

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

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Abstract: Ethylene copolymerizations with 4-methylcyclohexene (4-MeCHE), or 1-methylcyclopentene (1-MeCPE) have been explored by the aryloxo- or ketimide-modified half-titanocenes, Cp'TiCl₂(X) [X: O-2,6-^tPr₂C₆H₃, Cp': 1,2,4-Me₃C₅H₂ (**1**), ^tBuC₅H₄ (**2**), C₅Me₅ (Cp*)]; X: N=C^tBu₂, Cp': ^tBuC₅H₄, Cp, indenyl], linked half-titanocenes, [Me₂Si(C₅Me₄)(NR)]TiCl₂ (R = ^tBu, cyclohexyl), ordinary metallocenes, [Et(indenyl)₂]ZrCl₂, Cp₂ZrCl₂, in the presence of methylaluminoxane (MAO) cocatalyst. The aryloxo analogues (**1,2**) only showed rather efficient 4-MeCHE incorporations in 1,2- (or 2,1-) insertion manner, affording the copolymers with uniform molecular weight distributions (compositions), whereas as to the others they showed negligible incorporations under the same conditions. Only the 1,2,4-Me₃C₅H₂-aryloxo analogue (**1**) afforded the copolymers containing 1-MeCPE with uniform compositions and 1-MeCPE was incorporated with 1,2-insertion as well as after isomerization (**1,3-insertion**, incorporated as methylene cyclopentane units), whereas incorporation of 1-methylcyclohexene (1-MeCHE) was negligible.

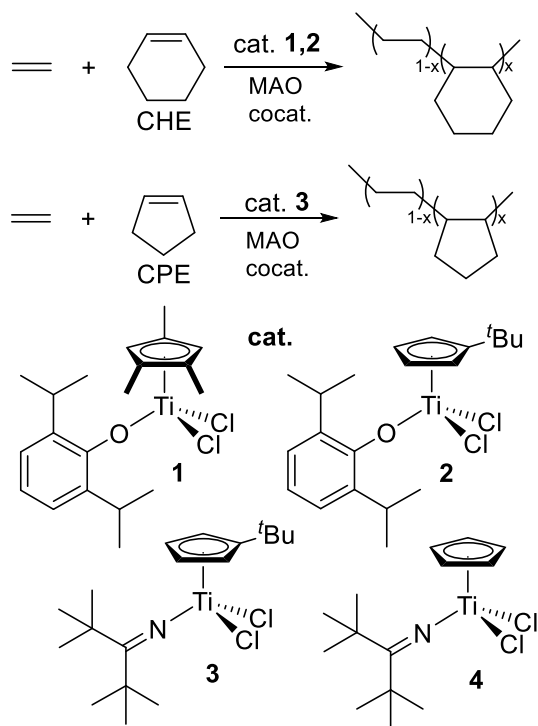
Introduction

Transition metal catalyzed olefin polymerization is a core technology for production of polyolefins [exemplified as linear high density polyethylene (HDPE), linear low density polyethylene (LLDPE), isotactic polypropylene (iPP) etc.] that covers almost 50 % production of commercialized synthetic polymers in the world. In this research field, considerable attention has been paid recently to the synthesis of new polymers that cannot be (or are very difficult to be) prepared by ordinary catalysts such as Ziegler-Natta, ordinary metallocene¹⁻⁴ linked-half metallocene so called constrained geometry (CGC) type,⁴⁻⁷ nonbridged half-metallocene,⁸⁻¹⁰ and so called non-metallocene type¹¹⁻¹⁶ catalysts. Since the copolymerization is an important method that usually allows the alteration of the (physical, mechanical, and electronic) properties in the resultant polymers by varying the ratio of individual components (each monomer), therefore, design of the molecular catalysts has been considered as attractive and important subject.¹⁻²⁵

Certain cyclic olefin (co)polymers are amorphous materials, highly transparent in the UV-vis region, endowed with high humidity-, and thermal-resistance, high glass transition temperature (T_g).²⁶⁻³² They are mostly prepared by coordination copolymerization of ethylene with cyclic olefins (called COC), or ring-opening metathesis polymerization of multi-cyclic olefins and subsequent hydrogenation (called COP). The copolymerization approach is promising in terms of modification of their compositions and microstructures.²⁶⁻³² Many reports on the copolymerization of ethylene with strained cyclic olefins like norbornene have been known,²⁶⁻³² and reports on the copolymerization with cyclopentene³³⁻⁴² have also been known. In contrast, reported examples for the ethylene/cyclohexene copolymerization still have been limited so far,⁴³ and no examples have been known concerning incorporation of 1-methylcyclohexene, 1-methylcyclopentene in ethylene copolymerization (trisubstituted olefins). Development of catalysts that enables incorporations

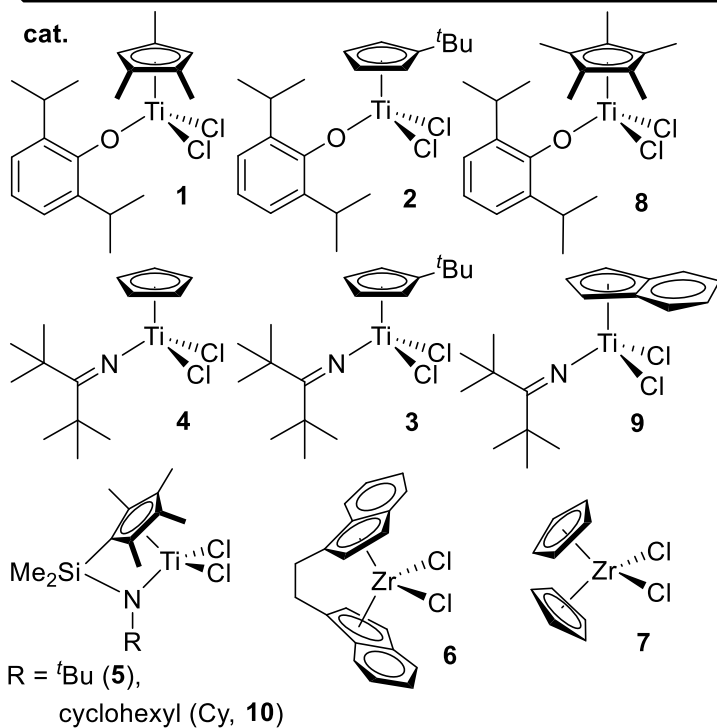
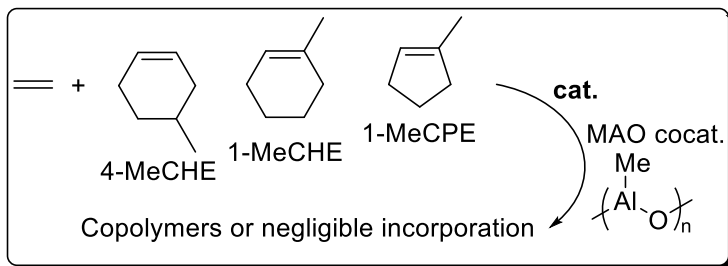
(especially with 1,2- or 2,1-insertion) of these monomers (di-, tri-substituted olefins), previously categorized as *traditionally inactive monomers* in transition metal catalyzed coordination polymerization,⁴⁴ has thus been considered a challenging subject.⁴⁵⁻⁵¹

