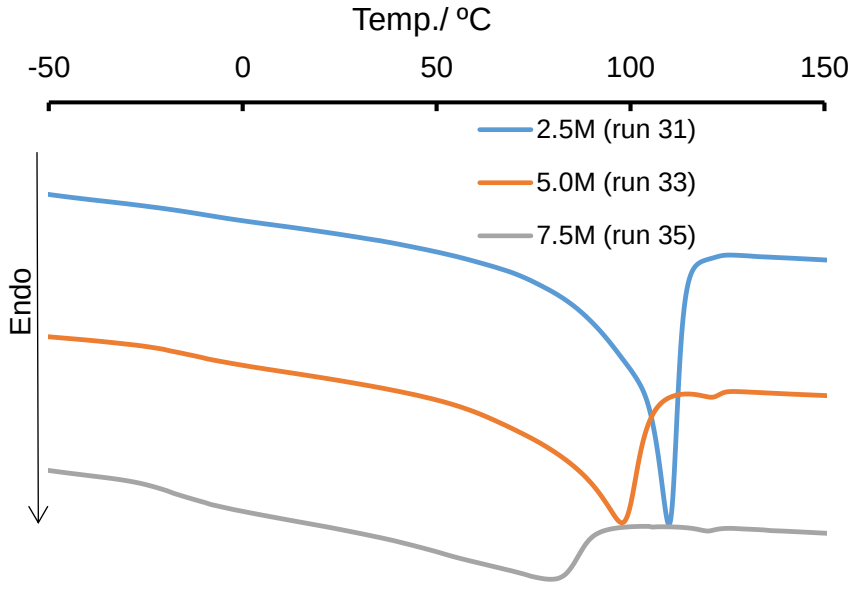


Figure S4-8. DSC thermograms of poly(ethylene-*co*-1-MeCPE)s by (1,2,4-$Me_3C_5H_2$)$TiCl_2$(O-2,6-$^{i}Pr_2C_6H_3$) (**1**) – MAO catalyst system. Detailed results are shown in Table 2 (runs 31,33,35).

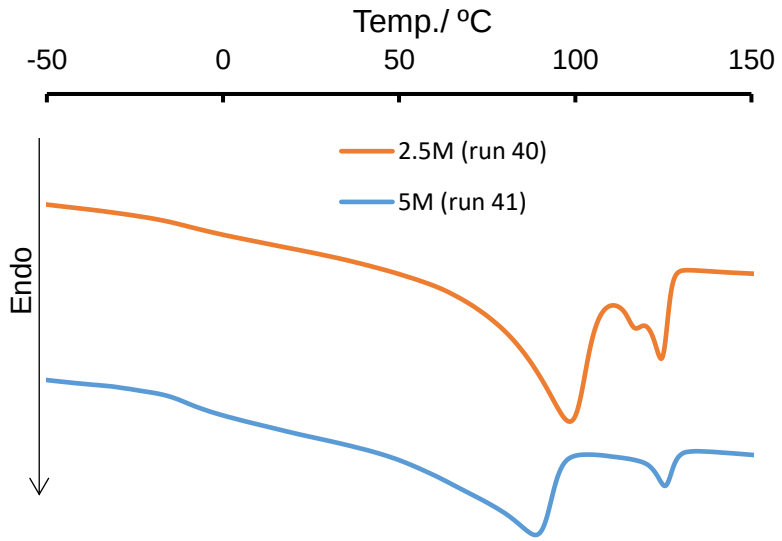


Figure S4-9. DSC thermograms of poly(ethylene-*co*-1-MeCPE)s by (^{t}BuC$_5$H$_4$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**2**) - MAO catalyst system. Detailed results are shown in Table 2 (runs 40,41).

