Communication

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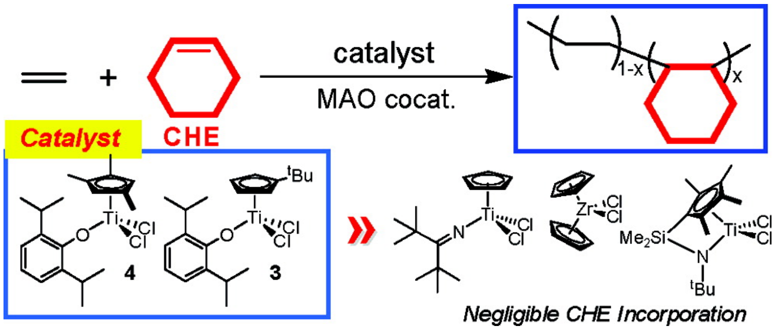

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Copolymerization of Ethylene with Cyclohexene (CHE) Catalyzed by *Nonbridged* Half-Titanocenes Containing Aryloxo Ligand: Notable Effect of Both Cyclopentadienyl and Anionic Donor Ligand for Efficient CHE Incorporation

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The design and synthesis of efficient transition-metal-complex catalysts that precisely control olefin coordination insertion polymerization are the key for evolution of new polyolefins that have never been prepared by conventional catalysts.[1] Some cyclic olefin copolymers are known to be amorphous materials with a promising combination of high transparency in the UV−vis region along with humidity-, and heat-resistance.[2,3] There have been many reports concerning the copolymerization of ethylene with *strained* cyclic olefins such as norbornene (NBE),[4,5] cyclopentene (CPE),[5b,6] etc.[7] However, there have been no previous reports on the successful copolymerization of ethylene with cyclohexene (CHE),[8] although CHE is widely used as a key intermediate in the chemical industry. In this communication, we present for the first time that the efficient incorporation of CHE in ethylene/CHE copolymerization can be achieved by using *nonbridged* half-titanocenes containing aryloxo ligands of the type Cp′$TiCl_2$(OAr) (OAr = O-2,6-$^iPr_2C_6H_3$) that exhibit some unique characteristics in olefin coordination polymerization (Scheme 1).[5,9,10]

Since the indenyl analogue, (indenyl)$TiCl_2$(OAr) (**1**), showed efficient NBE incorporation in ethylene/NBE copolymerization,[5] we first conducted the copolymerization under similar conditions (Table 1).[11] Although the observed catalytic activities seemed higher than those in the ethylene polymerization, the resultant polymer contained a trace amount of CHE (run 2), whereas the efficient incorporation of NBE was observed under the same conditions (runs 4, 5). The incorporation of a small amount of CHE as estimated from the ^{13}C NMR spectrum[12] for the resultant polymer could be seen under higher CHE concentrations (0.3 mol %, run 3). Therefore, we explored the polymerization conditions in more detail.

Four complexes, Cp′$TiCl_2$(OAr) [Cp′ = indenyl (**1**), Cp* (**2**), $^tBuC_5H_4$ (**3**), 1,2,4-$Me_3C_5H_2$ (**4**), Chart 1] were chosen as the catalyst precursors, since both the monomer reactivities and the microstructures in the copolymerization of ethylene with α-olefin,[9] styrene,[10] NBE,[5] and CPE[5b] depended on the cyclopentadienyl fragment (Cp′). Cp$TiCl_2$(N=C$^tBu_2$) (**5**) was also chosen for comparison, since **5** (MAO catalyst) exhibited notable catalytic activity in ethylene/1-hexene copolymerization.[13] Cp_2ZrCl_2 (**6**) and [$Me_2Si(C_5Me_4)(N^tBu)$]$TiCl_2$ (**7**) were also chosen for comparison. The results of copolymerization under the optimized conditions are summarized in Table 2.[11,12]

Scheme 1

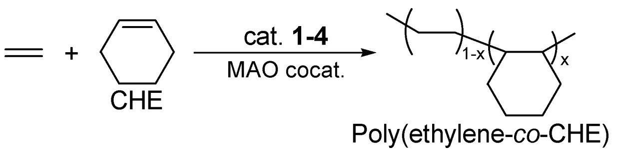
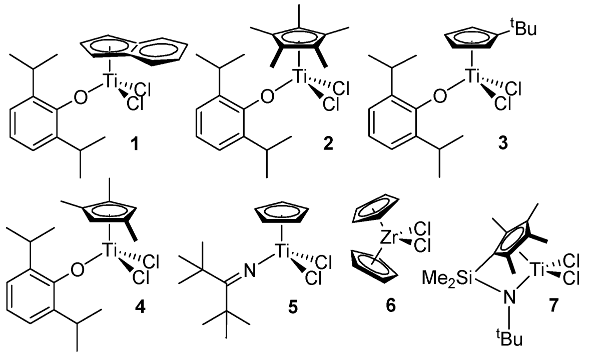


