

Effect of *para*-Substituents in Ethylene Copolymerizations with 1-Decene, 1-Dodecene, and with 2-Methyl-1-Pentene Using Phenoxide Modified Half-Titanocenes-MAO Catalyst Systems

Suphitchaya Kitphaitun, Qing Yan, and Kotohiro Nomura^{*[a]}

Effect of *para*-substituents in the ethylene (E) copolymerization with 1-decene (DC), 1-dodecene (DD), and with 2-methyl-1-pentene (2M1P) using a series of Cp^{*}TiCl₂(O-2,6-*i*-Pr₂-4-R-C₆H₂) [R=H (1), ^tBu (2), Ph (3), CHPh₂ (4), CPh₃ (5), SiMe₃ (6), SiEt₃ (7), and newly prepared 4-^tBuC₆H₄ (8) and 3,5-Me₂C₆H₃ (9)]-MAO catalyst systems has been studied. The activities in these copolymerization reactions were affected by the *para*-substituent, and the SiMe₃ (6), SiEt₃ (7) and 3,5-Me₂C₆H₃ (9) analogues showed the higher activities at 50 °C in the E copolymerization

reactions with DC (1.06–1.44 × 10⁶ kg-polymer/mol-Ti·h), DD (1.04–1.88 × 10⁶ kg-polymer/mol-Ti·h) than the others, whereas no significant differences were observed in the comonomer incorporations. Complexes 6 and 7 also showed the higher activities at 50 °C in the E/2M1P copolymerization, and the 2M1P incorporation was affected by the *para*-substituent and the polymerization temperature; complex 9 showed better 2M1P incorporation at 25 °C.

1. Introduction

Polyolefins, that account for ca. 50% commercialized synthetic polymers in the world, are widely used in our daily life, and transition metal catalyzed olefin coordination insertion polymerization has been the key technology. Synthesis of new polymers by the designed molecular catalysts has been considered as an important subject in the field of catalysis, organometallic chemistry, and of polymer chemistry.^[1,2] In particular, synthesis of the new copolymers (containing sterically encumbered monomers or cyclic olefins that are not incorporated by ordinary catalysts,^[3,4] or by incorporation of polar functionalities^[5,6]), have been one of the most fascinating goals in this research field. Modified half-titanocenes containing anionic ancillary donor ligands^[4] of type, Cp^{*}TiX₂(Y) (Cp^{*}=cyclopentadienyl; X=Cl, Me etc.; Y=anionic donor ligand such as phenoxide,^[7,8] ketimide,^[9,10] phosphinimide,^[11] iminoimidazolide,^[12] iminoimidazolidide^[13] etc.^[14]), have been the promising catalysts for the above purpose, because the catalysts enable synthesis of ethylene copolymers with disub-

stituted or branched α -olefins,^[15] cyclic olefins^[16] by the ligand modification.^[4]

In this paper, we focus on the Cp^{*}-phenoxide analogues with different *para*-substituents. This is because that the complexes of this type, Cp^{*}TiX₂(O-2,6-*i*-Pr₂C₆H₃) [Cp^{*}=C₅Me₅; X=Cl (1), Me], exhibit not only remarkable catalytic activities for ethylene/ α -olefin copolymerization,^[7b,15c] but also enable synthesis of ethylene copolymers by incorporation of 2-methyl-1-pentene,^[15a,c] vinylcyclohexane,^[15b] 3-methyl-1-pentene,^[15d] and cyclooctene^[16f] in the copolymerization. The catalysts also display unique characteristics for synthesis of unsaturated polymers by incorporation of non-conjugated dienes^[17] and of ultrahigh molecular weight long chain poly(α -olefins).^[18] More recently, we communicated an efficient synthesis of high-molecular-weight ethylene copolymers incorporating 9-decen-1-ol (or 5-hexen-1-ol) in the ethylene copolymerization by Cp^{*}TiCl₂(O-2,6-*i*-Pr₂-4-SiEt₃-C₆H₂)-MAO catalyst system.^[19] The complexes containing SiMe₃, SiEt₃ groups as the *para* substituent also exhibit high catalytic activities for ethylene copolymerization of 2-methyl-1-pentene, 1-decene and with 1-dodecene.^[19]

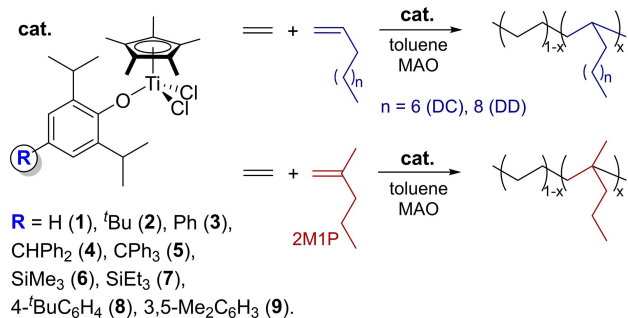
In this full article, we wish to present the explored results in detail concerning effect of *para*-substituents in the ethylene copolymerization with 1-decene (DC), 1-dodecene (DD), and with 2-methyl-1-pentene (2M1P) using a series of Cp^{*}TiCl₂(O-2,6-*i*-Pr₂-4-R-C₆H₂)-MAO catalyst systems [R=H (1), ^tBu (2), Ph (3), CHPh₂ (4), CPh₃ (5), SiMe₃ (6), SiEt₃ (7), 4-^tBuC₆H₄ (8), 3,5-Me₂C₆H₃ (9)] (Scheme 1); complexes 8 and 9 were newly prepared for this purpose. Through this study, we wish to represent thermally resistant new catalysts for the efficient ethylene copolymerization, and the activities were affected by the *para*-substituent employed.

[a] S. Kitphaitun, Dr. Q. Yan, Prof. Dr. K. Nomura
Department of Chemistry
Tokyo Metropolitan University
1-1 Minami Osawa, Hachioji
Tokyo 192-0397 (Japan)
E-mail: ktnomura@tmu.ac.jp

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/open.202100047>

International Symposium on Homogeneous Catalysis (Special Collection)

© 2021 The Authors. Published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.



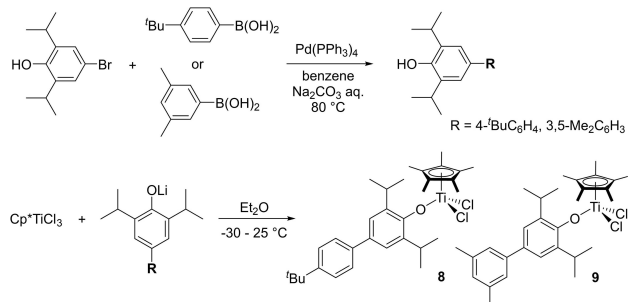
Scheme 1. Ethylene copolymerization with 1-decene (DC), 1-dodecene (DD), and with 2-methyl-1-pentene (2M1P) using Cp*TiCl₂(O-2,6-ⁱPr₂-4-R-C₆H₂)-MAO catalyst systems [R = H (1), ^tBu (2), Ph (3), CHPh₂ (4), CPh₃ (5), SiMe₃ (6), SiEt₃ (7), 4-^tBuC₆H₄ (8), 3,5-Me₂C₆H₃ (9)].

2. Results and Discussion

1. Ethylene Copolymerization with 1-Decene, 1-Dodecene Using Cp*TiCl₂(O-2,6-ⁱPr₂-4-R-C₆H₂)-MAO catalyst systems [R = H (1), ^tBu (2), Ph (3), CHPh₂ (4), CPh₃ (5), SiMe₃ (6), SiEt₃ (7), 4-^tBuC₆H₄ (8), 3,5-Me₂C₆H₃ (9)].

A series of the half-titanocene dichloride complexes containing different *para*-substituents on the 2,6-diisopropylphenoxy ligand, Cp*TiCl₂(O-2,6-ⁱPr₂-4-R-C₆H₂) [R = H (1), ^tBu (2), Ph (3), CHPh₂ (4), CPh₃ (5), SiMe₃ (6), SiEt₃ (7), 4-^tBuC₆H₄ (8), 3,5-Me₂C₆H₃ (9)], have been chosen for this study. Complexes 8 and 9 were newly prepared according to the analogous procedure for syntheses of 1–7,^[7,19,20] by treating Cp*TiCl₃ with the corresponding lithium phenoxides in Et₂O; the ligands, HO-2,6-ⁱPr₂-4-(4-^tBuC₆H₄)-C₆H₂ and HO-2,6-ⁱPr₂-4-(3,5-Me₂C₆H₃)-C₆H₂ were prepared from HO-2,6-ⁱPr₂-4-Br-C₆H₂ by coupling reactions in the presence of Pd catalysts (Scheme 2) (details are shown in the Experimental Section). The prepared complexes were identified by NMR spectra and elemental analysis. As reported in the crystal structures in 1,^[7a] 2,^[20] 6 and 7,^[19] the Ti–O–C(phenyl) bond angles [173.0(3), 174.0(3), 172.5(3), 174.62(19)° for 1, 2, 6, 7, respectively] are rather large compared to the others,^[7,20] which led to exhibiting the high activity by increased stabilization of the active species, cationic Ti(IV) alkyls,^[8a,21] by O→Ti π-donation.^[4c,19,20]

Ethylene (E) copolymerizations with 1-decene (DC), 1-dodecene (DD) (called long-chain α-olefins) using complexes 1–



Scheme 2. Synthesis of Cp*TiCl₂(O-2,6-ⁱPr₂-4-R-C₆H₂) [R = 4-^tBuC₆H₄ (8), 3,5-Me₂C₆H₃ (9)].