Nonbridged half-titanocenes containing anionic donor ligands of type, Cp'TiX₂(Y) (Cp' = cyclopentadienyl group, Y = aryloxo, ketimide, phosphinimide etc.), are known to be effective especially for syntheses of new polymers by ethylene copolymerizations.⁸⁻¹⁰ In particular, the aryloxo or the ketimide modified analogues, Cp'TiCl₂(O-2,6-*i*-Pr₂C₆H₃) or Cp'TiCl₂(N=C'^tBu₂), display promising characteristics especially for copolymerization of ethylene with sterically encumbered olefins⁵⁰⁻⁵⁵ or cyclic olefins (such as cyclopentene,⁴² cyclohexene,⁴³ Scheme 1). In this catalysis, the ligand modification plays an important role in obtaining the desired copolymerization in an efficient manner; as shown in Scheme 1, the aryloxo-modified catalysts [Cp'TiCl₂(O-2,6-*i*-Pr₂C₆H₃), Cp' = 1,2,4-Me₃C₅H₂ (**1**), ^tBuC₅H₄ (**2**)] are **highly** effective for ethylene/cyclohexene copolymerization,⁴³ whereas the ^tBuC₅H₄-ketimide analogue [(^tBuC₅H₄)TiCl₂(N=C'^tBu₂) (**3**)] is effective for the ethylene/cyclopentene copolymerization⁴² and the Cp-ketimide analogue [CpTiCl₂(N=C'^tBu₂) (**4**)] is the best suited for the copolymerization with norbornene.⁵⁶



Scheme 1. Ethylene copolymerizations with cyclopentene, cyclohexene with half-titanocene catalysts.

We thus herein report our results exploring possibilities for incorporations of 4-methylcyclohexene (4-MeCHE), 1-methylcyclohexene (1-MeCHE), and 1-methylcyclopentene (1-MeCPE) in the ethylene copolymerization using a series of (linked and nonbridged) half-titanocenes, and ordinary metallocenes in the presence of methylaluminoxane (MAO) cocatalyst (Scheme 2). In particular, we wish to demonstrate rare examples not only for incorporations of these monomers into the polymer main chains, but also for estimation of their insertion pathways in these catalysts (especially by **1** and **2**) through their microstructure analysis by NMR spectroscopy.



Scheme 2. Ethylene copolymerizations with 4-methylcyclohexene (4-MeCHE), 1-methylcyclohexene (1-MeCHE), and with 1-methylcyclopentene (1-MeCPE).

Results and Discussion

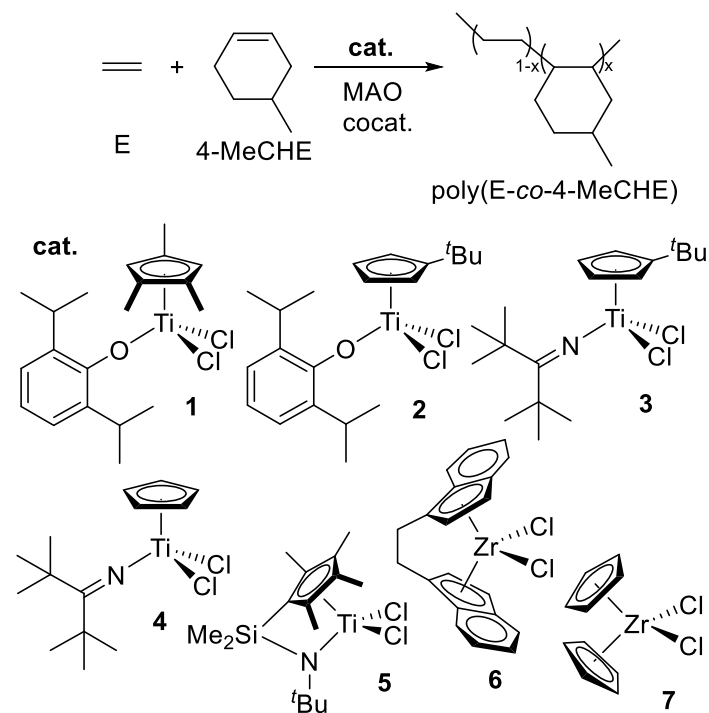
1. Copolymerization of Ethylene with 4-Methylcyclohexene (4-MeCHE), 1-Methylcyclopentene (1-MeCPE).

On the basis of results in the ethylene copolymerization with norbornene (NBE),⁵⁶ cyclopentene (CPE),⁴² and with cyclohexene (CHE),⁴³ modified half-titanocenes, Cp'TiCl₂(Y) [Y = O-2,6-ⁱPr₂C₆H₃, Cp' = 1,2,4-Me₃C₅H₂ (**1**), ^tBuC₅H₄ (**2**); Y = N=C^tBu₂, Cp': ^tBuC₅H₄ (**3**), C₅H₅ (Cp, **4**)] have been chosen for this study (Scheme 3). Linked half-titanocene (constrained geometry type), [Me₂Si(C₅Me₄)(N^tBu)]TiCl₂ (**5**), and ordinary metallocenes, [Et(indenyl)₂]ZrCl₂ (**6**), Cp₂ZrCl₂ (**7**), have also been chosen for comparison, because **5** and **6** incorporated NBE in rather efficient manner.⁵⁶⁻⁶⁰ MAO white solid (d-MAO) prepared by removing AlMe₃ and toluene from the commercially available samples (TMAO, 9.2 wt% in toluene, Tosoh Finechem Co.) was chosen, because it was effective in the preparation of high molecular weight copolymers with unimodal molecular weight distributions (as well as with uniform compositions).^{43,50-55} The polymerization conditions (amount of Ti charged, polymerization time etc.) were optimized on the basis of polymer yields in order to control the conversions of comonomers less than ca. 10 %. The results are summarized in Table 1.⁶¹

It turned out that the aryloxo modified half-titanocenes (**1,2**) incorporated 4-methylcyclohexene (4-MeCHE) in the copolymerization to afford high molecular weight polymers with unimodal molecular weight distributions. As described below, the resultant copolymers possessed uniform composition confirmed by DSC thermograms.⁶¹ It was revealed that the catalytic activity (based on the polymer yield) was affected by the 4-MeCHE concentration charged. As observed in the ethylene/CHE copolymerization (runs 1-3,11-13),⁴³ the activity by **1** increased upon increasing the 4-MeCHE concentration charged (2.5 → 5.0 M; runs 6-9), whereas the opposite trend was seen

when the copolymerizations by **2** were conducted at 2 atm (runs 15,16); further increase in the 4-MeCHE concentration (7.5 M) led to decrease in the activity (run 10,17,18). The activity by **2** was affected by ethylene pressure especially under high 4-MeCHE concentration (5.0 M, runs 20, 21), as also observed in the copolymerization with CHE (runs 12,13). The results (activity, melting temperature in the resultant copolymer by DSC thermograms etc.)⁶¹ are reproducible.

Incorporations of 4-MeCHE were confirmed by NMR spectra (shown below, Figure 1) and DSC thermograms;⁶¹ the melting temperature (T_m) decreased upon increasing the comonomer contents estimated by ¹³C NMR spectra.⁶¹ Glass transition temperatures (T_g) were also observed for samples with high 4-MeCHE contents (runs 10,17,18).⁶¹ On the basis of GPC data, NMR spectra, and DSC thermograms,⁶¹ it is clear that the resultant polymers are poly(ethylene-*co*-4-MeCHE)s with uniform compositions.



Scheme 3. Ethylene copolymerization with 4-methylcyclohexene (4-MeCHE).

In contrast, as shown in Table 1, 4-MeCHE incorporations were negligible when the polymerizations by the ketimide-modified half-titanocenes (**3,4**), which were effective for the ethylene copolymerizations with CPE, NBE, were conducted under the same conditions (runs 22,23, confirmed by DSC thermograms).⁶¹ Moreover, the resultant polymers by $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{TiCl}_2$ (**5**), ordinary metallocenes (**6,7**) were linear polyethylene with negligible 4-MeCHE incorporations (runs 25,27,29), confirmed by DSC thermograms.⁶¹ Therefore, the aryloxo-modified half-titanocenes (**1,2**) only incorporated 4-MeCHE affording the copolymer~~s~~s with uniform compositions.

