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# Communications to the Editor

## Efficient Incorporation of Vinylcylohexane in Ethylene/Vinylcyclohexane Copolymerization Catalyzed by Nonbridged Half-Titanocenes

**Kotohiro Nomura* and Koji Itagaki**

*Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST), 8916-5 Takayama, Ikoma, Nara 630-0101, Japan*

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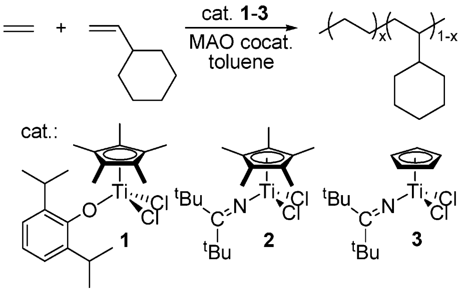
One of the most attractive subjects in the field of transition-metal-catalyzed coordination polymerization is the evolution of new polyolefins using newly designed polymerization catalysts because unique properties that have never been observed by the conventional catalysts can be highly expected, especially by the precise placement of chemical functionality and/or substituent.[1] Although copolymers prepared by the copolymerization of ethylene with α-olefin such as 1-butene, 1-hexene, and 1-octene are widely used as LLDPE, however, examples for the copolymerization of ethylene (or propylene) with vinylcyclohexane (VCH) have been limited so far.[2−4] For example, VCH contents in the ethylene/VCH copolymerization using $Cp_2ZrCl_2$, $Cp_2ZrMe_2$−methylaluminoxane (MAO) catalyst (at 25 or 70 °C) under excess VCH molar ratios were low (0.6−1.7 mol %), and the resultant copolymer possessed low $M_n$ values ($(5.0-6.1) \times 10^3$).[2] Moreover, the VCH contents in the ethylene/propylene/VCH terpolymers prepared by *rac*-$Me_2Si$[2-MeBenz[*e*]-Ind]$ZrCl_2$−MAO catalyst were low (0.6−0.9 mol %), although these copolymerizations were performed under relatively high VCH concentrations compared to ethylene and propylene.[3] In addition, an efficient VCH dimerization took place with exclusive selectivity in the presence of $Cp_2TiCl_2$, $Cp_2HfCl_2$, $Cp_2ZrCl_2$, or $[Me_2Si(Cp)_2]ZrCl_2$−MAO catalysts.[4] In contrast, one well-known successful example is the isospecific coordination polymerization of VCH using an “exposed” half-zirconocene containing an acetamidinate ligand as the catalyst precursor,[5] although the catalytic activity may not be fully sufficient.

**Scheme 1**



We recently presented that the 1,1-disubstituted α-olefin, 2-methyl-1-pentene (2M1P), has been efficiently copolymerized with ethylene by our original nonbridged half-titanocene $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1**, $Cp^* = C_5Me_5$)−MAO catalyst, even under moderate 2M1P/ethylene feed molar ratios, affording high molecular weight copolymers with uniform composition.[6] Since this copolymerization did not proceed efficiently by ordinary transition-metal complexes especially by metallocenes, these results thus encouraged us to explore the possibility of copolymerization of ethylene with the other monomers that have traditionally been difficult to be incorporated, especially by ordinary metallocenes. In this report, we thus wish to present the first example that VCH has been efficiently copolymerized with ethylene by using nonbridged half-titanocenes.[7]

Two complexes, $Cp^*TiCl_2(X)$ [$X = O\text{-}2,6\text{-}{}^iPr_2C_6H_3$ (**1**), $N = C^tBu_2$ (**2**)], were chosen as the catalyst precursors because **1** efficiently incorporates 2M1P in the ethylene/2M1P copolymerization.[6] The ketimide analogue **2** was also chosen because monomer reactivities in the copolymerization of ethylene with 1-hexene,[8] cyclohexene,[9] and styrene[10] as well as the corresponding microstructures were highly dependent upon the anionic donor ligand employed. The Cp−ketimide analogue, $CpTiCl_2$-

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* Corresponding author: tel +81-743-72-6041; fax +81-743-72-6049; e-mail nomurak@ms.naist.jp.