9 were conducted in toluene in the presence of AlMe₃-free MAO white solid (d-MAO). Table 1 summarizes results of the E/DC copolymerization by 1–9 – MAO catalyst systems. It turned out that the catalytic activities (on the basis of polymer yields) at 25 °C were affected by the *para*-substituent in the phenoxide ligand, and the activity increased in the order (also shown in Figure 1): R = Ph (3) < H (1) < ^tBu (2) < Ph₃C (5) < 4-^tBuC₆H₄ (8) < 3,5-Me₂C₆H₃ (9) < SiEt₃ (7) < Ph₂CH (4) < SiMe₃ (6). It also turned out that the activities by 2–9 at 50 °C are higher than those conducted at 25 °C, whereas a slight decrease in the activity was observed by 1 (3.46–3.50 × 10⁵ → 2.42 × 10⁵ kg-polymer/mol-Ti·h). In particular, the SiMe₃ analogue (6) showed a notable increase in the activity at 50 °C (8.04 × 10⁵ → 1.44 × 10⁶ kg-polymer/mol-Ti·h). As reported previously,^[19] the notable activities were observed by the SiMe₃ (6) and SiEt₃ (7) analogues at 50 °C even under the low catalyst concentration conditions (runs 17 vs 18, 21 vs 22). The resultant polymers were poly(E-co-DC)s that possess relatively high molecular weights with unimodal molecular weight distributions ($M_n = 1.38\text{--}1.97 \times 10^5$; $M_w/M_n = 1.48\text{--}1.85$) as well as with high DC contents (20.1–21.4 mol%).

Results in the E/DD copolymerization are summarized in Table 2. It was revealed that, as observed in the E/DC copolymerization, complexes 2, 6, 7 and 9 (7.39–10.4 × 10⁵ kg-polymer/mol-Ti·h) showed higher activities at 25 °C than 1 (6.44 × 10⁵ kg-polymer/mol-Ti·h). In particular, the SiMe₃ (6, run 40; activity 1.88 × 10⁶ kg-polymer/mol-Ti·h) and the SiEt₃ (7, run 44; 1.61 × 10⁶ kg-polymer/mol-Ti·h) analogues showed the highest activities. The activity at 25 °C increased in the order: R = Ph (3), Ph₃C (5), 4-^tBuC₆H₄ (8) < Ph₂CH (4) < H (1) < ^tBu (2) < 3,5-Me₂C₆H₃ (9) < SiMe₃ (6) < SiEt₃ (7). Moreover, the activity at 50 °C increased in the order: R = Ph (3) < 4-^tBuC₆H₄ (8) < Ph₃C (5), Ph₂CH (4) < H (1) < ^tBu (2), 3,5-Me₂C₆H₃ (9) < SiEt₃ (7) < SiMe₃ (6). The order is somewhat different from that in the E/DC copolymerization as well as that between 25 °C and 50 °C, although the reason is unclear at this moment.

Importantly, as shown in Figure 1, the activities by 2–9 increased at 50 °C in all cases, whereas slight decrease in the activity was observed by 1 at 50 °C (runs 28, 29). As described above, both the SiMe₃ (6) and the SiEt₃ (7) analogues showed the highest activities, and the 3,5-Me₂C₆H₃ analogue (9) also showed a notable increase in the activity at 50 °C (run 27,

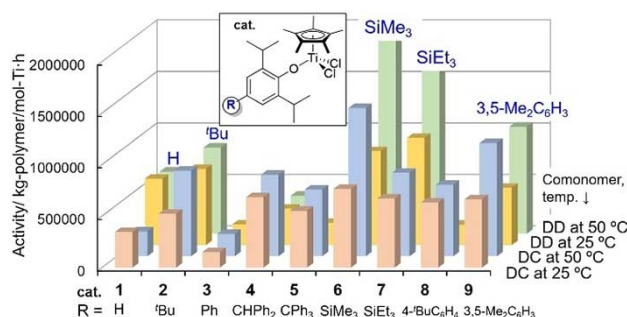


Figure 1. Effect of *para*-substituent in ethylene copolymerization with 1-decene (DC), 1-dodecene (DD) using Cp*TiCl₂(O-2,6-ⁱPr₂-4-R-C₆H₂) [R = H (1), ^tBu (2), Ph (3), CHPh₂ (4), CPh₃ (5), SiMe₃ (6), SiEt₃ (7), 4-^tBuC₆H₄ (8), 3,5-Me₂C₆H₃ (9)]-MAO catalyst systems (ethylene 6 atm, DC 0.88 M or DD 0.75 M in toluene at 25 or 50 °C).

Table 1. Ethylene copolymerization with 1-decene (DC) by Cp*TiCl₂(O-2,6-Pr₂-4-R-C₆H₂) [R = H (1), ^tBu (2), Ph (3), CHPh₂ (4), CPh₃ (5), SiMe₃ (6), SiEt₃ (7), 4-^tBuC₆H₄ (8), 3,5-Me₂C₆H₃ (9)]-MAO catalyst systems (ethylene 6 atm, toluene).^[a]

run	catalyst [μmol]	temp/ [°C]	yield/ [mg]	activity/ kg-polymer/mol-Ti-h	$M_n^{[b]}$ × 10 ⁻⁴	$M_w/M_n^{[b]}$	cont. ^[c] / [mol%]
1 ^[d]	1 [0.0050]	25	173	346000	19.7	1.61	21.4
2	1 [0.0050]	25	175	350000			
3 ^[d]	1 [0.0050]	50	121	242000	16.0	1.73	
4 ^[d]	2 [0.0025]	25	131	524000	19.5	1.71	
5	2 [0.0025]	25	128	512000			
6 ^[d]	2 [0.0010]	50	83.2	832000	15.5	1.79	
7 ^[d]	3 [0.0050]	25	75.3	151000	15.3	1.58	
8 ^[d]	3 [0.0050]	50	109	218000	14.6	1.52	
9	4 [0.0025]	25	171	684000	15.5	1.85	
10	4 [0.0025]	50	198	792000	16.7	1.58	
11	5 [0.0050]	25	281	562000			
12	5 [0.0025]	25	138	552000	13.8	1.54	21.1
13	5 [0.0050]	50	385	770000			
14	5 [0.0025]	50	162	648000	14.0	1.48	21.4
15 ^[d]	6 [0.0025]	25	191	764000	18.4	1.67	20.1
16	6 [0.0025]	25	201	804000			
17	6 [0.0025]	50	299	1200000			
18 ^[d]	6 [0.0010]	50	144	1440000	16.2	1.74	21.3
19 ^[d]	7 [0.0025]	25	168	672000	15.4	1.55	
20	7 [0.0025]	25	165	660000			
21	7 [0.0025]	50	266	1060000			
22 ^[e]	7 [0.0010]	50	81.1	811000	15.0	1.57	21.4
23	8 [0.0025]	25	158	632000	18.2	1.54	
24	8 [0.0025]	25	152	608000			
25	8 [0.0010]	50	69.5	695000	15.2	1.63	
26	9 [0.0025]	25	166	664000	15.4	1.53	
27	9 [0.0010]	50	110	1100000	16.0	1.71	21.1

[a] Conditions: toluene and 1-decene 5.0 mL (initial conc. 0.88 M) total 30.0 mL, ethylene 6 atm, 6 min, MAO 2.0 mmol. [b] GPC data in *o*-dichlorobenzene vs polystyrene standards. [c] 1-Decene (DC) content (mol%) estimated by ¹³C NMR spectra. [d] Cited from reference 19.

Table 2. Ethylene copolymerization with 1-dodecene (DD) by Cp*TiCl₂(O-2,6-Pr₂-4-R-C₆H₂) [R = H (1), ^tBu (2), Ph (3), CHPh₂ (4), CPh₃ (5), SiMe₃ (6), SiEt₃ (7), 4-^tBuC₆H₄ (8), 3,5-Me₂C₆H₃ (9)]-MAO catalyst systems (ethylene 6 atm, toluene).^[a]

run	catalyst [μmol]	temp/ [°C]	yield/ [mg]	activity/ kg-polymer/mol-Ti-h	$M_n^{[b]}$ × 10 ⁻⁴	$M_w/M_n^{[b]}$	cont. ^[c] / [mol%]
28 ^[d]	1 [0.0025]	25	161	644000	18.9	1.79	17.6
29 ^[d]	1 [0.0025]	50	151	604000	16.5	1.85	
30 ^[d]	2 [0.0010]	25	73.9	739000	18.4	1.60	18.3
31	2 [0.0025]	50	277	1110000			
32 ^[d]	2 [0.0010]	50	83.7	837000	16.9	1.67	
33 ^[d]	3 [0.0050]	25	99.8	200000	16.7	1.59	
34 ^[d]	3 [0.0025]	50	61.5	246000	15.4	1.52	
35 ^[d]	4 [0.0050]	25	176	352000	16.7	1.57	
36 ^[d]	4 [0.0050]	50	185	370000	15.2	1.54	17.5
37 ^[d]	5 [0.0050]	25	108	216000	16.9	1.52	
38	5 [0.0050]	50	196	392000	14.1	1.58	
39 ^[d]	6 [0.0010]	25	91.1	911000	15.0	1.62	
40 ^[d]	6 [0.0010]	50	188	1880000	15.3	1.54	16.3
41	7 [0.0025]	25	211	844000			
42 ^[d]	7 [0.0010]	25	104	1040000	16.7	1.62	15.3
43	7 [0.0025]	50	356	1420000			
44 ^[d]	7 [0.0010]	50	161	1610000	16.2	1.60	16.7
45	8 [0.0050]	25	98	196000	15.2	1.53	
46	8 [0.0010]	50	31.5	315000	15.2	1.54	
47	9 [0.0050]	25	447	894000			
48	9 [0.0010]	25	55.6	556000	15.2	1.61	17.6
49	9 [0.0010]	50	104	1040000	14.8	1.55	17.7