It was also revealed that incorporation of 1-methylcyclohexene (1-MeCHE) was suggested by DSC thermograms,⁶¹ when the ethylene copolymerizations with 1-MeCHE were conducted by **1,2** (runs 4,5,14); the melting temperature decreased upon increasing the 1-MeCHE concentration (runs 4,5). However, it seems difficult to estimate the contents precisely due to low intensity of the resonances in the ^{13}C NMR spectra.⁶¹ In contrast, 1-MeCHE incorporations in the resultant polymers were tiny trace (confirmed by DSC thermograms) in the attempted copolymerization by **5-7** under the same conditions.⁶¹

Table 1. Copolymerization of ethylene and 1-methylcyclohexene (1-MeCHE), 4-methylcyclohexene (4-MeCHE) by **1-7** — MAO catalyst systems.^a

run	catalyst (μmol)	comonomer (conc. ^b M)	ethylene / atm	yield / mg	activity ^c	M_n^d $\times 10^{-4}$	M_w/M_n^d	content ^e / mol%	T_m^f (T_g^f) / °C
1	1 (0.8)	CHE (1.0)	2	99.5	746	32.3	2.49	3.0	105
2	1 (0.8)	CHE (2.5)	2	178	1330	22.0	1.98	-	76
3	1 (0.8)	CHE (5.0)	2	205	1540	15.2	1.71	12.9	45
4	1 (0.8)	1-MeCHE (5.0)	2	117	878	13.2	2.11	-	128
5	1 (1.2)	1-MeCHE (7.5)	2	79.3	397	10.5	1.62	-	124
6	1 (0.3)	4-MeCHE (2.5)	2	160	3200	37.0	1.92	4.3	97
7	1 (0.3)	4-MeCHE (2.5)	2	141	2830	31.6	2.04		96
8	1 (0.2)	4-MeCHE (5.0)	2	187	5600	30.8	1.80		79
9	1 (0.2)	4-MeCHE (5.0)	2	206	6170	28.7	1.81	11.6	74
10	1 (0.5)	4-MeCHE (7.5)	2	166	1990	12.0	1.76	14.2	39 (-8.3)
11	2 (1.0)	CHE (2.5)	2	184	1100	20.9	1.85		75
12	2 (2.0)	CHE (5.0)	2	178	534	8.42	1.44	11.1	52
13	2 (2.0)	CHE (5.0)	4	565	1700	16.1	2.19		77
14	2 (2.0)	1-MeCHE (5.0)	2	150	449	7.40	1.68		119
15	2 (0.3)	4-MeCHE (2.5)	2	187	3740	31.0	2.43	6.3	80
16	2 (0.3)	4-MeCHE (5.0)	2	162	3250	16.4	1.82	12.3	56
17	2 (0.3)	4-MeCHE (7.5)	2	142	2850	10.2	1.86	19.4	37 ^g (-10)
18	2 (0.3)	4-MeCHE (7.5)	2	127	2530	7.7	1.67		40 ^g (-8)
19	2 (0.2) ^h	4-MeCHE (2.5)	4	74	3720	24.8	2.04	2.0	97
20	2 (0.1)	4-MeCHE (5.0)	4	116	6940	23.7	1.69	8.0	71
21	2 (0.1)	4-MeCHE (5.0)	4	105	6320	33.3	2.45		77
22	3 (0.1)	4-MeCHE (5.0)	2	146	8730	insoluble			127
23	4 (1.0)	4-MeCHE (5.0)	2	288	1730	42.4	14.5		123
24	5 (1.0)	1-MeCHE (5.0)	2	192	1150	23.6	2.98		131
25	5 (1.0)	4-MeCHE (5.0)	2	207	1240	24.4	2.50		130
26	6 (1.0)	1-MeCHE (5.0)	2	839	5030	19.1	2.51		130
27	6 (1.0)	4-MeCHE (5.0)	2	913	5480	18.0	2.55		130
28	7 (1.0)	1-MeCHE (5.0)	2	976	2930	39.5	2.58		132
29	7 (1.0)	4-MeCHE (5.0)	2	502	1500	35.4	2.11		131

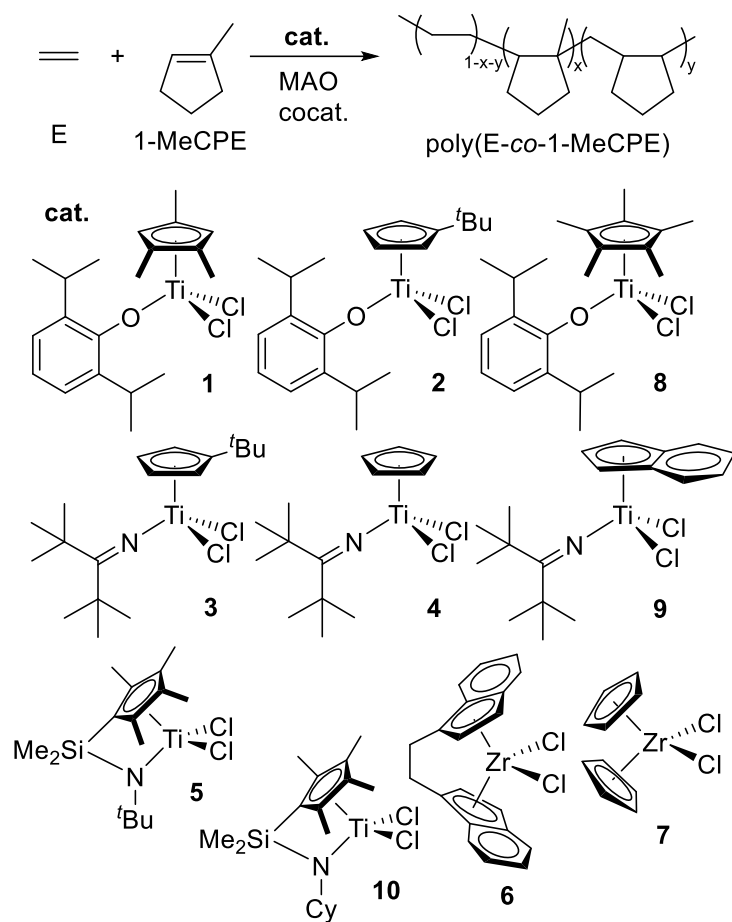
^aConditions: toluene+comonomer total 10 mL, 25 °C, 10 min, MAO 3.0 mmol. ^bInitial comonomer concentration (mol/L). ^cActivity in kg-polymer/mol-Ti·h. ^dGPC data in *o*-dichlorobenzene vs polystyrene standards. ^eComonomer content (mol%) estimated by ¹³C NMR spectra.⁶¹ ^fBy DSC thermograms.⁶¹ ^gSmall T_m shoulder at ca.120 °C was also observed on the DSC thermogram.⁶¹ ^hPolymerization time 6 min.

Table 2 summarizes results for polymerization of ethylene with 1-methylcyclopentene (1-MeCPE) using modified half-titanocenes, $\text{Cp}'\text{TiCl}_2(\text{Y})$ [$\text{Y} = \text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$, $\text{Cp}' = 1,2,4\text{-Me}_3\text{C}_5\text{H}_2$ (**1**), $t\text{BuC}_5\text{H}_4$ (**2**), C_5Me_5 (Cp^* , **8**); $\text{X} = \text{N}=\text{C}'\text{Bu}_2$, $\text{Cp}' = t\text{BuC}_5\text{H}_4$ (**3**), C_5H_5 (Cp , **4**), indenyl (**9**)], in the presence of MAO cocatalyst. The results by linked half-titanocene, $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{NR})]\text{TiCl}_2$ [$\text{R} = t\text{Bu}$ (**5**), cyclohexyl (**10**)], and ordinary metallocenes (**6,7**) conducted under the same conditions are also placed for comparison.