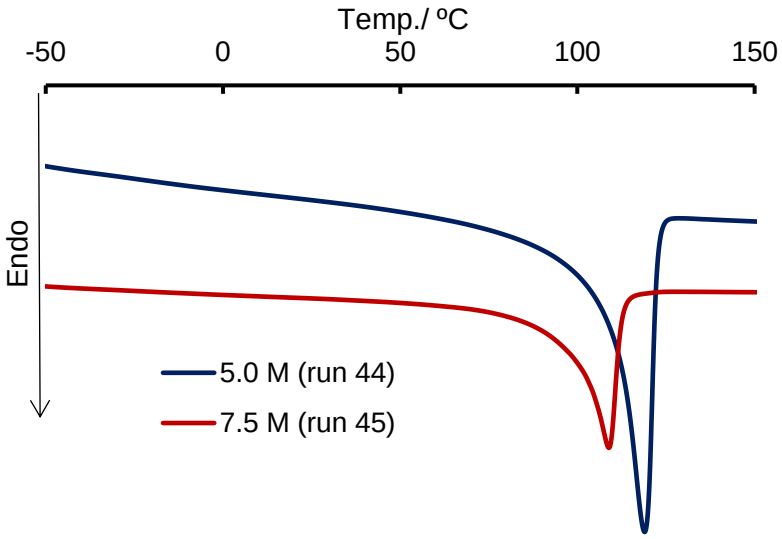


Figure S4-10. DSC thermograms of poly(ethylene-*co*-1-MeCPE)s by Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**8**) - MAO catalyst system. Detailed results are shown in Table 2 (runs 44,45).

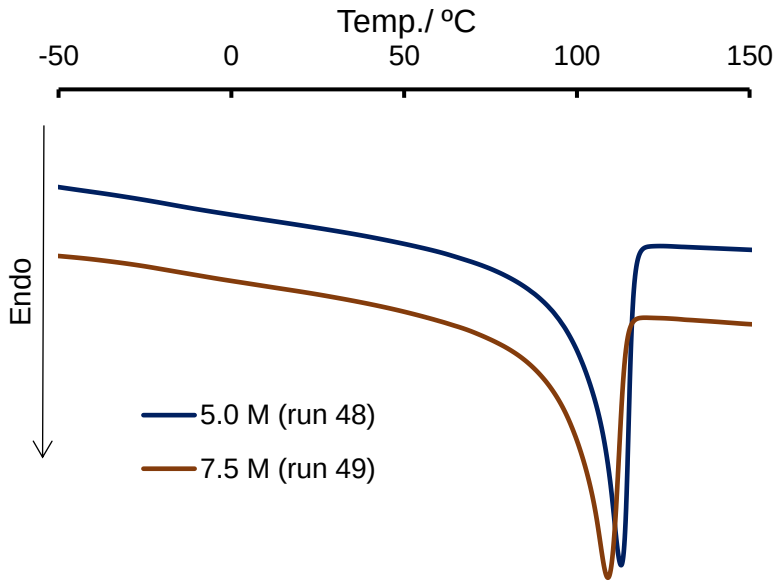


Figure S4-11. DSC thermograms of polymers prepared by (^{t}BuC$_5$H$_4$)TiCl$_2$(N=C^{t}Bu$_2$) (**3**) - MAO catalyst system in ethylene polymerization in the presence of 1-MeCPE. Detailed results are shown in Table 2 (runs 48,49).

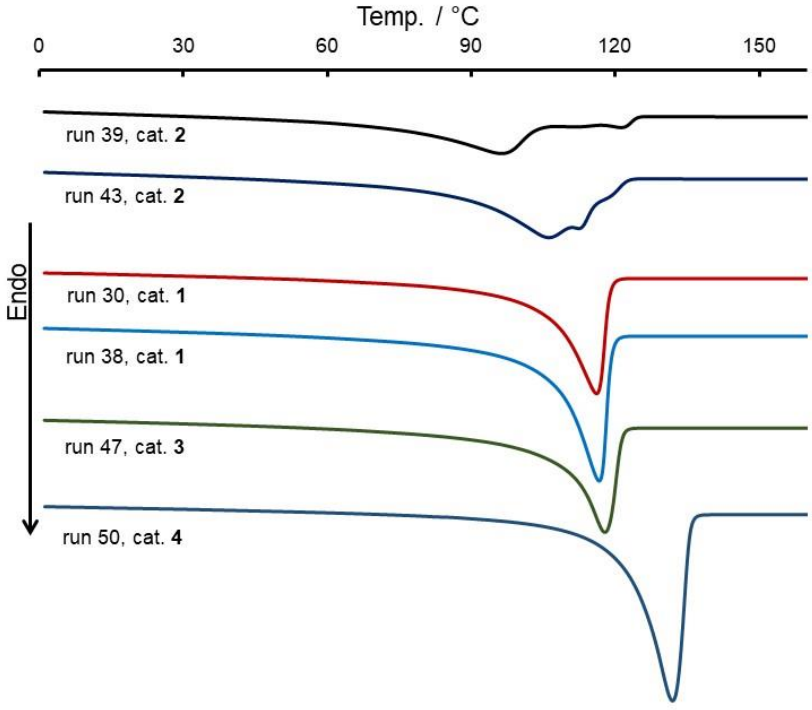


Figure S4-12. DSC thermograms of polymers prepared by **1-4** - MAO catalyst systems in ethylene polymerization in the presence of 1-MeCPE. Detailed results are shown in Table 2.