Table 1. Copolymerization of Ethylene with Norbornene (NBE) or Cyclohexene (CHE) by **1**−MAO Catalyst System (ethylene 6 atm)[a]

run	CHE or NBE (concn/M)	polymer yield/mg	activity[c]	CHE or NBE content[d]/%	M_n[e] $\times 10^{-4}$	M_w/M_n[e]
1	− (−)	232	6960	−	22.5	1.88
2	CHE (0.20)	268	8040	n.d.	18.1	2.07
3	CHE (1.0)	283	8490	0.3	8.84	3.77
4	NBE (0.20)	350	10500	14.0	14.6	1.56
5	NBE (1.0)	192	2300	35.2	5.87	1.82

[a] Conditions: complex **1** 0.20 μmol (run 5, 0.50 μmol), ethylene 6 atm, 25 °C, 10 min, MAO 3.0 mmol, toluene + comonomer = 50 mL. [b] NBE or CHE concentration charged (mol/L). [c] Activity in kg of polymer/mol-Ti·h. [d] CHE or NBE content (mol %) estimated by ^{13}C NMR spectra. [e] GPC data in *o*-dichlorobenzene vs polystyrene standards.

Chart 1



Both the *tert*-BuCp analogue (**3**) and the Me_3Cp analogue (**4**) showed better CHE incorporation than **1**, and the resultant polymer possessed high molecular weights with unimodal molecular weight distributions ($M_n = 3.12-9.06 \times 10^4$, $M_w/M_n = 1.45-2.07$). On the basis of the above results, the ^{13}C NMR spectra[12] and DSC thermograms,[14] it is clear that the resultant polymers are poly(ethylene-*co*-CHE)s with uniform CHE incorporation. The observed activities by **3** decreased at higher CHE concentrations, whereas the activities by **4** were higher than those in ethylene polymerization. The activities by **3** increased at higher ethylene pressure, and the M_n values decreased with an increase in the CHE content. In contrast, the resultant polymers by the Cp* analogue (**2**) and Cp-ketimide analogue (**5**) contained trace or negligible amounts of CHE,[12] indicating that the substituents on both Cp′ and the anionic donor ligand *directly affect* CHE incorporation. Moreover, no CHE incorporation was observed in polymers prepared by **6** or **7**, as assumed from the previous reports.[1,2,12] These results clearly indicate that **3** and **4** give the highest CHE incorporation among these catalyst precursors.

Figure 1 shows a typical ^{13}C NMR spectrum for the poly(ethylene-*co*-CHE)s. The resonances were identified by comparison with the dept spectrum[12] and with spectra for poly(ethylene-*co*-

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Table 2. Copolymerization of Ethylene with Cyclohexene (CHE) by **1**−**7**−MAO Catalyst Systems (ethylene 2 atm)[a]

run	catalyst (μmol)	CHE concn[b]/M	polymer yield/mg	activity[c]	CHE content[d]/ mol%	M_n[e] $\times 10^{-4}$	M_w/M_n[e]
6	**1** (1.0)	−	166	996	−	14.1	2.96
7	**1** (1.0)	5.0	195	1170	3.2	2.82	1.90
8	**2** (1.0)	−	413	2478	−	22.0	1.77
9	**2** (1.0)	5.0	333	1998	trace	24.7	1.79
10	**3** (1.0)	−	102	612	−	7.87	1.97
11	**3** (1.0)	2.5	123	738	10.0	6.22	1.45
12	**3** (1.0)	5.0	82	492		3.12	1.70
13	**3** (2.0)	5.0	141	423	16.2	3.23	1.70
14[f]	**3** (2.0)	5.0	460	1380	8.2	6.58	1.82
15[g]	**3** (5.0)	5.0	843	1012	7.9	6.35	1.89
16[h]	**3** (2.0)	5.0	790	2370	5.4	8.80	1.84
17	**4** (0.5)	−	89	1068	−	9.15	1.79
18	**4** (0.5)	1.0	112	1344	3.5	9.06	2.07
19	**4** (0.5)	2.5	153	1836	9.3	7.71	1.57
20	**4** (0.5)	5.0	138	1656	14.1	4.31	1.94
21	**5** (1.0)	5.0	324	1944	0.3	4.98	1.83
22	**6** (1.0)	5.0	92	532	trace	6.11	1.76
23	**7** (1.0)	5.0	427	2562	trace	10.4	2.71