It should be noted that the observed catalytic activity in the copolymerization by $(1,2,4\text{-Me}_3\text{C}_5\text{H}_2)\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ (**1**) was affected by ethylene pressure and the 1-MeCPE concentration (runs 30-38) changed, and the activity decreased upon increasing the 1-MeCPE concentration (runs 30-36). The resultant polymers were poly(ethylene-co-1-MeCPE)s that possess unimodal molecular weight distributions (by GPC traces) and compositions confirmed by DSC thermograms [single melting temperature (T_m)];⁶¹ the T_m value decreased upon increasing the 1-MeCPE content (estimated by ^{13}C NMR spectra, described below). The results (activities, M_n values, and T_m values in the resultant polymers) were reproducible (runs 30-36). In contrast, the resultant polymers prepared by the $t\text{BuC}_5\text{H}_4$ -aryloxo analogue (**2**) possess several melting temperatures, suggesting that these polymers are a mixture of several compositions. Although we are unsure of the exact reason for the observed difference, one probable cause would be a steric bulk of 1,1-disubstituted olefins, which might hinder coordination, as observed in the ethylene copolymerization with 2-methyl-1-pentene.^{9,50,51} The polymerization by the Cp^* -aryloxo analogue (**8**), which has been known as the effective catalyst for certain ethylene copolymerizations (with 2-methyl-1-pentene,^{50,51} vinylcyclohexane⁵² etc.),⁸⁻¹⁰ afforded polymers possessing less 1-MeCPE incorporation (estimated by T_m values in the DSC thermograms) compared to those by **1**.⁶¹

The similar ethylene polymerizations in the presence of 1-MeCPE were conducted by the ketimide-modified half-titanocenes (**3,4,9**), because these catalysts showed efficient CPE incorporation in the ethylene/CPE copolymerization (exemplified in run 46).⁴² The resultant polymers by **3** possessed high molecular weights with uniform molecular weight distributions, suggesting that the polymerization proceeded with uniform catalytically active species. **Although** the T_m value in the DSC thermograms decreased upon increasing the 1-MeCPE concentration charged, suggesting that the resultant polymers incorporated 1-MeCPE (runs 47,48),⁶¹ **however**, the contents were low (less than ca. 3 mol% **on the basis of T_m**). Moreover, the melting temperatures in the resultant polymers prepared by the Cp-ketimide (**4**), and the indenyl-ketimide (**9**) analogues were higher than those by **3**, strongly **suggesting that** the resultant polymers prepared by **4,9** possessed negligible 1-MeCPE incorporations.⁶¹

Moreover, the resultant polymers prepared by using the liked half-titanocene (**5**), and ordinary metallocene (**6,7**), **conducted under the similar** polymerization **conditions, did not** incorporate 1-MeCPE (or negligible incorporation) on the basis of DSC thermograms (ca. 130 °C). The cyclohexyl analogue (**10**) exhibited low catalytic activity, affording polymer with bimodal molecular weight distributions (run 54).⁶¹ Therefore, **it is concluded that** only the 1,2,4-Me₃C₅H₂-aryloxo analogue (**1**) afforded the copolymers with rather high 1-MeCPE contents.



Scheme 4. Ethylene copolymerization with 1-methylcyclopentene (1-MeCPE).

Table 2. Copolymerization of ethylene with 1-methylcyclopentene (1-MeCPE), by **1-10** — MAO catalyst systems.^a

run	catalyst (μmol)	ethylene / atm	1-MeCPE conc. ^b / M	yield / mg	activity ^c	M_n^d $\times 10^{-4}$	M_w/M_n^d	content ^e / mol%	T_m^f / $^{\circ}\text{C}$
30	1 (0.5)	2	2.0	142	1700	14.4	1.62		116
31	1 (0.5)	2	2.5	130	1560	6.28	1.40	3.2	110
32	1 (0.5)	2	2.5	129	1540	6.29	1.49		111
33	1 (0.5)	2	5.0	122	1470	4.22	1.42	4.4	98
34	1 (0.5)	2	5.0	111	1330	4.54	1.38		101
35	1 (0.5)	2	7.5	87	1040	2.58	1.46	7.1	80
36	1 (0.5)	2	7.5	81	971	2.50	1.53		
37	1 (0.5)	4	5.0	186	2230	14.6	1.51		114
38	1 (0.5)	4	5.0	176	2120	15.9	1.51		117
39	2 (1.0)	2	2.0	294	1760	9.61	1.32		104,113,120
40	2 (1.0)	2	2.5	231	1380	8.33	1.48	-	98,117,124
41	2 (1.0)	2	5.0	155	928	5.87	1.42	(8.2) ^h	87,125
42	2 (1.0)	2	5.0	151	907	4.89	1.37		82,127
43	2 (1.0)	4	5.0	437	2620	11.3	1.36		106,113
44	8 (0.5)	2	5.0	186	2230	77.2	2.07	-	118
45	8 (0.5)	2	7.5	124	1490	10.8	1.50	-	108
46	3^g (0.1)	2	5.0	372	22600	13.4	1.69	43.6	-
47	3 (1.0)	2	5.0	405	2430	78.8	2.42		118
48	3 (0.1)	2	5.0	127	7600	163	2.05		113
49	3 (0.1)	2	7.5	76	4550	127	2.04		108
50	4 (1.0)	2	5.0	29	173	93.1	3.24		131
51	4 (1.0)	2	5.0	46	276	bimodal			125
52	9 (0.02)	2	5.0	82	24600	95.7	2.84	-	124
53	9 (0.02)	2	5.0	75	22600	88.9	2.63		127
54	5 (1.0)	2	5.0	248	1490	35.8	2.03		130
55	10 (3.0)	2	5.0	29.1	58.2	bimodal			106,128
56	6 (1.0)	2	5.0	844	5100	16.9	3.11		129
57	7 (1.0)	2	5.0	552	1660	28.0	2.54		135

^aConditions: toluene + 1-MeCPE total 10 mL, 25 $^{\circ}\text{C}$, 10 min, MAO 3.0 mmol. ^bInitial comonomer concentration (mol/L). ^cActivity in kg-polymer/mol-Ti \cdot h. ^dGPC data in *o*-dichlorobenzene vs polystyrene standards. ^eComonomer content (mol%) estimated by ^{13}C NMR spectra.⁶¹ ^fBy DSC thermograms.⁶¹ ^gCopolymerization with cyclopentene cited from reference 42. ^h1-MeCPE content in the whole polymer estimated by ^{13}C NMR spectrum.⁶¹

2. Microstructural Analysis of Poly(ethylene-co-4-MeCHE)s and Poly(ethylene-co-1-MeCPE)s.

Figure 1 shows the ^{13}C NMR spectra for poly(ethylene-co-4-methylcyclohexene) with different comonomer (4-MeCHE) contents prepared with ($t\text{BuC}_5\text{H}_4$) $\text{TiCl}_2(\text{O}-2,6\text{-Cl}_2\text{C}_6\text{H}_3)$ (**2**) - MAO catalyst system, and a dept spectrum.⁶¹

