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Efficient Synthesis of Functionalized Polyolefin by Incorporation of 4-Vinylcyclohexene in Ethylene Copolymerization Using Half-Titanocene Catalysts

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ABSTRACT: Copolymerizations of ethylene with vinylcyclohexene (VCHen) by using $Cp'TiCl_2(X)$ [X = O-2,6-$^iPr_2C_6H_3$, Cp′ = Cp* (**1**); X = N=C$^tBu_2$, Cp′ = Cp* (**2**) and Cp (**3**)] catalyst systems with MAO have been explored. The copolymerizations proceeded via vinyl addition/insertion affording high molecular weight copolymers containing cyclohexenyl side chains (with uniform compositions as well as with unimodal molecular weight distributions) accompanied with certain degree of side reaction (intramolecular cyclization after VCHen insertion). Degree of the side reaction (cyclization) was dependent upon the catalyst employed, polymerization temperature, but was not affected by the time course, the Al/Ti molar ratios. The Cp−ketimide analogue (**3**) showed the best catalyst performance in terms of both the catalytic activity and the selectivity (lowest degree of the subsequent intramolecular cyclization) in the copolymerization. Quantitative epoxidation of the olefinic double bonds in the resultant copolymer has been achieved by using *m*-chloroperbenzoic acid under mild conditions; a facile, precise synthesis of functionalized polyolefin has thus been demonstrated by adopting this approach.

Introduction

Precise, efficient synthesis of polyolefin containing polar functionality is one of the most attractive goals in the field of transition metal catalyzed coordination polymerization.[1] Although the direct copolymerization of ethylene/propylene with polar monomers (such as acrylates, methacrylates etc.) is the most desirable approach, the approach faces a difficulty of notable decrease in the catalytic activity as well as of lowering the molecular weight in the resultant copolymer due to the catalyst poisoning of the active metal center by interaction with the polar functional groups (generating dormant or inactive species).[2−7] Postpolymerization modification of saturated polyolefins by transition metal catalyzed C−H bond activation[8] or grafting by free radical reaction[9] are known as the other approaches. However, these methods require harsh reaction conditions, and control of their contents/compositions of polar functionality should be difficult; the latter method accompanies unfavorable side reactions such as degradation, cross-linking, etc.

As the alternative approach, considerable attention has been paid recently to an approach by adopting controlled synthesis of unsaturated polyolefins by ethylene copolymerization with nonconjugated dienes,[1d,10−18] which can be subsequently introduced polar functionality through chemical modifications under mild conditions. In order to introduce the olefinic double bonds in the pendent side chains without accompanying cyclization and/or cross-linking as the probable side reactions,[19] nonconjugated dienes containing two olefins with different reactivities, such as 1,4-hexadiene,[12] 7-methyl-1,6-octadiene,[13,14] dicyclopentadiene,[15] and 5-vinyl-2-norbornene,[16] were chosen to improve the selectivity of incorporation of the monoolefin or strained cyclic olefin units in the two olefinic double bonds.

In this context, 4-vinylcyclohexene (VCHen), commercially produced by dimerization of butadiene, should be one of the promising nonconjugated dienes for the above purpose, especially from the practical viewpoint. Several examples were reported for copolymerization of ethylene or propylene with VCHen.[18,20,21] For example, the VCHen contents in the copolymerization of ethylene and/or propylene with VCHen using the *rac*-$[Et(indenyl)_2]ZrCl_2$−methylaluminoxane (MAO) catalyst system were low (< 5 mol %) even under excess VCHen molar ratios,[21a,21b] and the ethylene/propylene/VCHen terpolymerization prepared by *rac*-$[Me_2Si(2\text{-}MeBenz[e]Ind)_2]ZrCl_2$−MAO catalyst system afforded copolymers with negligible VCHen contents (0.6−0.9 mol %) even under relatively high VCHen concentration conditions (compared to ethylene and propylene).[21c] The ethylene/VCHen copolymerization by the $[Ph_2C(Cp)(Flu)]ZrCl_2$−MAO catalyst system at 0 °C afforded the copolymer with 33 mol % VCHen content (but with low catalytic activity, 10 kg-polymer/mol-Zr·h), but the contents drastically decreased to 8 mol % when the copolymerization was conducted at 30 °C.[18] Therefore, the successful catalytic copolymerizations exhibiting high catalytic activities with efficient VCHen incorporations have never been reported so far. This seems to be probably somewhat related to the low efficiency of incorporation of vinyl group in VCHen as seen in the ethylene/vinylcyclohexane (VCH) copolymerization using ordinary metallocenes.[22]

We communicated that half-titanocenes containing anionic ancillary donor ligand (X) of the type, $Cp'TiCl_2(X)$ [X = O-2,6-$^iPr_2C_6H_3$, Cp′ = Cp* (**1**); X = N=C$^tBu_2$, Cp′ = Cp* (**2**), Cp (**3**)], exhibited both high catalytic activity and efficient comonomer incorporation in the ethylene/VCH copolymerization in the presence of MAO cocatalyst (Scheme 1).[23] These catalysts showed negligible comonomer incorporation in the ethylene/cyclohexene copolymerization,[24,25] although $(^tBuC_5H_4)TiCl_2$(O-2,6-$^iPr_2C_6H_3$) showed rather efficient cyclohexene incorporation