[a] Conditions: ethylene 2 atm, 25 °C, 10 min, toluene + CHE = 10 mL, MAO 3.0 mmol. [b] CHE concentration (mol/L). [c] Activity in kg of polymer/mol-Ti·h. [d] CHE content (mol %) estimated by ^{13}C NMR spectra. [e] GPC data in *o*-dichlorobenzene vs polystyrene standards. [f] Ethylene 4 atm. [g] Ethylene 4 atm, toluene + CHE = 20 mL, MAO 6.0 mmol. [h] Ethylene 6 atm.

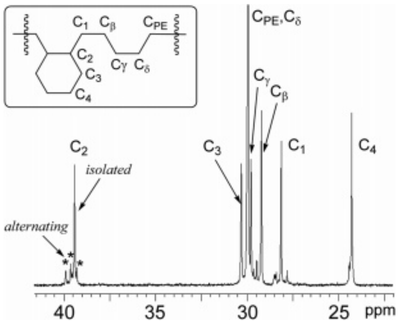

Figure 1. ^{13}C NMR spectrum (in benzene-d_6/1,2,4-trichlorobenzene at 110 °C) for poly(ethylene-*co*-cyclohexene) prepared by **4**−MAO catalyst system (run 20, CHE content 14.1 mol %).

CPE)s reported previously.[5b] It is clear that CHE was incorporated in a 1,2-insertion manner without 1,3-insertion via β-hydrogen elimination (and then isomerization) after CHE insertion,[15] which is often seen in poly(ethylene-*co*-CPE)s prepared by ordinary zirconocene catalysts.[6a−d] 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.[5b,6e,f,] The microstructure for the resultant copolymer possessed both isolated and alternating CHE sequences,[12] and the degree of alternating sequences seemed to depend on the Cp′ employed, as observed in ethylene/NBE copolymerization.[5] No CHE repeat units were observed, which suggests that it may be difficult to prepare a copolymer with higher CHE content.

We have shown as the first example that CHE can be incorporated in ethylene/CHE copolymerization by transition-metal-catalyzed coordination polymerization. Since we believe that this is a unique characteristic of this catalysis, we are now exploring other possibilities for the evolution of new polyolefins by the incorporation of other traditionally unreactive olefins.[16]

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Supporting Information Available: General experimental details, additional polymerization results, ^{13}C NMR (dept) spectra for poly(ethylene-*co*-CHE)s, and typical DSC thermograms for the copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) For detailed experimental procedures, additional polymerizatioin results (effect of Al/Ti molar ratio, reproducibility, etc.), see the Supporting Information.

(12) For estimation of CHE content based on ^{13}C NMR spectra (assignments of each resonances), DSC thermograms, see the Supporting Information.

(13) (a) Ethylene/1-hexene copolymerization by various $Cp'TiCl_2(N{=}C^tBu_2)$−MAO catalysts, Nomura, K.; Fujita, K.; Fujiki, M. *J. Mol. Catal. A: Chem.* **2004**, *220*, 133. (b) Olefin polymerization results, McMeeking, J.; Gao, X.; Spence, R. E. v. H.; Brown, S. J.; Jerermic, D. U.S. Patent 6,114,481, 2000.

(14) DSC thermograms for resultant polymers showed melting temperatures (T_m) at 98.7 (run 18), 68.9 (run 19), 49.5 °C (run 20), and glass transition temperature (T_g) at −20.7 °C (run 20). These results indicate that resultant copolymers possessed uniform CHE incorporation. More details are shown in the Supporting Information.

(15) In fact, we might observe resonances (ca. 34 and 38 ppm) probably due to the 1,3-inserted unit in the copolymer by **3** (runs 11 and 13), and the resonances disappeared upon increasing the ethylene pressure (runs 13−14). In contrast, no resonances due to the 1,3-insertion were observed in the copolymer prepared by **4**. For more details, see the Supporting Information.

(16) Example of copolymerization of ethylene with 2-methyl-1-pentene: Nomura, K.; Itagaki, K.; Fujiki, M. *Macromolecules* **2005**, in press.

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