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**Table 1. Copolymerization of Ethylene with 1-Octene, 2-Methyl-1-pentene (2M1P), and Vinylcyclohexane (VCH) by Cp′TiCl$_2$(X) [X = O-2,6-$^i$Pr$_2$C$_6$H$_3$, Cp′ = Cp* (1); X = N=C$^t$Bu$_2$, Cp′ = Cp* (2), Cp (3)]−MAO Catalysts[a]**

| run | complex (μmol) | comonomer (mL) | time (min) | yield (mg) | activity[c] | $M_n$[d] × $10^{-4}$ | $M_w/M_n$[d] | comonomer[e] (mol %) |
|---|---|---|---|---|---|---|---|---|
| 1[f] | **1** (0.5) | | 6 | 530 | 6360 | 49 | 2.1 | |
| 2 | **1** (0.02) | 1-octene (10.0) | 6 | 301 | 151000 | 12 | 2.1 | 38.8 |
| 3[f] | **1** (0.2) | 2M1P (10.0) | 10 | 480 | 5760 | 7.2 | 1.8 | 5.7 |
| 4 | **1** (0.2) | VCH (5.0) | 6 | 334 | 16700 | 19 | 2.0 | 22.5 |
| 5 | **1** (0.2) | VCH (10.0) | 6 | 282 | 14100 | 10 | 2.3 | 31.9 |
| 6 | **2** (0.2) | 1-octene (10.0) | 6 | 214 | 10700 | 22 | 2.9 | 31.5 |
| 7[f] | **2** (0.2) | 2M1P (10.0) | 10 | 259 | 7770 | 63 | 1.9 | 0.30 |
| 8 | **2** (1.0) | VCH (10.0) | 6 | 522 | 5220 | | | |
| 9 | **2** (0.1) | VCH (10.0) | 6 | 52 | 5200 | 32 | 3.1 | 10.9 |
| 10 | **3** (0.02) | 1-octene (10.0) | 6 | 326 | 163000 | 53 | 3.4 | 34.1 |
| 11[f] | **3** (0.2) | 2M1P (10.0) | 10 | 232 | 6960 | 34 | 1.8 | 0.27 |
| 12 | **3** (0.2) | VCH (10.0) | 6 | 143 | 7150 | 28 | 2.9 | 24.5 |

[a] Conditions: toluene + comonomer total 30 mL (the initial 1-octene, VCH, 2M1P concentrations were 2.12, 2.44, and 2.70 mmol/mL, respectively, runs 2, 3, 5−11), MAO white solid (prepared by removing toluene and AlMe$_3$ from PMAO) 3.0 mmol (run 3, 4.50 mmol), ethylene 6 atm, 25 °C. [b] Molar ratio of Al/Ti. [c] Activity in kg of polymer/(mol of Ti h). [d] GPC data in *o*-dichlorobenzene vs polystyrene standard. [e] Comonomer content estimated by $^{13}$C NMR spectra. [f] Cited from ref 6.

**Table 2. Copolymerization of Ethylene with Vinylcyclohexane (VCH) by Cp*TiCl$_2$((O-2,6-$^i$Pr$_2$C$_6$H$_3$) (1)−MAO Catalyst[a]**

| run | complex (μmol) | Al/Ti[b] × $10^{-3}$ | ethylene (atm) | VCH (mL) | time (min) | yield (mg) | activity[c] | $M_n$[d] × $10^{-4}$ | $M_w/M_n$[d] | VCH[e] (mol %) | $T_g$ ($T_m$)[f] (°C) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 13 | **1** (0.2) | 15.0 | 8 | 5 | 6 | 438 | 21900 | 23 | 2.1 | 18.2 | |
| 14 | **1** (0.2) | 7.50 | 6 | 5 | 10 | 647 | 19400 | 15 | 2.3 | | −26 |
| 15 | **1** (0.2) | 15.0 | 6 | 5 | 10 | 692 | 20800 | 13 | 2.4 | 22.5 | −27 |
| 16 | **1** (0.2) | 22.5 | 6 | 5 | 10 | 590 | 17700 | 15 | 2.3 | | −25 |
| 17 | **1** (0.1) | 30.0 | 6 | 5 | 10 | 245 | 14700 | | | | |
| 4 | **1** (0.2) | 15.0 | 6 | 5 | 6 | 334 | 16700 | 19 | 2.0 | 22.5 | −27 |
| 5 | **1** (0.2) | 15.0 | 6 | 10 | 6 | 282 | 14100 | 10 | 2.3 | 31.9 | −12 |
| 18 | **1** (0.2)[g] | 15.0 | 6 | 10 | 6 | 338 | 16900 | 14 | 1.8 | 33.2 | |
| 19 | **1** (0.2) | 15.0 | 4 | 5 | 6 | 128 | 6400 | 13 | 2.0 | 29.7 | −14 |
| 20 | **1** (0.2) | 15.0 | 4 | 10 | 6 | 113 | 5650 | 11 | 1.8 | 38.1 | −5 |