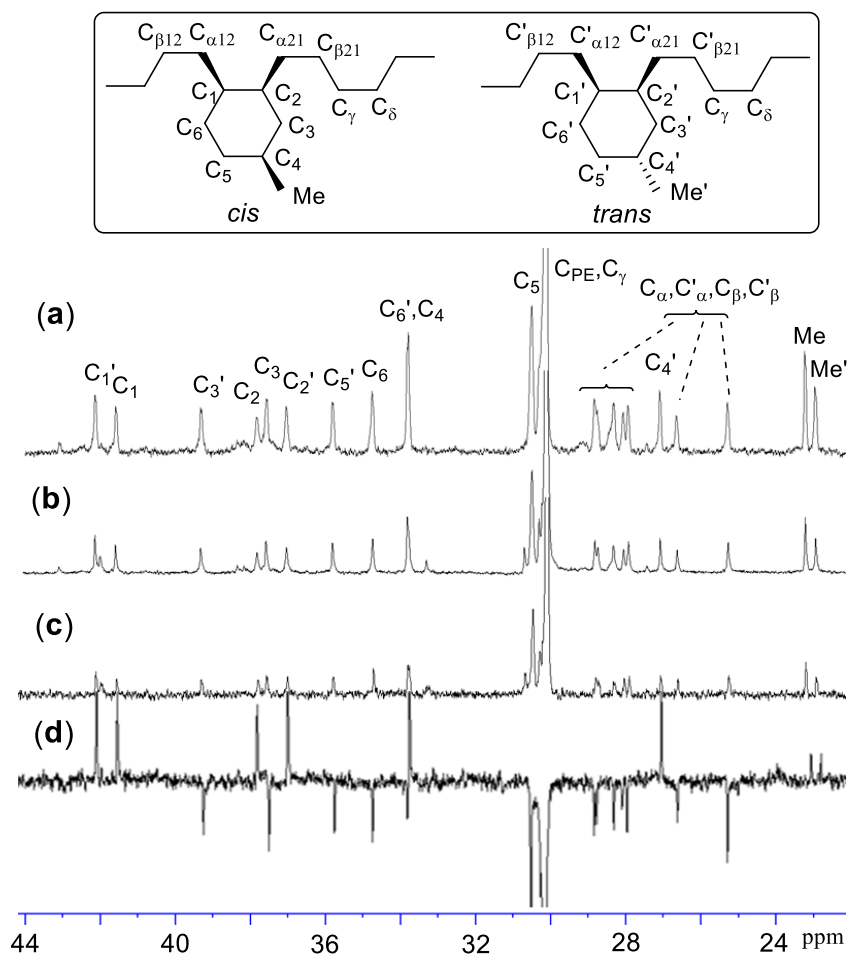
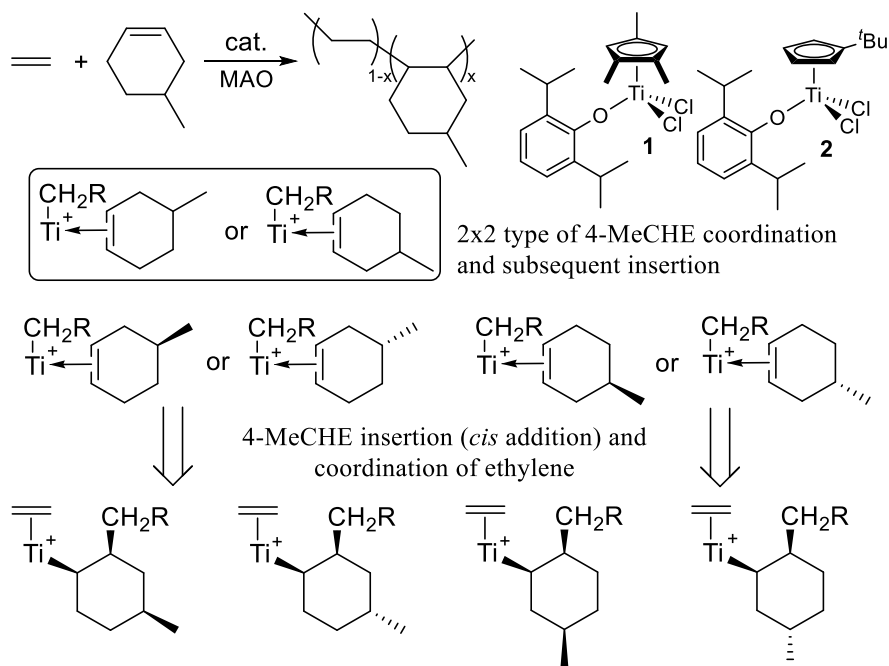


Figure 1. ^{13}C NMR spectra (a-c) and (d) the dept spectrum for poly(ethylene-co-4-MeCHE)s [4-MeCHE content: (a) 19.4 mol% (run 17 in Table 1), (b) 12.3 mol% (run 16), and (c,d) 6.3 mol% (run 15)] prepared by ($t\text{BuC}_5\text{H}_4$) $\text{TiCl}_2(\text{O}-2,6\text{-Cl}_2\text{C}_6\text{H}_3)$ (**2**) - MAO catalyst system (in 1,1,2,2-tetrachloroethane- d_2 at 110 °C).⁶¹

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, **that it is assumed to be *cis***, 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 ^1H - ^{13}C HSQC (Heteronuclear Single Quantum Coherence) and HMBC (Heteronuclear Multiple Bond Correlation) spectra (see Supporting Information, **Figures S2-1,2**),⁶¹ on the basis of comparison with the ^{13}C NMR spectra of poly(ethylene-*co*-CHE)s,⁴³ and considering possible stereo-chemical shifts, originated from the conformational characteristics of the copolymer chain.

As shown in Scheme 5, 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.



Scheme 5. Possible *cis* (1,2- and 2,1-) insertion modes in copolymerization of ethylene with 4-methylcyclohexene (**4-MeCHE**).

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-position is *cis* or *trans* with respect to the first CH₂ of the polymer chain (see **Chart 1**). Such a difference can have big effect on the chemical shifts of the carbons.^{62, 63}

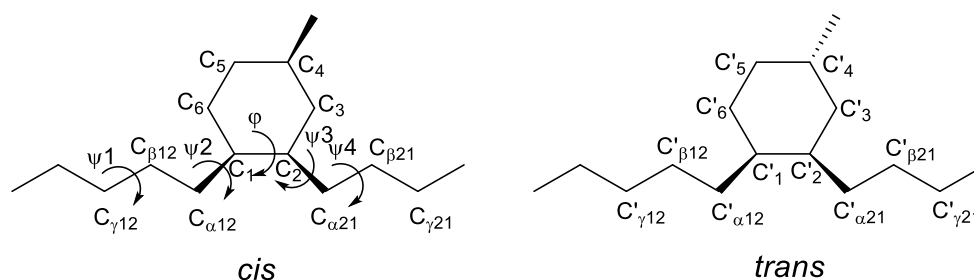


Chart 1. Two possible stereoisomers in poly(ethylene-*co*-4-MeCHE) with isolated comonomer incorporation.

In order to understand if there are differences in the ¹³C 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. 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, CH₂₍₁₂₎, and CH₂₍₂₁₎ substituents and on their interactions in each conformer (**Chart 2**). The ¹³C chemical shifts are influenced by γ -gauche effects in the allowed conformations and by the populations of the different conformers. In Table **S2-1** the possible conformers of the *trans* and *cis* isomers are described.

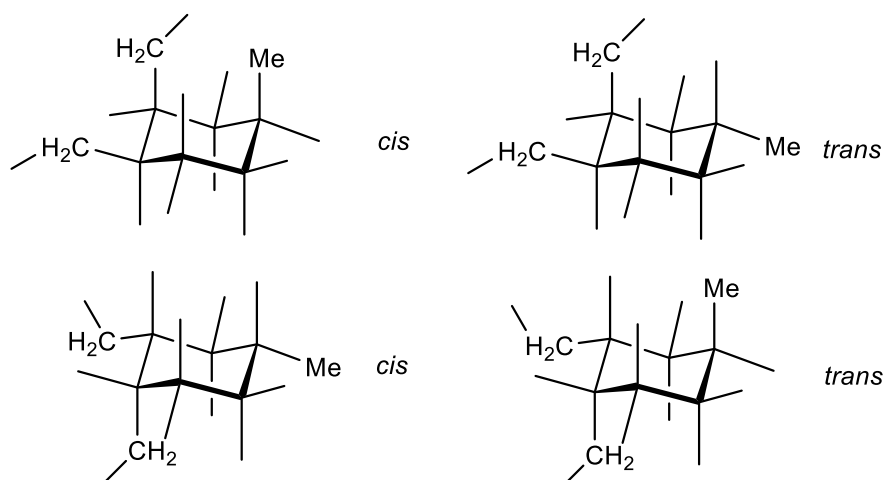


Chart 2. Possible four conformations (chair forms), stereo isomers considered in 4-MeCHE incorporation into methylene (linear polyethylene) units.