[a] Conditions: toluene and 1-dodecene 5.0 mL (initial conc. 0.75 M) total 30.0 mL, ethylene 6 atm, 6 min, MAO 2.0 mmol. [b] GPC data in *o*-dichlorobenzene vs polystyrene standards. [c] 1-Dodecene (DD) content (mol%) estimated by ¹³C NMR spectra. [d] Cited from reference 19.

activity 1.10 × 10⁶ kg-polymer/mol-Ti-h; run 49, activity 1.04 × 10⁶ kg-polymer/mol-Ti-h). The resultant poly(E-co-DD)s possessed rather high molecular weights with unimodal molecular

weight distributions ($M_n = 1.41\text{--}1.89 \times 10^5$; $M_w/M_n = 1.52\text{--}1.85$) as well as with high DD contents (15.3–18.3 mol%). Significant differences in the DD incorporation (DD contents in the

copolymers) were not observed in the resultant poly(E-co-DC) and poly(E-co-DD)s prepared by 1–9-MAO catalyst systems. Moreover, no significant differences in the DC/DD contents in the copolymers prepared between 25 °C and 50 °C, although 1-hexene content in poly(ethylene-co-1-hexene)s prepared by 1-MAO catalyst system slightly increased at 50 °C probably due to decrease in solubility of ethylene in toluene.^[22,23]

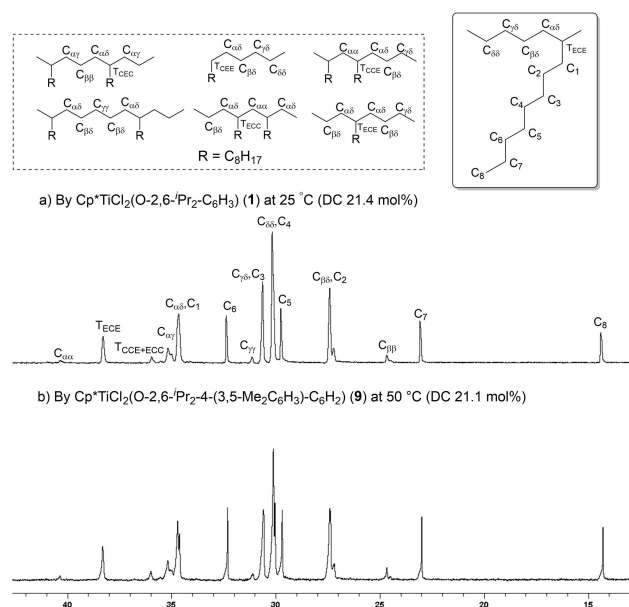


Figure 2. ^{13}C NMR spectra (in 1,1,2,2-tetrachloroethane- d_2 at 110 °C) for poly(ethylene-co-DC)s prepared by a) $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{-Pr}_2\text{-C}_6\text{H}_3)$ (1, run 1, DC 21.4 mol%) and b) $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{-Pr}_2\text{-}4\text{-(3,5-Me}_2\text{C}_6\text{H}_3)\text{-C}_6\text{H}_2)$ (9, run 27, DC 21.1 mol%).

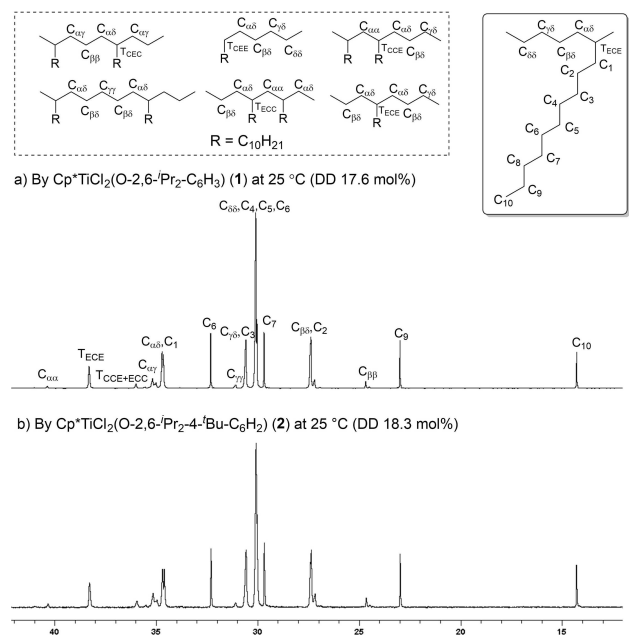


Figure 3. ^{13}C NMR spectra (in 1,1,2,2-tetrachloroethane- d_2 at 110 °C) for poly(ethylene-co-DD)s prepared by a) $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{-Pr}_2\text{-C}_6\text{H}_3)$ (1, run 28, DD 17.6 mol%) and b) $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{-Pr}_2\text{-}4\text{-}i\text{-Bu-C}_6\text{H}_2)$ (2, run 30, DD 18.3 mol%).

Figure 2 shows selected ^{13}C NMR spectra (in 1,1,2,2-tetrachloroethane- d_2 at 110 °C) of poly(ethylene-co-DC)s prepared by 1 (at 25 °C),^[19] 9 (at 50 °C), and Figure 3 shows the spectra of poly(ethylene-co-DD)s by 1, 2 – MAO catalyst systems (at 25 °C). Additional ^{13}C NMR spectra of poly(ethylene-co-DC)s and poly(ethylene-co-DD)s by 4–7, 9 at 25 and 50 °C are also shown in Figures S2-1-S2-11 in the Supporting Information.^[24] All resonances could be assigned according to the previous reports,^[15d,19] and the resultant copolymers [poly(ethylene-co-DC)s, poly(ethylene-co-DD)s] possessed resonances ascribed to the isolated DC or DD insertion in addition to resonances ascribed to the alternating sequence [assigned as $\text{C}_{\beta\beta}$, $\text{C}_{\alpha\gamma}$ and T_{ECE}]. Moreover, the resonance ascribed to repeated comonomer insertion were also observed ($\text{T}_{\text{ECC}+\text{CCE}}$, $\text{C}_{\alpha\alpha}$). The resultant polymers thus possessed random α -olefin (DC, DD) incorporation as also described below on the basis of analysis of monomer sequence distributions (Table 3).

Table 3 summarizes the triad sequence distribution, the dyads, r_E , r_C and $r_E r_C$ values (C = comonomer, DC, DD) on the basis of microstructure analysis estimated by the ^{13}C NMR spectra of poly(ethylene-co-DC)s and poly(ethylene-co-DD)s.^[25] The relative reactivity ratio, r_E , r_C can be used to evaluate the efficiency in the comonomer incorporation especially in the ethylene/ α -olefin copolymerization,^[7b,9b,14c,15d,18,22] because the large r_E value (also defined as $k_{\text{EE}}/k_{\text{EC}}$, k_{EE} is the reaction rate for ethylene insertion after ethylene incorporation and k_{EC} is the reaction rate for DC or DD insertion after incorporation of ethylene) expresses less comonomer incorporation compared to ethylene after ethylene insertion. The r_E values of a series of the dichloride complexes containing various *para*-substituents, $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{-Pr}_2\text{-}4\text{-R-C}_6\text{H}_2)$ [$\text{R}=\text{CPh}_3$ (5) and SiMe_3 (6)], are 2.94 (run 12, at 25 °C) and 3.60 (run 15, at 25 °C), respectively. Moreover, the r_E values in this series of *para*-substituted complexes (5–7, 9 at 50 °C) are close ($r_E=2.92\text{--}3.41$) to that by 1 (run 1, $r_E=3.12$). These values are smaller than those by $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^i\text{Bu})]\text{TiCl}_2$ (called constrained geometry type, $r_E=4.26, 4.31$), and Cp_2ZrCl_2 ($r_E=49$) in E/DD copolymerization.^[15d] Furthermore, $r_E r_C$ values estimated from analysis in poly(ethylene-co-DC)s by these *para*-substituted complexes possessed rather small ($r_E r_C=0.37\text{--}0.54$), which are close to that ($r_E r_C=0.37$) by complex 1. These results thus clearly indicate that these E/DC copolymerization reactions by 1–9 proceed in a random manner (1-decene incorporations are random in the copolymerization) with a rather alternating fashion (as observed in the trace CCC sequence).

2. Ethylene Copolymerization with 2-Methyl-1-Pentene (2M1P) Using $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{-Pr}_2\text{-}4\text{-R-C}_6\text{H}_2)$ –MAO catalyst systems [$\text{R}=\text{H}$ (1), $i\text{Bu}$ (2), Ph (3), CHPh_2 (4), CPh_3 (5), SiMe_3 (6), SiEt_3 (7), $4\text{-}i\text{BuC}_6\text{H}_4$ (8), $3,5\text{-Me}_2\text{C}_6\text{H}_3$ (9)].