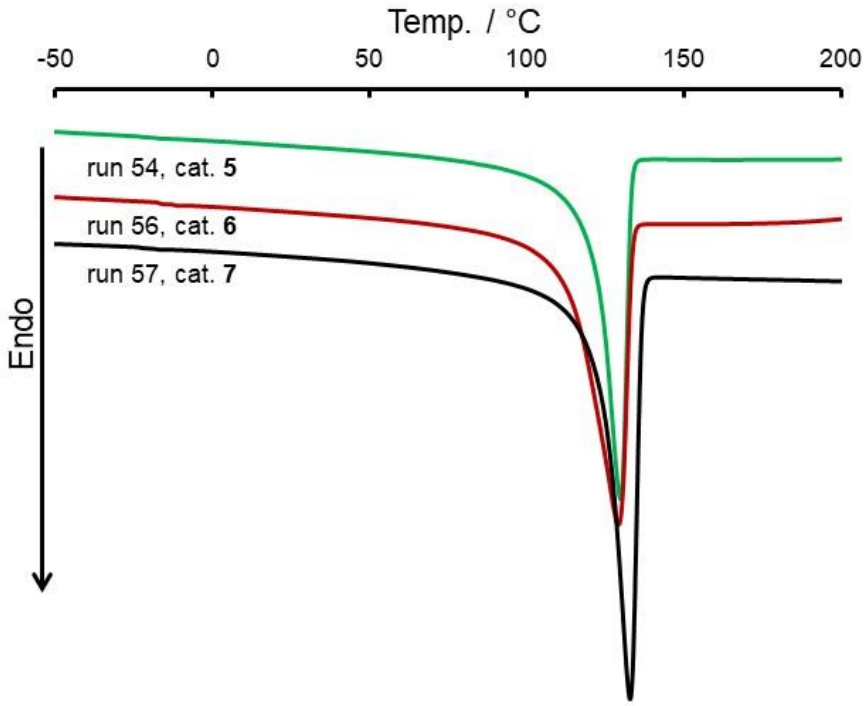


Figure S4-13. DSC thermograms of polymers prepared by **5-7** - MAO catalyst systems in ethylene polymerization in the presence of 1-MeCPE. Detailed results are shown in Table 2.

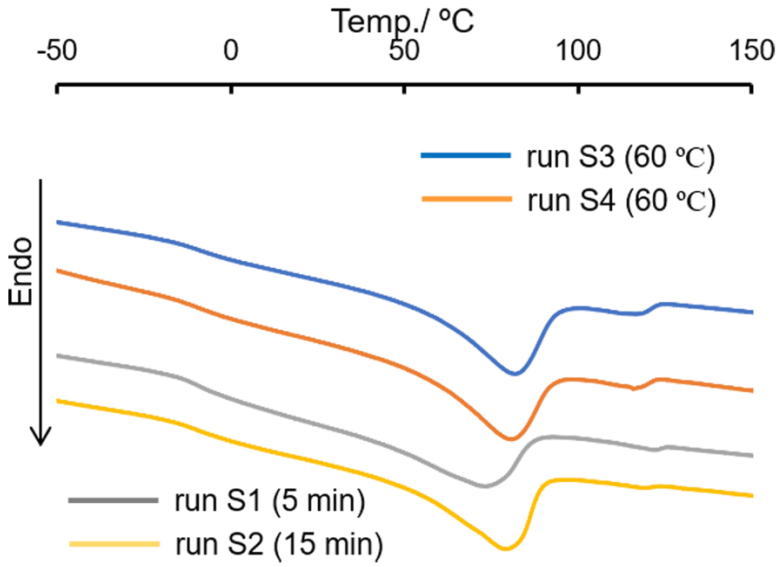


Figure S4-14. DSC thermograms of poly(ethylene-*co*-1-MeCPE)s by (1,2,4-$Me_3C_5H_2$)$TiCl_2$(O-2,6-$^{i}Pr_2C_6H_3$) (**1**) – MAO catalyst system. Detailed results are shown in Table S1-1.