In each stereoisomer the two CH₂ of ethylene units adjacent to cyclohexane ring are one axial and one equatorial (named C_{α21} and C_{α12} in Chart 1). The methyl in position 4 causes steric interactions when in the axial position. When the methyl of the *cis* isomer is axial, it has a strong interaction with the axial CH₂, 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.

Observing the ¹³C spectrum of run containing 4-MeCHE, 6.3 mol%, in Figure 1, two methyls are present at 22.69 and 23.01 ppm, that were assigned to *trans* and *cis* stereoisomers, respectively, basing on conformational effects. The complex pattern of signals was assigned analyzing the 2D data. Following the correlations of the two methyls in the HMBC spectrum, along the proton dimension, (0.82 ppm protons of methyl at 22.69 ppm; 0.84 ppm protons of methyl at 23.01 ppm) it was possible to assign the closest carbon atoms C₃, C₄, and C₅. The methyl protons at 0.82 ppm, (CH₃ at 22.69 ppm) correlate with three carbons at 26.77, 35.65, and 39.34 ppm, respectively. As the carbon at 26.77 ppm was the only methyne from dept spectrum, it identified the C₄ atom. C₃

and C₅ were distinguished by considering a β additional effect on C₃ with respect to C₅, as C₃ has in β both the CH₂ of the polymer chain and the methyl group. Considering this effect and conformational considerations, the signal at 39.34 ppm was assigned to the C₃ methylene of *trans* stereoisomer, and the remaining carbon atom at 35.65 ppm to C₅. In the same way, from HMBC spectrum, the resonances of the *cis* stereoisomer positioning at 30.36 ppm, 33.59 ppm, and 37.56 ppm were assigned to C₅, C₄, and C₃, respectively (Figure S2-2).

According to the conformational effects and from 2D results, the remaining carbons of the structure were assigned as follows: 42.18 ppm to C₁; 37.14 ppm to C₂; 33.73 ppm to C₆ of the *trans* stereoisomer; 41.58 ppm to C₁; 37.89 ppm to C₂; 34.64 ppm to C₆ of the *cis* stereoisomer.

The CH₂ 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_{α21}, C_{α12}, C'_{α21}, and C'_{α12} for *cis* and *trans* isomers.

It turned out that cyclohexene moiety was incorporated in a *cis* 1,2-insertion manner without 1,3-insertion via β-hydrogen elimination (then isomerization) after CHE insertion,⁴³ which is often seen in poly(ethylene-*co*-cyclopentene)s prepared by ordinary zirconocene catalysts.³³⁻³⁵ This exclusive selectivity may be due to the lower tendency to undergo β-hydrogen elimination compared to the use of zirconocene catalysts as proposed previously.³⁶⁻⁴² The microstructure for the resultant copolymer possessed isolated 4-MeCHE sequences,⁶¹ while no alternating and 4-MeCHE dyads repeat units were observed, as in the poly(ethylene-*co*-CHE)s,⁴³ due to a difficulty to be incorporated.

Figure 2 shows ^{13}C NMR spectra and a dept spectrum (in 1,2,4-trichlorobenzene- d_6 at 110 °C) for poly(ethylene-*co*-1-MeCPE) prepared by ($^t\text{BuC}_5\text{H}_4$)TiCl₂(O-2,6-Cl₂C₆H₃) - MAO (**2**) and (1,2,4-Me₃C₅H₂)TiCl₂(O-2,6-Cl₂C₆H₃) (**1**) - MAO catalyst systems.⁶¹

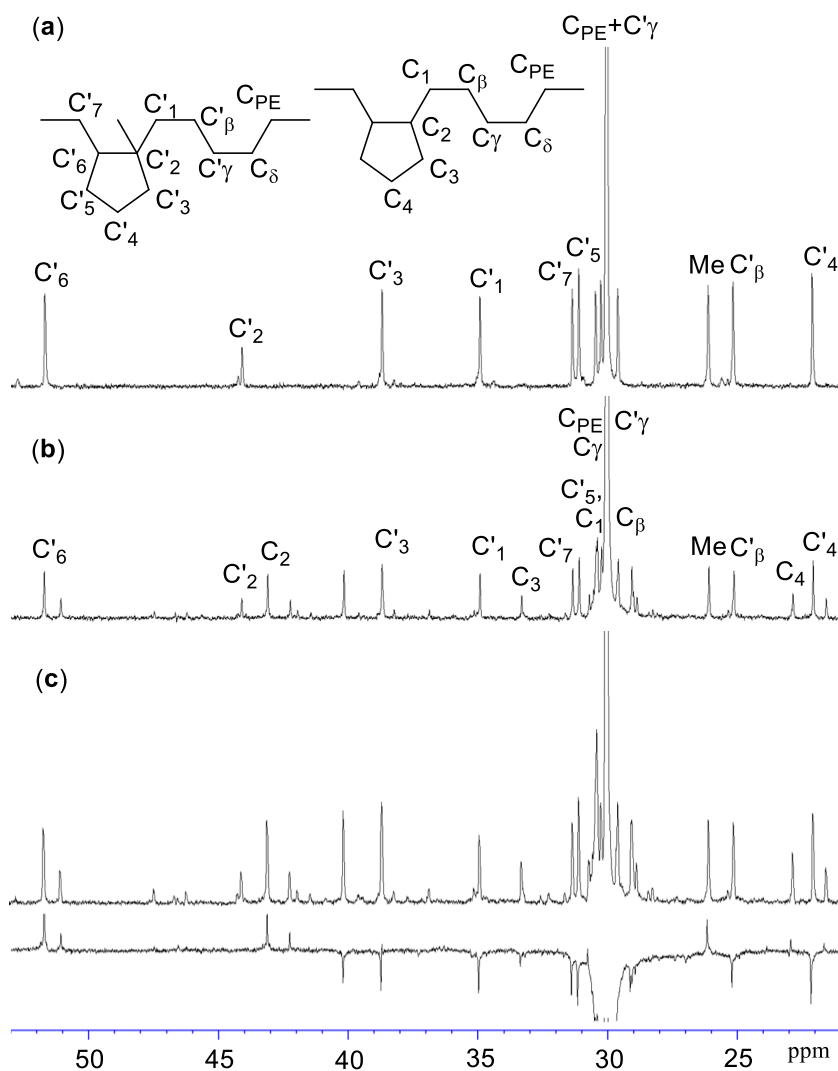
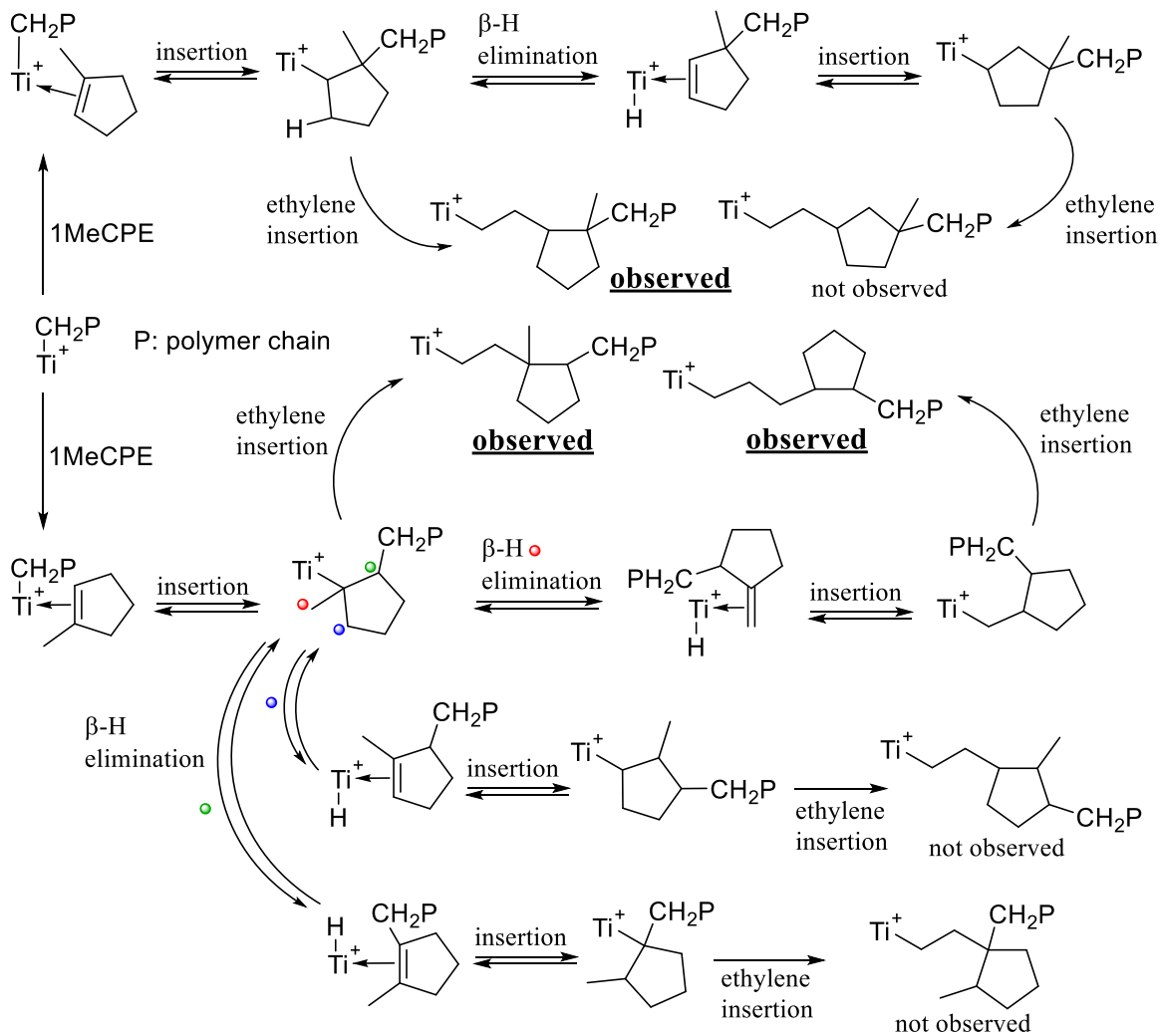
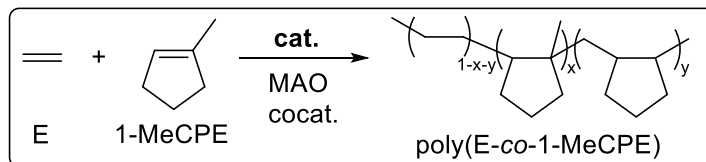