Table 4 summarizes results in the ethylene (E) copolymerization with 2-methyl-1-pentene (2M1P) at 25, 50, or 80 °C using $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{-Pr}_2\text{-}4\text{-R-C}_6\text{H}_2)$ [$\text{R}=\text{H}$ (1), $i\text{Bu}$ (2), Ph (3), CHPh_2 (4), CPh_3 (5), SiMe_3 (6), SiEt_3 (7), $4\text{-}i\text{BuC}_6\text{H}_4$ (8), $3,5\text{-Me}_2\text{C}_6\text{H}_3$ (9)] in the presence of MAO cocatalyst. It turned out that the activity at 25 °C increased in the order: 1 ($\text{R}=\text{H}$, activity 5000 kg-polymer/mol-Ti h), 8 ($4\text{-}i\text{BuC}_6\text{H}_4$, 5270) < 9 ($3,5\text{-Me}_2\text{C}_6\text{H}_3$, 8200) < 7 (SiEt_3 , 9070) < 5 (CPh_3 , 12700) < 3 (Ph, 15000) < 6 (SiMe_3 , 19700) < 4

Table 3. Monomer sequence distributions of poly(ethylene-co-DC)s and poly(ethylene-co-DD)s prepared by Cp*TiCl₂(O-2,6-*i*-Pr₂-4-R-C₆H₂) [R = H (1), ^tBu (2), CHPh₂ (4), CPh₃ (5), SiMe₃ (6), SiEt₃ (7), 3,5-Me₂C₆H₃ (9)] –MAO catalyst systems. (ethylene 6 atm, toluene).^[a]

run	cat.	comonomer	content ^[b] / [mol %]	triad sequence distribution ^[c] [%]					dyads ^[d] [%]			$r_E^{[e]}$	$r_C^{[e]}$	$r_E r_C^{[f]}$	
				EEE	EEC + CEE	CEC	ECE	CCE + ECC	CCC	EE	EC + CE				CC
1	1	DC	21.4	39.6	31.5	6.73	18.0	4.25	–	55.3	42.6	2.12	3.12	0.12	0.37
12	5	DC	21.1	36.0	34.5	7.62	15.6	6.20	–	53.3	43.6	3.10	2.94	0.17	0.50
14	5	DC	21.4	42.8	28.9	5.69	17.6	4.98	–	57.3	40.3	2.49	3.41	0.15	0.51
15	6	DC	20.1	43.9	29.9	4.75	17.5	4.07	–	58.8	39.2	2.04	3.60	0.12	0.45
18	6	DC	21.3	39.2	32.4	5.71	18.3	4.48	–	55.4	42.4	2.24	3.14	0.13	0.40
22	7	DC	21.4	36.4	34.4	6.94	17.6	4.67	–	53.6	44.1	2.33	2.92	0.13	0.37
27	9	DC	21.1	41.9	26.3	9.31	16.6	5.98	–	55.0	42.0	2.99	3.14	0.17	0.54
28	1	DD	17.6	47.8	30.6	3.67	14.9	3.03	–	63.1	35.3	1.52	3.68	0.09	0.33
30	2	DD	18.3	50.1	27.4	4.81	14.2	3.46	0.76	63.8	34.4	2.49	3.82	0.15	0.57
36	4	DD	17.5	47.2	31.8	3.42	13.5	4.04	–	63.1	34.9	2.02	3.73	0.12	0.45
40	6	DD	16.3	50.4	29.6	3.28	14.1	2.62	–	65.2	33.5	1.31	4.02	0.08	0.32
42	7	DD	15.3	52.4	29.0	3.04	13.2	2.29	–	66.9	31.9	1.14	4.32	0.07	0.32
44	7	DD	16.7	46.0	33.0	3.43	14.5	3.08	–	62.5	36.0	1.54	3.58	0.09	0.32
48	9	DD	17.6	49.3	28.9	4.16	14.9	2.80	–	63.7	34.9	1.40	3.76	0.08	0.31
49	9	DD	17.7	45.9	30.7	5.30	14.0	4.13	–	61.2	36.7	2.06	3.44	0.12	0.40

[a] Detailed polymerization conditions, see Tables 1 and 2, C = comonomer [1-decene (DC), 1-dodecene (DD)]. [b] Comonomer contents in copolymer estimated by ¹³C NMR spectra. [c] Calculated by ¹³C NMR spectra, E = ethylene, C = comonomer [DC, DD]. [d] [EE] = [EEE] + 1/2[EEC + CEE], [EC] = [CEC] + [ECE] + 1/2[[EEC + CEE] + [CCE + ECC]], [CC] = [CCC] + 1/2[CCE + ECC]. [e] $r_E = [C]_0/[E]_0 \times 2[EE]/[EC + CE]$, $r_C = [E]_0/[C]_0 \times 2[CC]/[EC + CE]$. [f] $r_E r_C = 4[EE][CC]/[EC + CE]^2$.

(CHPh₂, 26800) < 2 (^tBu, 30800). It should be noted that most of all *para*-substituted complexes (2–7,9) showed higher catalytic activities than the unsubstituted 1. It also turned out that the activities by 1–9 at 50 °C were higher than those conducted at 25 °C, and the activity at 50 °C conducted under the same conditions (ethylene 4 atm, 2M1P 1.35 M) increased in the order: 5 (21400, run 67), 9 (21900, run 92), 4 (26600, run 63) < 8 (30200, run 89) < 1 (34100, run 51), 3 (35000, run 60) < 6 (43900, run 73), 7 (46100, run 82) < 2 (65300, run 56). In particular, complexes 2, 6 and 7 showed higher activities, whereas the activity by 4 increased upon addition of MAO (run 64); as observed in the above ethylene copolymerizations (with DC, DD), both the SiMe₃ (6) and SiEt₃ (7) were effective. No apparent decreases in the activities were observed between 5–15 minutes in the copolymerizations using 6 and 7 (runs 72–74, and runs 80–83).

In contrast, a trend in the activities at 80 °C were affected by the *para*-substituents employed; the activity by the SiEt₃ analogue (7) further increased at 80 °C (run 85, 53800 kg-polymer/mol-Ti h), whereas decreases in the activities by 1, 2, 6 were observed. Moreover, effect of 2M1P concentration toward the activities also seemed to be affected by the *para* substituents. The activities by 2 and 6 increased upon the increasing 2M1P concentration charged (runs 57 vs 58, runs 73 vs 75), whereas the opposite trend was observed by 7 (runs 85 vs 87). It was revealed that the activities by 6, 7 on the basis of polymer yields were not dependent on the polymerization time between 5–15 minutes (runs 72–74, 80–83), suggesting no significant catalyst deactivations were occurred during the copolymerization. The activity was affected by MAO charged; the activities by 2, 4, 6 and 7 in the presence of 5.0 mmol of MAO were higher than those in the presence of 1.0 or 3.0 mmol of MAO (runs 55, 64, 71, 79 vs 56, 63, 69–70, 77–78, respectively). These complexes afforded high molecular weight poly(ethylene-co-2M1P)s with unimodal molecular weight dis-

tributions ($M_n = 2.02–13.3 \times 10^4$; $M_w/M_n = 1.36–2.05$) and their compositions are uniform confirmed by DSC thermograms as observed sole T_m (Figure 4) with efficient 2M1P incorporations (2M1P 1.7–3.9 mol %).

Moreover, no apparent differences in the T_m , M_n , M_w/M_n values and the 2M1P contents were observed in the resultant copolymers prepared by 1–9 under the same conditions, except that the T_m value in the copolymer by 5 (CPh₃) at 25 and 50 °C was rather high (run 66, 67, $T_m = 113, 120$ °C, less 2M1P content) compared to those by the others. (Figures 4, S3-1 in the Supporting Information).^[24] One probable reason we may take into consideration that these results would be due to an electronic effect of the CPh₃ substituent. Importantly, the T_m value in the copolymer by the Ph analogue (3) and 3,5-Me₂C₆H₃ analogue (9) prepared at 25 °C, 50 °C and 80 °C (Figure S3-2 in

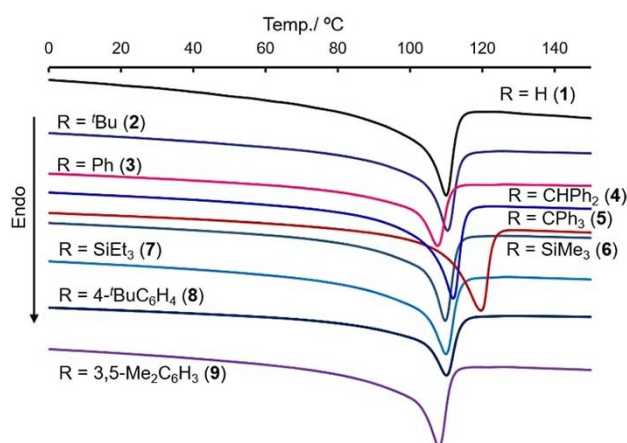


Figure 4. DSC thermograms of poly(ethylene-co-2M1P)s prepared by Cp*TiCl₂(O-2,6-*i*-Pr₂-4-R-C₆H₂) [R = H (1), ^tBu (2), Ph (3), CHPh₂ (4), CPh₃ (5), SiMe₃ (6), SiEt₃ (7), 4-^tBuC₆H₄ (8), 3,5-Me₂C₆H₃ (9)]–MAO catalyst systems at 50 °C. Detailed results are shown in Table 4 (runs 51, 56, 60, 63, 67, 73, 81, 89, 92).