[a] Conditions: toluene + vinylcyclohexane (VCH) total 30 mL, MAO white solid (prepared by removing toluene and AlMe$_3$ from PMAO), 25 °C. [b] Molar ratio of Al/Ti. [c] Activity in kg of polymer/(mol of Ti h). [d] GPC data in *o*-dichlorobenzene vs polystyrene standard. [e] VCH content estimated by $^{13}$C NMR spectra. [f] By DSC thermograms. [g] Polymerization at 40 °C.

(N=C$^t$Bu$_2$) (**3**), was also chosen because the **3**−MAO catalyst exhibited remarkable catalytic activity for ethylene/1-hexene copolymerization.[8b] The results for the ethylene/VCH copolymerization are summarized in Table 1,[11,12] and the copolymerizations of ethylene with 1-octene and 2M1P[6] by the **1**−**3**−MAO catalysts under similar conditions were also performed for comparison.

It was revealed that the copolymerizations by the **1**−MAO catalyst took place, affording relatively high molecular weight polymers with unimodal molecular weight distributions ($M_n$ = (1.0−1.9) × $10^5$, $M_w/M_n$ = 2.0−2.3). The observed activities calculated on the basis of the polymer yields were higher than that in the ethylene polymerization (runs 4 and 5), but the activity decreased upon increasing the VCH concentration (runs 4 and 5). The resultant polymers were poly(ethylene-*co*-VCH)s confirmed by both DSC thermograms ($T_m$ and/or $T_g$ values)[11] and the $^{13}$C NMR spectrum (Figure 1), as shown below, and the copolymers possessed uniform VCH distributions. These results thus strongly suggest that the copolymerization took place with a single catalytically active species. The VCH content by **1** was higher than 2M1P but lower than 1-octene under similar conditions (runs 2, 3, and 5), suggesting that the steric bulk around the olefinic bond affects the comonomer incorporations.

Although trace amounts of 2M1P incorporations were observed in the copolymerization of ethylene with 2M1P by the **2**−**3**−MAO catalysts (runs 7 and 11), **3** showed relatively efficient VCH incorporation under similar conditions, affording high molecular weight copolymer with unimodal molecular weight distribution (run 12). The Cp*−ketimide analogue (**2**) also incorporated VCH, but the VCH content in the copolymer was lower than that by **3** (run 9). The fact suggests that the substituent on the Cp′ affects the VCH incorporation, although, as suggested previously in the ethylene/1-hexene copolymerization,[8b] no significant differences in the 1-octene incorporations by **2**−**3**−MAO catalysts were observed in the ethylene/1-octene copolymerization under these conditions (runs 6 and 10). Since the VCH incorporations in the ethylene/VCH copolymerization by ordinary metallocene catalysts seemed difficult, as described above, these should be one of the most unique characteristics for using nonbridged half-titanocenes in olefin polymerization.

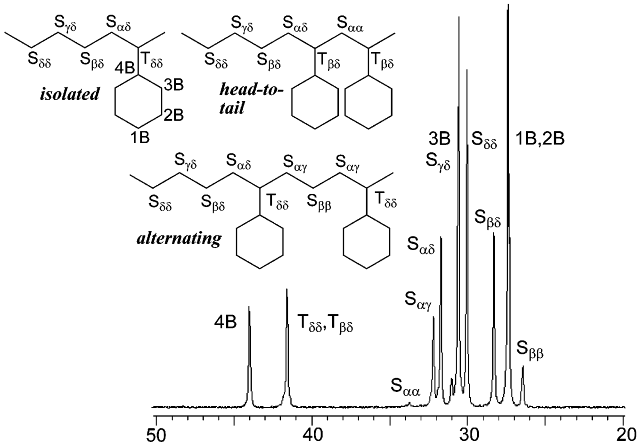

**Figure 1.** $^{13}$C NMR spectrum for poly(ethylene-*co*-vinylcyclohexane) prepared by the **1**−MAO catalyst (run 19, VCH content 29.7 mol %).