Figure 2. ^{13}C NMR spectra and the dept spectrum for poly(ethylene-*co*-1-MeCPE)s prepared by: (a) ($^t\text{BuC}_5\text{H}_4$)TiCl₂(O-2,6-Cl₂C₆H₃) - MAO catalyst system [**2**, run 41 (1-MeCPE 8.2 mol%)]; (b,c) (1,2,4-Me₃C₅H₂)TiCl₂(O-2,6-Cl₂C₆H₃) (**1**) - MAO catalyst system [1-MeCPE content: (b) 4.4 mol% (run 33), and (c) 7.1 mol% (run 35)] (in 1,1,2,2-tetrachloroethane- d_2 at 110 °C).⁶¹

Most of all resonances could be assigned on the basis of poly(ethylene-*co*-CPE),³³⁻⁴² poly(ethylene-*co*-methylene cyclopentane),^{18a,b} and the dept spectra.⁶¹ Scheme 6 describes possible insertion patterns in incorporation of 1-MeCPE in the copolymerization.

The spectrum of the copolymer prepared with (^tBuC₅H₄)TiCl₂(O-2,6-Cl₂C₆H₃) (**2**) – MAO catalyst system in Figure 2a is rather simple. Besides the (CH₂)_n peak at about 30 ppm there are 9 peaks, which should arise from the different environment of *cis* 1,2 insertion of 1-MeCPE. Resonance at 25.7 ppm is due to the methyl on CPE, while resonances at 51.42 and 31.3 ppm are easily assigned to C₆' and C₇', respectively from dept spectrum and by comparison with spectra of poly(ethylene-*co*-CPE). The other carbon atoms were assigned combining results from 2D NMR spectroscopy and from additive rules, by adding the methyl effect to the chemical shifts of a poly(ethylene-*co*-CPE) taken as a model. Considering the long term correlations of the methyl protons in the HMBC spectrum (Figure S2-4),⁶¹ it was possible to assign C₂' at 43.77 ppm; C₃' at 38.17 ppm; and C₁' at 34.18 ppm. The other signals are easily assigned for comparison to spectra of poly(ethylene-*co*-CPE). The spectra of copolymer prepared with (1,2,4-Me₃C₅H₂)TiCl₂(O-2,6-Cl₂C₆H₃) (**1**) - MAO catalyst system (Figure 2b,c) show resonances ascribed to 1,2- and 1,3- (formed as methylene cyclopentane unit) incorporations. Although compositions in the resultant polymers prepared by (^tBuC₅H₄)TiCl₂(O-2,6-Cl₂C₆H₃) (**2**) – MAO catalyst system were not uniform (containing polyethylene containing negligible 1-MeCPE incorporation), the polymer only possessed microstructure of ~~only~~ 1,2- (or 2,1-) insertion. Thus, this ~~it~~ would be an interesting fact that the microstructure ~~is~~ affected by the cyclopentadienyl fragment [1,2,4-Me₃C₅H₂ (**1**) vs ^tBuC₅H₄ (**2**)].⁶⁴



Scheme 6. Possible insertion modes in copolymerization of ethylene with 1-methylcyclopentene.