Table 4. Ethylene copolymerization with 2-methyl-1-pentene (2M1P) by $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{-Pr}_2\text{-4-R-C}_6\text{H}_4)$ [R = H (1), $t\text{-Bu}$ (2), Ph (3), CHPh_2 (4), CPh_3 (5), SiMe_3 (6), SiEt_3 (7), $4\text{-}^i\text{BuC}_6\text{H}_4$ (8), $3,5\text{-Me}_2\text{C}_6\text{H}_3$ (9)] –MAO catalysts. (ethylene 4 atm, toluene).^[a]

run	cat. [μmol]	MAO/ [mmol]	2M1P ^[b] / [M]	Time/ [min]	temp./ [$^{\circ}\text{C}$]	yield/ [mg]	activity ^[c]	M_n ^[d] $\times 10^{-4}$	M_w/M_n ^[d]	T_m ^[e] / [$^{\circ}\text{C}$]	2M1P ^[f] / [mol %]
50 ^[g]	1 [0.050]	3.0	1.35	10	25	41.7	5000	10.7	1.64	102	3.9
51	1 [0.025]	3.0	1.35	10	50	142	34100	7.35	1.68	111	
52	1 [0.025]	2.0	1.35	10	80	74.5	17900	3.25	1.50	120	
53	2 [0.050]	1.0	1.35	10	25	96.3	11600	10.6	1.78	105	
54	2 [0.050]	3.0	1.35	10	25	257	30800	11.2	1.72	104	
55	2 [0.025]	3.0	1.35	10	25	94.5	22700	12.1	1.84	104	3.4
56	2 [0.0125]	3.0	1.35	10	50	136	65300	8.01	1.77	111	2.4
57	2 [0.025]	2.0	1.35	10	80	113	27100	6.61	1.70	120	2.3
58	2 [0.025]	2.0	2.03	10	80	132	31700	3.35	1.70	115	
59	3 [0.050]	3.0	1.35	10	25	125	15000	12.5	1.60	101	
60	3 [0.025]	3.0	1.35	10	50	146	35000	5.62	1.82	108	
61	3 [0.025]	2.0	1.35	10	80	81.4	19500	2.02	1.75	115	
62	4 [0.050]	3.0	1.35	10	25	223	26800	12.2	1.65	109	
63	4 [0.025]	3.0	1.35	10	50	111	26600	7.29	1.85	112	
64	4 [0.025]	5.0	1.35	10	50	267	64100	9.60	1.60	112	
65	4 [0.025]	2.0	1.35	10	80	239	57400	4.64	1.51	119	
66	5 [0.025]	3.0	1.35	10	25	52.8	12700	11.4	1.65	113	
67	5 [0.0125]	3.0	1.35	10	50	44.5	21400	4.50	1.57	120	
68	5 [0.025]	2.0	1.35	10	80	121	29000	3.71	1.67	117	
69	6 [0.050]	1.0	1.35	10	25	104	12500	9.24	1.72	103	
70	6 [0.050]	3.0	1.35	10	25	164	19700	10.7	1.65	101	
71	6 [0.050]	5.0	1.35	10	25	283	34000	11.0	1.64	101	
72	6 [0.025]	3.0	1.35	5.0	50	78.0	37400	5.36	1.70	111	
73 ^[g]	6 [0.025]	3.0	1.35	10	50	183	43900	5.29	1.60	110	3.3
74	6 [0.025]	3.0	1.35	15	50	266	42600	5.78	1.61	111	
75	6 [0.025]	3.0	2.03	10	50	240	57600	5.88	1.57	107	
76 ^[g]	6 [0.025]	2.0	1.35	10	80	148	35500	2.05	1.98	116	2.6
77	7 [0.050]	1.0	1.35	10	25	38.4	4610	9.52	1.68	105	
78	7 [0.050]	3.0	1.35	10	25	75.6	9070	9.29	1.63	102	
79 ^[g]	7 [0.050]	5.0	1.35	10	25	98.5	11800	10.9	1.54	105	
80	7 [0.025]	3.0	1.35	5.0	50	92.0	44200	6.01	1.73	109	
81 ^[g]	7 [0.025]	3.0	1.35	10	50	168	40300	6.19	1.58	110	2.9
82	7 [0.025]	3.0	1.35	10	50	192	46100	6.35	1.60	110	
83	7 [0.025]	3.0	1.35	15	50	232	37100	6.31	1.53	111	
84 ^[g]	7 [0.025]	3.0	2.03	10	50	148	35500	3.79	1.74	105	
85 ^[g]	7 [0.0125]	2.0	1.35	10	80	112	53800	2.37	1.83	119	1.7
86	7 [0.025]	1.0	2.03	10	80	67.1	16100	2.09	1.99	117	
87 ^[g]	7 [0.025]	2.0	2.03	10	80	154	37000	2.44	2.05	117	
88	8 [0.050]	3.0	1.35	10	25	43.9	5270	12.1	1.63	100	
89	8 [0.025]	3.0	1.35	10	50	126	30200	5.21	1.56	110	
90	8 [0.025]	2.0	1.35	10	80	147	35300	2.59	1.80	116	
91	9 [0.050]	3.0	1.35	10	25	68.3	8200	13.3	1.55	99.4	
92	9 [0.025]	3.0	1.35	10	50	91.1	21900	6.43	1.50	108	
93	9 [0.025]	2.0	1.35	10	80	190	45600	3.45	1.71	116	

[a] Conditions: toluene and 2M1P total 30.0 mL, ethylene 4 atm. [b] Initial 2M1P concentration (mol/L). [c] Activity = kg-polymer/mol-Ti·h. [d] GPC data in *o*-dichlorobenzene vs polystyrene standards. [e] By DSC thermograms. [f] 2M1P content (mol%) estimated by ^{13}C NMR spectra. [g] Cited from reference 19.

the Supporting Information)^[24] seems rather low (run 59–61, 91–93), and the results also suggest a possibility that an electronic factor play a role toward the 2M1P incorporation. The M_n values were slightly decreased upon increasing the reaction temperature (25–80 $^{\circ}\text{C}$) with decrease in the 2M1P contents, which are corresponded to the increases in the T_m values in the copolymers at 50 and 80 $^{\circ}\text{C}$ consistent with possessing their uniform compositions confirmed by their DSC thermograms (Figure 5).

Figure 5 shows the selected DSC thermograms of poly(ethylene-*co*-2M1P)s prepared by $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{-Pr}_2\text{-4-}^i\text{Bu-C}_6\text{H}_4)$ (2)-MAO catalyst system (at 25, 50 and 80 $^{\circ}\text{C}$). As described above, the T_m values in the resultant poly(E-*co*-2M1P)s increased at higher temperature (50 and 80 $^{\circ}\text{C}$) along with decrease in the 2M1P contents [T_m 104 \rightarrow 111 \rightarrow 120 $^{\circ}\text{C}$, content 3.4 \rightarrow 2.4 \rightarrow

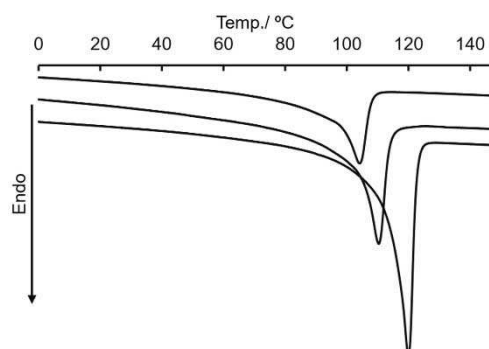


Figure 5. DSC thermograms of poly(ethylene-*co*-2M1P)s prepared by $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{-Pr}_2\text{-4-}^i\text{Bu-C}_6\text{H}_4)$ (2)-MAO catalyst system at 25, 50 and 80 $^{\circ}\text{C}$. Detailed results are shown in Table 4 (runs 55–57).

2.3 mol% (run 55–57)] as well as consisting with uniform compositions. The similar trends in the DSC thermograms (and 2M1P contents) in the copolymers prepared were observed by the other complexes (1 and 3–4, 6–9, Figures S3–3–S3-5, S3-7–S3-10, in the Supporting Information),^[24] whereas the slight decrease of T_m value in the copolymer by complex 5 at 80 °C was observed (T_m 120→117 °C; see Figure S3-6, in the Supporting Information).^[24] The T_m values were not affected by the amount of MAO charged and the polymerization time (see Figures S3-11–S3-17 in the Supporting Information).^[24] The T_m values decreased upon increasing 2M1P concentration charged along with increase the 2M1P contents in the copolymers (see Figures S3-18–S3-21 in the Supporting Information).^[24] The observed temperature dependence is unique contrast to those observed in the ethylene copolymerization with 1-hexene,^[22] 1-dodecene and with 1-dodecene.