The ethylene/VCH copolymerizations by the **1**−MAO catalyst under various conditions are summarized in Table 2.[11] The catalytic activity was dependent upon the Al/Ti molar ratios (runs 14−17), but both the VCH contents and the $M_n$ values were unchanged under these conditions. The observed catalytic activities based on the polymer yields decreased at higher VCH/ethylene molar ratios under lower ethylene pressure (runs 4, 5, 19, and 20), whereas the VCH contents in the resultant copolymer increased under higher VCH/ethylene molar ratios. The activity did not change or slightly increased at higher polymerization temperature (40 °C, run 18). The DSC thermograms[11] showed sole glass transition temperatures ($T_g$), and the copolymers also exhibited melting temperatures ($T_m$) for the low VCH content indicating substantial crystalline poly(ethylene),[11] suggesting that the resultant copolymers possess uniform VCH incorporation. The $T_g$ values increased upon increasing the VCH contents,[11] suggesting that the resultant copolymers are amorphous as demonstrated by some ethylene/cyclic olefin copolymers such as poly(ethylene-*co*-norbornene)s[13] and poly(ethylene-*co*-cyclohexene)s.[9]

Figure 1 shows a typical $^{13}$C NMR spectrum in poly(ethylene-*co*-VCH) (run 19, in benzene-$d_6$/1,2,4-trichlorobenzene at 110 °C), and all resonances were identified by the dept analysis[11] as well as by comparison with the poly(VCH)[5] and poly(ethylene-*co*-cyclohexene)s[9] reported previously. The resultant copolymer possessed isolated VCH inserted unit among the repeated ethylene insertions, and the alternating sequence (assigned as $\beta\beta$ and $\alpha\gamma$) was also present with low extent.[11] The resonances ascribed to the repeated VCH insertion were negligible, and the fact may clearly explain that negligible or no catalytic activity was observed in an attempted homopolymerization of VCH by the **1**−MAO catalyst. These facts also indicate that the VCH incorporation was not so efficient as the 1-octene incorporation under the similar conditions, and preparation of the copolymer with VCH content higher than 50 mol % seems difficult in this catalysis.

We have shown that vinylcyclohexane (VCH) has been efficiently copolymerized with ethylene by using our original complex catalyst of nonbridged half-titanocenes containing an aryloxo ligand (even under moderate VCH/ethylene feed molar ratios[14]), affording high molecular weight copolymer with uniform composition. It was also revealed that both the cyclopentadienyl fragment and the anionic donor ligand directly affect the VCH incorporation and that the VCH incorporations by **1**−**3** were not so efficient as the 1-octene incorporations but were more efficient than the 2M1P incorporations. Encouraged by the above findings, we are exploring other possibilities for preparing new polyolefins by copolymerization of ethylene with other substituted olefins that have traditionally been difficult to be incorporated by ordinary catalysts in the presence of our original nonbridged half-titanocenes.

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**Supporting Information Available:** Detailed experimental procedures, $^{13}$C NMR spectra for poly(ethylene-*co*-VCH)s, and poly(ethylene-*co*-1-octene)s prepared by **1**−**3**−MAO catalysts, DSC thermograms for poly(ethylene-*co*-VCH)s, and plots of glass transition temperatures ($T_g$) vs VCH contents in the copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Zhang, H.; Nomura, K. *J. Am. Chem. Soc.* **2005**, *127*, 9364−9365.

(11) The general polymerization procedures, $^{13}$C NMR spectra for poly(ethylene-*co*-VCH)s and poly(ethylene-*co*-1-octene)s, DSC thermograms for resultant copolymer, and plots of glass transition temperatures ($T_g$) vs VCH contents are shown in the Supporting Information.

(12) To obtain the copolymer with uniform compositions, the polymerization should be terminated at the initial stage. MAO white solid was prepared by removing toluene and $AlMe_3$ from the commercially available MAO (PMAO-S, Tosoh Finechem. Co.), and a certain excess amount of MAO was required for exhibiting high catalytic activity, as shown in Table 2.

(13) For example: (a) Kaminsky, W. *Adv. Catal.* **2001**, *46*, 89−159. (b) Kaminsky, W.; Beulich, I.; Arndt-Rosenau, M. *Macromol. Symp.* **2001**, *173*, 211−225. (c) Nomura, K.; Tsubota, M.; Fujiki, M. *Macromolecules* **2003**, *36*, 3797−3799.

(14) The initial feed molar ratios of VCH/E in Tables 1 and 2 are ca. 1.26 (ethylene 8 atm, VCH 5.0 mL) and 5.02 (ethylene 4 atm, VCH 10.0 mL).

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