Summary

We have shown that 4-methylcyclohexene (4-MeCHE) **has been** incorporated in the ethylene copolymerization **for the first time** by using the aryloxo modified half-titanocenes, Cp'TiCl₂(O-2,6-*i*-Pr₂C₆H₃) [Cp' = 1,2,4-Me₃C₅H₂ (**1**), ^tBuC₅H₄ (**2**)], and the resultant copolymers possessed uniform molecular weight distributions as well as compositions confirmed by DSC thermograms. On the basis of microstructural analysis in the NMR spectra, 4-MeCHE was incorporated in 1,2- (or 2,1-) insertion manner and the resonances of carbons ascribed to isolated 4-MeCHE incorporations were observed. In contrast, the ketimide analogues, Cp'TiCl₂(N=C^tBu₂) [Cp' = ^tBuC₅H₄ (**3**), Cp (**4**)], linked half-titanocenes, [Me₂Si(C₅Me₄)(N^tBu)]TiCl₂ and ordinary metallocenes, [Et(indenyl)₂]ZrCl₂, Cp₂ZrCl₂, afforded polymers with negligible 4-MeCHE incorporations under the same conditions. It also turned out that the complex **1** only afforded copolymers with rather efficient comonomer incorporations in the ethylene copolymerization with 1-methylcyclopentene (1-MeCPE), affording poly(ethylene-*co*-1-MeCPE)s with uniform molecular weight distributions and compositions (confirmed by DSC thermograms). In contrast, the ^tBuC₅H₄ analogue (**2**) afforded polymers with a mixture of several compositions (confirmed by DSC thermograms) and the Cp* analogue showed less efficient 1-MeCPE incorporation (affording the copolymers with uniform compositions but negligible **1-MeCPE** incorporations) under the same conditions. The attempted copolymerization with the ketimide analogues [Cp' = ^tBuC₅H₄ (**3**), Cp (**4**), indenyl], linked half-titanocenes, [Me₂Si(C₅Me₄)(NR)]TiCl₂ (R = ^tBu, cyclohexyl), ordinary metallocenes, [Et(indenyl)₂]ZrCl₂, Cp₂ZrCl₂, afforded polymers with negligible 1-MeCPE incorporations. On the basis of microstructural analysis in the NMR spectra, 1-MeCPE was incorporated in 1,2- (or 2,1-) insertion in addition to 1,3-insertion (incorporated as methylene cyclopentane) manner. As far as we know, this is a very rare example of incorporation

of tri-substituted olefins into polyethylene by 1,2-incorporation. Attempted ethylene copolymerizations with 1-methylcyclohexene (1-MeCHE) afforded polymers with negligible comonomer incorporations, although the melting temperatures (T_m) in resultant polymers prepared by **1,2** were rather low compared to the polyethylene and the value decreased upon increasing the 1-MeCHE charged (conducted under high 1-MeCHE concentration).

We thus highly believe that the present results should introduce a new promising possibility for the synthesis of new polyolefins, and should also be of interest for the purpose of designing efficient molecular catalysts.

Experimental Section

General Procedures. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox unless otherwise specified. All chemicals used were of reagent grade and were purified by the standard purification procedures. Anhydrous grade toluene (Kanto Chemical Co., Inc.) was transferred into a bottle containing molecular sieves (mixture of 3 Å 1/16 and 4 Å 1/8, and 13X 1/16) under a nitrogen stream in the drybox and was used without further purification. Reagent grade 1-methylcyclohexene (Tokyo Chemical Industry Co., Ltd.), 4-methylcyclohexene (Tokyo Chemical Industry Co., Ltd.) and 1-methylcyclopentene (Sigma-Aldrich) were stored in bottles in the drybox in the presence of molecular sieves and were passed through an alumina short column before use. Toluene and AlMe₃ in the commercially available methylaluminoxane [TMAO, 9.5 wt% (Al) toluene solution; Tosoh Finechem Co.] were removed under reduced pressure (at ca. 50 °C for removing toluene and AlMe₃ and then heated at >100 °C for 1 h for completion) in the drybox to give white solids. (1,2,4-Me₃C₅H₂)TiCl₂(O-2,6-ⁱPr₂C₆H₃) (**1**),⁶⁵ (^tBuC₅H₄)TiCl₂(O-2,6-ⁱPr₂C₆H₃) (**2**),⁶⁶ (^tBuC₅H₄)TiCl₂(N=C^tBu₂) (**3**)⁶⁷ and CpTiCl₂(N=C^tBu₂) (**4**)⁶⁸ were prepared according to previous reports. [Me₂Si(C₅Me₄)(NR)]TiCl₂ [R = ^tBu, Cy] was prepared according to a reported procedure,⁶⁹ *rac*-[Et(indenyl)₂]ZrCl₂ (Strem Chemicals Inc.), Cp₂ZrCl₂ (Kanto Chemical Co., Inc.) were used as received. Ethylene for polymerization was of polymerization grade (purity >99.9%; Sumitomo Seika Co., Ltd.) and was used as received.

¹H and ¹³C NMR spectra were recorded on a Bruker AV500 spectrometer (500.13 MHz, ¹H; 125.77 MHz, ¹³C) and all chemical shifts are given in ppm and are referred to SiMe₄. ¹³C NMR spectra for the resultant polymers were recorded with proton decoupling, and the pulse interval was 5.2 sec, the acquisition time was 0.8 sec, the pulse angle was 90°, and the number of transients

accumulated was ca. 6000. The copolymer samples for analysis were prepared by dissolving the polymers in 1,1,2,2-tetrachloroethane- d_2 solution (for ^1H NMR spectra) or in 1,2,4-trichlorobenzene-benzene- d_6 (for ^{13}C NMR spectra), and the spectra were measured at 80 °C or 110 °C (for ^1H , ^{13}C NMR spectra, respectively).⁶¹

2D experiments were recorded on Bruker DMX spectrometers operating at 11.7 and 14 T, equipped with a 5 mm PFG probe. The working temperature was 60 °C. Samples were dissolved in 1,1,2,2-tetrachloroethane- d_2 , and chemical shifts were referenced to the polyethylene signal at 30.00 ppm, in the ^{13}C spectra; in the ^1H spectra the residual signal of the solvent was placed at 5.94 ppm. The 90° pulse was calculated for each sample.

g-HSQC experiments were carried out with a delay of 1.92 ms, corresponding to a $^1J_{\text{CH}} = 130$ Hz. g-HMBC experiments, optimized on long range couplings, were carried out with a delay of 125 ms for the evolution of long-range coupling.

Molecular weights and molecular weight distributions for the resultant polymers were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) using a RI-8022 detector (for high temperature; Tosoh Co.) with a polystyrene gel column (TSK gel GMHHR-H HT \times 2, 30 cm \times 7.8 mm i.d.), ranging from $<10^2$ to $<2.8 \times 10^8$ MW) at 140 °C using *o*-dichlorobenzene containing 0.05 wt/v% 2,6-di-*tert*-butyl-*p*-cresol as the solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples. Differential scanning calorimetric (DSC) data for the polymer were recorded by means of Hitachi DSC-7020 instrument under a nitrogen atmosphere (Preheating: from 30 to 250 °C (20 °C/min). Samples were heated from -100 °C to 250 °C at a rate of 10 °C/min and then cooled at the same rate. This heating and cooling was repeated two times. T_m values were determined from the middle point of the phase transition of the second heating scan.⁶¹

Copolymerization of ethylene with methylcyclohexenes, 1-methylcyclopentene. The typical reaction procedure for ethylene/4-methylcyclohexene (4-MeCHE) copolymerization (Table 1, run 4) is as follows. Toluene (3 mL), d-MAO solid (174 mg, 3.0 mmol), and 4-MeCHE (50 mmol) were added into the autoclave (100 mL scale, stainless steel) under stirring in the box, and the reaction apparatus was then filled with ethylene (absolute pressure 1 atm) at room temperature. A toluene solution (1.00 mL) containing **1** (2.0 μmol) was then added into the autoclave, and the reaction apparatus was then immediately pressurized to 1 atm (absolute pressure 2 atm). The mixture was magnetically stirred for 10 min, ethylene remained was purged after reaction, and the mixture was then poured into MeOH (150 mL) containing HCl (10 mL). The resultant polymer was collected on a filter paper by filtration, and was adequately washed with MeOH, and was then dried *in vacuo* for several hours. Experimental procedures for ethylene/1-methylcyclohexene (1-MeCHE) and ethylene/1-methylcyclopentene (1-MeCPE) copolymerizations were the same as those for the ethylene/4-MeCHE copolymerizations except that a prescribed amount of comonomer was charged and the total volume of toluene and comonomer was set to 10 mL.

Supporting Information. The following materials are available free of charge via the Internet at <http://pubs.acs.org>.”

Selected NMR spectra and DSC thermograms in the resultant polymers, assignment of resonances in the copolymers.

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

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