Figure 6 shows typical ¹³C NMR spectrum in poly(ethylene-co-2M1P) prepared by 2-MAO catalyst system (run 55 1,1,2,2-tetrachloroethane-*d*₂ solution at 110 °C). Selected ¹³C NMR spectra in poly(ethylene-co-2M1P)s by 2, 6, 7 – MAO catalyst systems are also shown in Figures S2-12–S2-17 in the Supporting Information.^[24] All resonances could be assigned according to the previous report,^[15c] and the resultant copolymer possessed resonances ascribed to the isolated 2M1P inserted unit in addition to resonances due to alternating 2M1P incorporations (assigned as C_{ββ} and C_{αγ}). No resonances ascribed to the repeated 2M1P insertion were observed, and the fact could explain that negligible or no catalytic activity was observed in an attempted 2M1P homopolymerization by the 2-MAO catalyst system. The results also explain that 2M1P incorporation is less efficient compared to DC and DD incorporations in this catalysis, as observed in the ordinary metallocenes (in the ethylene/isobutene copolymerization)^[28] and the linked half-titanocenes like [Me₂Si(C₅Me₄)(N^tBu)]TiCl₂.^[15a]

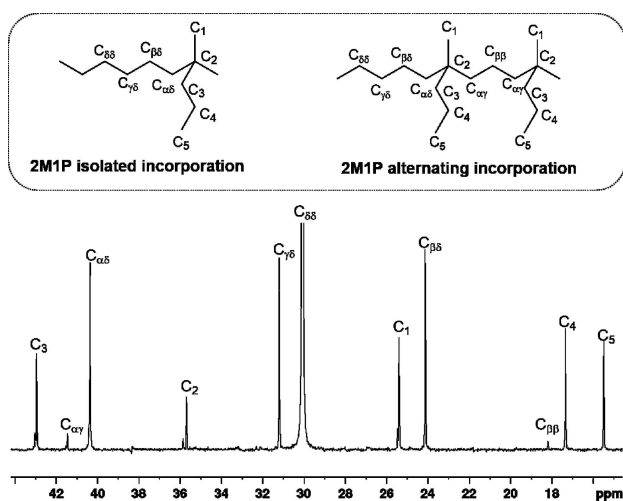


Figure 6. ¹³C NMR spectrum (in 1,1,2,2-tetrachloroethane-*d*₂ at 110 °C) for poly(ethylene-co-2M1P) prepared by Cp*TiCl₂(O-2,6-*i*-Pr₂-4-*t*-Bu-C₆H₃) (2)-MAO catalyst system (run 55, 2M1P 3.4 mol%).

3. Conclusion

In this paper, effect of phenoxide *para*-substituents in the ethylene copolymerization with 1-decene (DC), 1-dodecene (DD), and with 2-methyl-1-pentene (2M1P) using a series of Cp*TiCl₂(O-2,6-*i*-Pr₂-4-R-C₆H₃) [R = H (1), ^tBu (2), Ph (3), CHPh₂ (4), CPh₃ (5), SiMe₃ (6), SiEt₃ (7), 4-^tBuC₆H₄ (8) and 3,5-Me₂C₆H₃ (9)]-MAO catalyst systems were explored. Complexes 8 and 9 were newly prepared, identified for the purpose. The results can be summarized as follows.

The activity in the ethylene copolymerization with DC, DD was affected by the *para*-substituent, and the SiMe₃ (6), SiEt₃ (7) and 3,5-Me₂C₆H₃ (9) analogues showed the higher activities at 50 °C in the ethylene copolymerizations with DC (1.06–1.44 × 10⁶ kg-polymer/mol-Ti·h), DD (1.04–1.88 × 10⁶ kg-polymer/mol-Ti·h) than the others, whereas no significant differences were observed in the comonomer incorporations (evaluated as r_E values). No significant temperature dependences toward the DC, DD incorporation were observed between 25 and 50 °C, and, as reported in the ethylene/1-hexene copolymerization by 1-MAO catalyst system,^[22] the facts are unique contrast to that observed by the ordinary metallocene catalysts (the r_E values increased at high temperature).^[1c,26,27]

The activity in the ethylene copolymerization with 2M1P was affected by the *para*-substituent, and complexes 6 and 7 also showed the higher activities at 50 °C. The 2M1P incorporation was affected by the *para*-substituent and the polymerization temperature. In the copolymerization at 25 °C, the phenyl (3) and the 3,5-Me₂C₆H₃ (9) analogues showed better 2M1P incorporation but the CPh₃ analogue (5) showed less 2M1P incorporation, suggesting that an electronic factor would play a role toward the 2M1P incorporation.

On the basis of structural analysis in complexes 1,^[7] 2,^[20] 5–7,^[19] and the others,^[20,29] both Cp* and diisopropylphenyl ligands form unique Ti–O–C(phenyl) bond angles [173.0(3)–174.62(19)°], which could contribute to better stabilization of the proposed cationic alkyl species for exhibiting remarkable activity.^[4a–c] Therefore, it seems in high certainty that the observed effect could be considered as an electronic effect in the *para* substituent,^[30] unique characteristics in the activity observed in the SiMe₃ (6) and SiEt₃ (7) could be speculated due to better stabilization of the proposed active species.^[19] It also thus seems likely that observed difference in the 2M1P incorporation could be assumed as due to an electronic effect that affects the coordination energy of 2M1P, considered as an important factor for incorporation of sterically encumbered olefins as well as cyclic olefins.^[4c,15c,16e] We are exploring the possibility whether these effects were also observed in the other cyclopentadienyl analogues or not, including more details in effect of the *para*-substituents. This should be helpful for more precise catalyst design to proceed the desired (co) polymerization that cannot be performed in the conventional catalysts.

Experimental Section

General Procedure 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 of toluene (Kanto Kagaku Co. Ltd) was transferred into a bottle containing molecular sieves (mixture of 3 A and 4 A 1/16, and 13X) in the drybox, and was used without further purification. Ethylene for polymerization was of polymerization grade (purity >99.9%; Sumitomo Seika Co., Ltd.) and was used as received. Reagent grade 1-decene (DC, Tokyo Chemical Industry Co., Ltd.), 1-dodecene (DD, Tokyo Chemical Industry Co., Ltd.), 2-methyl-1-pentene (2M1P) (Tokyo Chemical Industry Co., Ltd.), were stored in bottles in the drybox with molecular sieves and were passed through an alumina short column before use. Toluene and AlMe₃ in the commercially available methylaluminoxane (MAO) [TMAO-S, 9.5 wt% (Al) toluene solution, Tosoh Finechem Co.] was taken to dryness under reduced pressure (at ca. 50 °C for removing toluene, Me₃Al, and then heated at >100 °C for 1 h for completion) in the drybox to give d-MAO white solids.^[7b,9b] Cp*TiCl₂(O-2,6-ⁱPr₂C₆H₃) (1),^[7b] Cp*TiCl₂(O-2,6-ⁱPr₂-4-^tBuC₆H₄) (2),^[20] Cp*TiCl₂(O-2,6-ⁱPr₂-4-R-C₆H₂) [R=Ph (3), CHPh₂ (4), CPh₃ (5), SiMe₃ (6), SiEt₃ (7)]^[19] and 4-Br-2,6-ⁱPr₂C₆H₂OH^[19] were prepared according to the reported procedure.

All 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. Elemental analyses were performed by using EAI CE-440 CHN/O/S Elemental Analyzer (Exeter Analytical, Inc.). 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×2, 30 cm ×7.8 mm i.d.), ranging from <10² to <2.8×10⁸ 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 (Pre-heating: 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 were repeated two times. *T*_m values were determined from the middle point of the phase transition of the second heating scan.

Synthesis of Cp*TiCl₂(O-2,6-ⁱPr₂-4-(4-^tBuC₆H₄)-C₆H₂) (8). (i) Synthesis of 4-(4-^tBuC₆H₄)-2,6-ⁱPr₂C₆H₂OH. A suspension of 4-Br-2,6-ⁱPr₂C₆H₂OH (823 mg, 3.2 mmol), 4-^tBu-phenylboronic acid (534.1 mg, 3.00 mmol), tetrakis(triphenylphosphine)palladium (3 mol%, 104 mg, 0.09 mmol), sodium carbonate (aqueous solution, 1 mol/L, 6.0 mmol) and benzene was stirred overnight at 80 °C. The suspension was cooled, filtered through Celite pad, and washed with hexane. The filtrates were successively washed with water and brine, and extracted with hexane. The organic layer was collected and dried over MgSO₄. The mixture was filtered to remove the MgSO₄, and the organic layer collected and dried under reduced pressure to give crude product. The crude product was then dissolved in minimum of hexane and placed in freezer (-30 °C) give the pure product (287.8 mg). Yield: 30.9%. ¹H NMR (CDCl₃): δ 7.49 (d, *J*=8.2 Hz, 2H), 7.44 (d, *J*=8.2 Hz, 2H), 7.26 (s, 2H), 4.78 (s, 1H), 3.20 (sept, *J*=6.8 Hz, 2H), 1.36 (s, 9H), 1.31 (d, *J*=6.8 Hz, 12H). ¹³C

NMR (CDCl₃): δ 149.4, 149.4, 139.2, 133.8, 133.7, 126.6, 125.6, 122.4, 34.5, 31.4, 27.3, 22.8.

(ii) Synthesis of Cp*TiCl₂(O-2,6-ⁱPr₂-4-(4-^tBuC₆H₄)-C₆H₂) (8). To an Et₂O solution (40 mL) containing Cp*TiCl₃ (289 mg, 1.0 mmol) was added and 4-(4-^tBuC₆H₄)-2,6-ⁱPr₂C₆H₂OLi (316.4 mg, 1.0 mmol) as one portion at -30 °C. The reaction mixture was warmed slowly to room temperature, and the mixture was then stirred for overnight. The solution was passed through a Celite pad, and the filter cake was washed with Et₂O. The combined organic layer was placed in a rotary evaporator to remove the volatiles. The crude product was dissolved in a minimum amount of Et₂O and layer by *n*-hexane. The chilled solution placed in the freezer (-30 °C) afforded orange crystals (350 mg). Yield 62.1%. ¹H NMR (CDCl₃) δ 7.53 (d, *J*=8.2 Hz, 2H), 7.47 (d, *J*=8.2 Hz, 2H), 7.29 (s, 2H), 3.22 (m, 2H), 2.20 (s, 15H), 1.37 (s, 9H), 1.25 (d, *J*=6.8 Hz, 12H). ¹³C NMR (CDCl₃) δ 159.2, 149.9, 139.6, 138.6, 136.0, 132.4, 126.6, 125.6, 121.9, 34.5, 31.4, 26.9, 24.0, 12.9. Anal. Calcd. C₃₂H₄₄Cl₂O₂Ti: C, 68.21; H, 7.87; N Found: C, 67.97; H, 7.75.

Synthesis of Cp*TiCl₂[O-2,6-ⁱPr₂-4-(3,5-Me₂C₆H₃)-C₆H₂] (9). (i) Synthesis of 4-(3,5-Me₂C₆H₃)-2,6-ⁱPr₂C₆H₂OH. was conducted by the similar procedure for 4-(4-^tBuC₆H₄)-2,6-ⁱPr₂C₆H₂OH, except that 3,5-dimethylphenylboronic acid (450 mg, 3.00 mmol) was used in place of 4-^tBu-phenylboronic acid. Yield: 580 mg (68.5%). ¹H NMR (CDCl₃): δ 7.24 (s, 2H), 7.15 (s, 2H), 6.95 (s, 1H), 4.79 (s, 1H), 3.20 (m, 2H), 2.38 (s, 6H), 1.32 (d, *J*=6.9 Hz, 12H). ¹³C NMR (CDCl₃): δ 149.5, 142.0, 138.1, 134.0, 133.8, 128.2, 124.9, 122.5, 27.4, 22.8, 21.4.

(ii) Synthesis of Cp*TiCl₂[O-4-(3,5-Me₂C₆H₃)-2,6-ⁱPr₂C₆H₂] (9). The procedure for synthesis of 9 was conducted by the similar procedure for 8, except that 4-(3,5-Me₂C₆H₃)-2,6-ⁱPr₂C₆H₂OLi (288.4 mg, 1.00 mmol) was used in place of 4-(4-^tBuC₆H₄)-2,6-ⁱPr₂C₆H₂OLi. Yield: 330 mg (61.6%). ¹H NMR (CDCl₃) δ 7.26 (s, 2H), 7.18 (s, 2H), 6.97 (s, 1H), 3.21 (m, 2H), 2.39 (s, 6H), 2.19 (s, 15H), 1.25 (d, *J*=6.8 Hz, 12H). ¹³C NMR (CDCl₃) δ 159.2, 141.5, 139.6, 138.2, 136.4, 132.4, 128.6, 124.9, 122.0, 26.9, 24.0, 21.4, 12.9. Anal. Calcd. C₃₀H₄₀Cl₂O₂Ti: C, 67.30; H, 7.53; found: C, 67.01; H, 7.59.

Ethylene copolymerization with long-chain α -olefins [1-decene (DC), 1-dodecene (DD)]. The typical reaction procedure for ethylene/DC or DD copolymerization (Table 1, 2) is as follows. The prescribed amounts of DC or DD, MAO and toluene (total 29 mL) were added into a 100 mL scale autoclave with stirring in the drybox. The reaction apparatus was then filled with ethylene (1 atm), and a toluene solution containing prescribed amount of complex (1.0 mL) was added into the autoclave. The reaction apparatus was then immediately pressurized with ethylene to 5 atm (total 6 atm) and the mixture was magnetically stirred for 6 min (ethylene pressure was kept constant during the reaction) at prescribed temperature. After the reaction, the autoclave was placed in an ice bath to purge ethylene unreacted. The reaction solution was poured into methanol (100 mL) containing HCl (10 mL) and was stirred for 15 min. The resultant precipitates were then collected through the suction filtration and was adequately washed with methanol. The resultant polymer was then dried in vacuo at 60 °C for 6 h.

Ethylene copolymerization with 2-methyl-1-pentene (2M1P). These copolymerizations were conducted in the similar procedure as that conducted for ethylene copolymerization with DC or DD except that prescribed amount of 2-methyl-1-pentene (2M1P) was charged instead of DC or DD. After the reaction for prescribed time, the autoclave was placed in an ice bath to purge ethylene unreacted. The reaction solution was poured into a mixed solution of hydrochloric acid and methanol and was stirred for 15 min. The resultant precipitates were then collected through the suction

filtration and was adequately washed with methanol. The resultant polymer was then dried *in vacuo* at 60 °C for 6 h.

Supporting Information

Additional results in ethylene copolymerization with 2-methyl-1-pentene (2M1P), selected NMR spectra in the copolymers, and selected DSC thermograms in the copolymers.

Acknowledgements

This project was partly supported by Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS, Grant No. 18H01982, 21H01942). The authors express their heartfelt thanks to Tosoh Finechem Co. for donating MAO.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: ethylene copolymerization · half-titanocenes · homogeneous catalysis · ligand effects · titanium catalysts

- [1] For Example (selected books, and reviews in early transition metal catalysts): a) *Organometallic Reactions and Polymerization* (Ed.: K. Osakada), Springer-Verlag, Berlin, **2014**; b) *Handbook of Transition Metal Polymerization Catalysts*, 2nd ed. (Ed.: R. Hoff), Wiley, Hoboken, NJ, **2018**; c) W. Kaminsky, *Macromol. Chem. Phys.* **1996**, *197*, 3907–3945; d) A. L. McKnight, R. M. Waymouth, *Chem. Rev.* **1998**, *98*, 2587–2598; e) K. Nomura, S. Zhang, *Chem. Rev.* **2011**, *111*, 2342–2362; f) H. Makio, H. Terao, A. Iwashita, T. Fujita, *Chem. Rev.* **2011**, *111*, 2363–2449; g) M. C. Baier, M. A. Zuideveld, S. Mecking, *Angew. Chem. Int. Ed.* **2014**, *53*, 9722–9744; *Angew. Chem.* **2014**, *126*, 9878–9902.
- [2] For example (selected reviews in late transition metal catalysts): a) S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169–1203; b) V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283–316; c) H. L. Mu, L. Pan, D. P. Song, Y. S. Li, *Chem. Rev.* **2015**, *115*, 12091–12137; d) C. L. Chen, *Nat. Chem. Rev.* **2018**, *2*, 6–14; e) F. Z. Wang, C. L. Chen, *Polym. Chem.* **2019**, *10*, 2354–2369.
- [3] a) H. Li, T. J. Marks, *Proc. Nat. Acad. Sci. USA* **2006**, *103*, 15295–15302; b) M. Delferro, T. J. Marks, *Chem. Rev.* **2011**, *111*, 2450–2485; c) J. P. McInnis, M. Delferro, T. J. Marks, *Acc. Chem. Res.* **2014**, *47*, 2545–2557.
- [4] a) K. Nomura, J. Liu, S. Padmanabhan, B. Kitiyanan, *J. Mol. Catal. A* **2007**, *267*, 1–29; b) K. Nomura, *Dalton Trans.* **2009**, 8811–8823; c) K. Nomura, J. Liu, *Dalton Trans.* **2011**, *40*, 7666–7682; d) G. van Doremaele, M. van Duin, M. Valla, A. Berthoud, *J. Poly. Sci. Part A: Polym. Chem.* **2017**, *55*, 2877–2891.
- [5] For example,^[2] a) L. S. Boffa, B. M. Novak, *Chem. Rev.* **2000**, *100*, 1479–1494; b) A. Nakamura, S. Ito, K. Nozaki, *Chem. Rev.* **2009**, *109*, 5215–5244; c) E. Y.-X. Chen, *Chem. Rev.* **2009**, *109*, 5157–5214; d) N. M. G. Franssen, J. N. H. Reek, B. de Bruin, *Chem. Soc. Rev.* **2013**, *42*, 5809–5832; e) A. Nakamura, T. M. J. Anselment, J. Claverie, B. Goodall, R. F. Jordan, S. Mecking, B. Rieger, A. Sen, P. W. N. M. van Leeuwen, K. Nozaki, *Acc. Chem. Res.* **2013**, *46*, 1438–1449; f) C. Tan, C. L. Chen, *Angew. Chem. Int. Ed.* **2019**, *58*, 7192–7200; *Angew. Chem.* **2019**, *131*, 7268–7276.
- [6] For selected more recent examples, see: a) W. J. Tao, R. Nakano, S. Ito, K. Nozaki, *Angew. Chem. Int. Ed.* **2016**, *55*, 2835–2839; *Angew. Chem.* **2016**, *128*, 2885–2889; b) S. Dai, C. L. Chen, *Angew. Chem. Int. Ed.* **2016**, *55*, 13281–13285; *Angew. Chem.* **2016**, *128*, 13475–13479; c) B. S. Xin, N. Sato, A. Tanna, Y. Oishi, Y. Konishi, F. Shimizu, *J. Am. Chem. Soc.* **2017**, *139*, 3611–3614; d) M. Chen, C. L. Chen, *ACS Catal.* **2017**, *7*, 1308–1312; e) S. Dai, S. Li, G. Xu, C. L. Chen, *Macromolecules* **2020**, *53*, 2539–2546; f) T. Liang, S. B. Goudari, C. L. Chen, *Nat. Commun.* **2020**, *11*, 372.
- [7] a) K. Nomura, N. Naga, M. Miki, K. Yanagi, A. Imai, *Organometallics* **1998**, *17*, 2152–2154; b) K. Nomura, N. Naga, M. Miki, K. Yanagi, *Macromolecules* **1998**, *31*, 7588–7597.
- [8] Other reports for modifications of (cyclopentadienyl)titanium(IV) complexes containing phenoxide ligands for ethylene (co)polymerization, a) T. A. Manz, K. Phomphrai, G. Medvedev, B. B. Krishnamurthy, S. Sharma, J. Haq, K. A. Novstrup, K. T. Thomson, W. N. Delgass, J. M. Caruthers, M. M. Abu-Omar, *J. Am. Chem. Soc.* **2007**, *129*, 3776–3777; b) T.-J. Kim, S.-K. Kim, B.-J. Kim, J. S. Hahn, M.-A. Ok, J. H. Song, D.-H. Shin, J. Ko, M. Cheong, J. Kim, H. Won, M. Mitoraj, M. Srebro, A. Michalak, S. O. Kang, *Macromolecules* **2009**, *42*, 6932–6943.
- [9] a) K. Nomura, K. Fujita, M. Fujiki, *Catal. Commun.* **2004**, *5*, 413–417; b) K. Nomura, K. Fujita, M. Fujiki, *J. Mol. Catal. A* **2004**, *220*, 133–144; c) H. Zhang, K. Nomura, *J. Am. Chem. Soc.* **2005**, *127*, 9364–9365.
- [10] a) J. McMeeking, X. Gao, R. E. v. H. Spence, S. J. Brown, D. Jeremic, WO9914250 A1 (1999); b) A. R. Dias, M. T. Duarte, A. C. Fernandes, S. Fernandes, M. M. Marques, A. M. Martins, J. F. da Silva, S. S. Rodrigues, *J. Organomet. Chem.* **2004**, *689*, 203–213; c) A. M. Martins, M. M. Marques, J. R. Ascenso, A. R. Dias, M. T. Duarte, A. C. Fernandes, S. Fernandes, M. J. Ferreira, I. Matos, M. C. Oliveira, S. S. Rodrigues, C. Wilson, *J. Organomet. Chem.* **2005**, *690*, 874–884; d) M. J. Ferreira, A. M. Martins, *Coord. Chem. Rev.* **2006**, *250*, 118–132.
- [11] a) D. W. Stephan, J. C. Stewart, F. Guérin, R. E. v. H. Spence, W. Xu, D. G. Harrison, *Organometallics* **1999**, *18*, 1116–1118; b) D. W. Stephan, J. C. Stewart, S. J. Brown, J. W. Swabey, Q. Wang, EP881233 A1 (1998); c) D. W. Stephan, J. C. Stewart, F. Guérin, S. Courtenay, J. Kickham, E. Hollink, C. Beddie, A. Hoskin, T. Graham, P. Wei, R. E. v. H. Spence, W. Xu, L. Koch, X. Gao, D. G. Harrison, *Organometallics* **2003**, *22*, 1937–1947.
- [12] a) M. Tamm, S. Randoll, T. Bannenberg, E. Herdtweck, *Chem. Commun.* **2004**, 876–877; b) M. Tamm, S. Randoll, E. Herdtweck, N. Kleigrewe, G. Kehr, G. Erker, B. Rieger, *Dalton Trans.* **2006**, 459–467; c) S. H. Stelzig, M. Tamm, R. M. J. Waymouth, *Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 6064–6070; d) K. Nomura, H. Fukuda, W. Apisuk, A. G. Trambitas, B. Kitiyanan, M. Tamm, *J. Mol. Catal. A* **2012**, *363–364*, 501–511.
- [13] a) W. P. Kretschmer, C. Dijkhuis, A. Meetsma, B. Hessen, J. H. Teuben, *Chem. Commun.* **2002**, 608–609; b) K. Nomura, H. Fukuda, H. Matsuda, S. Katao, S. Patamma, *J. Organomet. Chem.* **2015**, *798*, 375–383; c) K. Nomura, S. Patamma, H. Matsuda, S. Katao, K. Tsutsumi, H. Fukuda, *RSC Adv.* **2015**, *5*, 64503–64513.
- [14] Other selected examples, a) E. G. Ijpeij, B. Coussens, M. A. Zuideveld, G. H. J. van Doremaele, P. Mountford, M. Lutz, A. L. Spek, *Chem. Commun.* **2010**, *46*, 3339–3341; b) I. Saeed, S. Katao, K. Nomura, *Inorg. Chem.* **2009**, *48*, 5011–5020; c) K. Nomura, G. Nagai, A. Nasr, K. Tsutsumi, Y. Kawamoto, K. Koide, M. Tamm, *Organometallics* **2019**, *38*, 3233–3244.
- [15] a) K. Nomura, K. Itagaki, M. Fujiki, *Macromolecules* **2005**, *38*, 2053–2055; b) K. Nomura, K. Itagaki, *Macromolecules* **2005**, *38*, 8121–8123; c) K. Itagaki, M. Fujiki, K. Nomura, *Macromolecules* **2007**, *40*, 6489–6499; d) K. Kakinuki, M. Fujiki, K. Nomura, *Macromolecules* **2009**, *42*, 4585–4595; e) F. Z. Khan, K. Kakinuki, K. Nomura, *Macromolecules* **2009**, *42*, 3767–3773.
- [16] a) K. Nomura, M. Tsubota, M. Fujiki, *Macromolecules* **2003**, *36*, 3797–3799; b) W. Wang, M. Fujiki, K. Nomura, *J. Am. Chem. Soc.* **2005**, *127*, 4582–4583; c) K. Nomura, W. Wang, M. Fujiki, J. Liu, *Chem. Commun.* **2006**, 2659–2661; d) J. Liu, K. Nomura, *Adv. Synth. Catal.* **2007**, *349*, 2235–2240; e) W. Zhao, K. Nomura, *Macromolecules* **2016**, *49*, 59–70; f) H. Harakawa, S. Patamma, A. Boccia, L. Boggioni, D. Ferro, S. Losio, K. Nomura, I. Tritto, *Macromolecules* **2018**, *51*, 8538–63; g) H. Harakawa, M. Okabe, K. Nomura, *Polym. Chem.* **2020**, *11*, 5590–5600.
- [17] a) K. Nomura, J. Liu, M. Fujiki, A. Takemoto, *J. Am. Chem. Soc.* **2007**, *129*, 14170–14171; b) W. Apisuk, K. Nomura, *Macromol. Chem. Phys.* **2014**, *215*, 1785–1791; c) K. Nomura, S. Pengoubol, W. Apisuk, *Polymer* **2020**, *12*, 3.
- [18] a) K. Nomura, S. Pengoubol, W. Apisuk, *RSC Adv.* **2016**, *6*, 16203–16207; b) K. Nomura, S. Pengoubol, W. Apisuk, *Molecules* **2019**, *24*, 1634.
- [19] S. Kitphaitun, Q. Yan, K. Nomura, *Angew. Chem. Int. Ed.* **2020**, *59*, 23072–23076; *Angew. Chem.* **2020**, *132*, 23272–23276.
- [20] K. Nomura, A. Tanaka, S. Katao, *J. Mol. Catal. A: Chem.* **2006**, *254*, 197–204.
- [21] For example, K. Nomura, I. Izawa, J. Yi, N. Nakatani, H. Aoki, T. Ina, T. Mitsudome, N. Tomotsu, S. Yamazoe, *Organometallics* **2019**, *38*, 4497–4507.

- [22] a) K. Nomura, K. Oya, T. Komatsu, Y. Imanishi, *Macromolecules* **2000**, *33*, 3187–3189; b) K. Nomura, K. Oya, Y. Imanishi, *J. Mol. Catal. A* **2001**, *174*, 127–140.
- [23] For example, A. Sahgal, H. M. La, W. Hayduk, *Can. J. Chem. Eng.* **1978**, *56*, 354–357.
- [24] Additional NMR spectra in the resultant copolymers and DSC thermograms in poly(ethylene-co-2M1P)s are shown in the Supporting Information.
- [25] The calculation of r_E and r_C [C = 1-decene (DC), 1-dodecene (DD)] values are based on dyads and the initial monomer concentrations, according to the reported method.^[7b,9b,14c,15d,18,22] Solubility data in toluene was cited from reference 23.
- [26] K. Heiland, W. Kaminsky, *Makromol. Chem.* **1992**, *193*, 601–610.
- [27] a) J. Suhm, M. J. Schneider, R. Mülhaupt, *J. Mol. Catal. A* **1998**, *128*, 215–227; b) J. Suhm, M. J. Schneider, R. Mülhaupt, *J. Polym. Sci.: Part A, Polym. Chem.* **1997**, *35*, 735–740.
- [28] W. Kaminsky, A. Bark, R. Spiehl, N. Möller-Linderhof, S. Niedoba, In *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; W. Kaminsky, H. Sinn, H., Eds.; Springer-Verlag: Berlin, 1988; pp 291–301.
- [29] a) K. Nomura, A. Fudo, *Inorg. Chim. Acta* **2003**, *345*, 37–43; b) K. Nomura, Y. Hatanaka, *Inorg. Chem. Commun.* **2003**, *6*, 517–522.
- [30] It was assumed that an introduction of SiMe₃, SiEt₃ group could contribute to a stabilization of the active species leading to the higher activity (by PM3 calculation, unpublished results).^[4c]

Manuscript received: February 24, 2021
Revised manuscript received: May 21, 2021