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Scheme 1

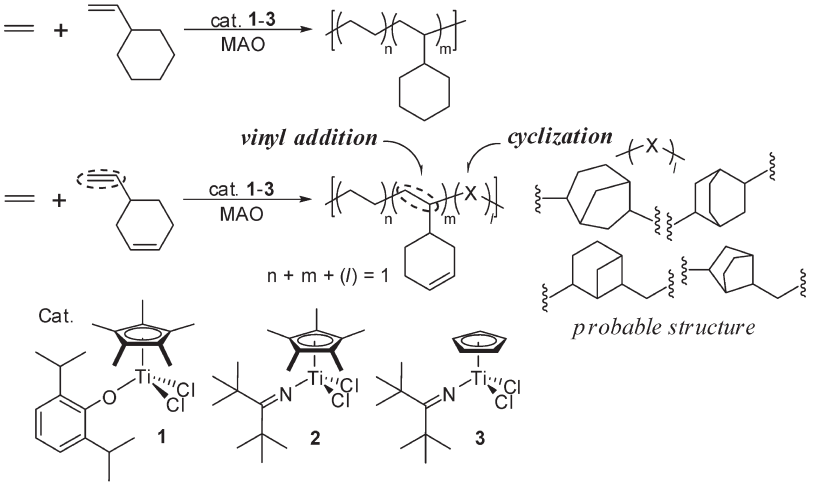


Table 1. Copolymerizations of Ethylene with 4-Vinylcyclohexene (VCHen), Vinylcyclohexane (VCH) by Cp′TiCl$_2$(X) [X = O-2,6-^{i}Pr$_2$C$_6$H$_3$, Cp′ = Cp* (1); X = N=C^{t}Bu$_2$, Cp′ = Cp* (2), Cp (3)]−MAO Catalyst Systems[a]

run	catalyst (μmol)	comonomer (M)	yield/mg	activity[b]	M_n[c] × 10^{-4}	M_w/M_n[c]	C_6 branch[d]/mol %	S[e]	T_m (T_g)[f]/°C
1	**1** (2.0)	VCHen (1.22)	264	1320	4.4	2.1	9.3	0.39	
2	**1** (2.0)	VCHen (2.43)	194	970	2.6	2.3	15.5	0.35	(−13)
3	**1** (0.2)	VCH (1.22)	334	16700	18.7	2.0	22.5		(−27)
4	**1** (0.2)	VCH (2.43)	282	14100	10.0	2.3	31.9		(−12)
5	**2** (1.0)	VCHen (1.22)	371	3710	38.8	2.4		1.37	105
6	**2** (1.0)	VCHen (2.43)	185	1850	25.6	2.6	2.5	1.17	90
7	**2** (1.0)	VCH (2.43)	522	5220	31.6	3.1	10.9		65
8	**3** (0.1)	---	118	11800	46.7	2.0			137
9	**3** (0.1)	VCHen (0.61)	184	18400	49.0	1.7	2.6	0.23	104
10	**3** (0.1)	VCHen (2.43)	233	23300	50.8	2.0	10.0	0.13	57
11	**3** (0.1)	VCHen (4.86)	195	19500	54.8	2.1	16.1	0.13	(−18)
12	**3** (0.2)	VCH (2.43)	143	7150	27.8	2.9	24.5		(−25)

[a] Conditions: VCHen or VCH + toluene total 30 mL, MAO (prepared by removing toluene and AlMe$_3$ from ordinary MAO) 3.0 mmol, ethylene 6 atm, 25 °C, 6 min. [b] Activity in kg-polymer/mol-Ti·h. [c] GPC data in *o*-dichlorobenzene vs polystyrene standards. [d] Content of cyclohexenyl or cyclohexyl (C_6) branch unit in the copolymers by vinyl addition [m × 100; m in Scheme 1]. [e] Degree of side reaction (intramolecular cyclization), and the details are shown in the Supporting Information.[26] [f] Measured by DSC thermograms.

under certain conditions.[24] On the basis of these results in addition to the facts reported previously,[18,20,21] we thus have an interest to explore a possibility for efficient synthesis of copolymers containing cyclohexene units as the pendent side chain in the ethylene/VCHen copolymerization using these half-titanocenes (**1**−**3**). We present herewith that the copolymerizations especially by **1**,**3**−MAO catalyst systems proceeded with efficient incorporation of vinyl group accompanied with certain degree of cyclization (Scheme 1) on the basis of detailed assignments of resonances in the ^{13}C NMR spectra in the resultant copolymers under various conditions. We also wish to present that an efficient synthesis of polymer containing polar functionality has been achieved by the subsequent chemical modification (epoxidation using *m*-chloroperbenzoic acid) under mild conditions.

Results and Discussion

Copolymerization of Ethylene with 4-Vinylcyclohexene (VCHen) Using Half-Titanocenes−MAO Catalyst Systems. Table 1 summarizes results in copolymerizations of ethylene with 4-vinylcyclohexene (VCHen) by using Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**), Cp′TiCl$_2$(N=C^{t}Bu$_2$) [Cp′ = Cp* (**2**) and Cp (**3**)] in toluene at 25 °C in the presence of methylaluminoxane (MAO) (Scheme 1).[26] MAO white solids, prepared by removing AlMe$_3$ and toluene from the commercially available sample (PMAO-S, 6.8 wt % in toluene, Tosoh Finechem Co.), were chosen as the cocatalyst, because they were effective for preparation of high molecular weight copolymers with unimodal molecular weight distributions in the copolymerization of ethylene with vinylcyclohexane (VCH) catalyzed by **1**−**3**.[23] These copolymerizations were terminated after 10 min (at the initial stage), and the termination with the comonomer (VCHen) conversion less than 10% are important to obtain the copolymer with uniform composition distributions. The results in the ethylene/VCH copolymerization communicated previously[23] are also shown for comparison.

It turned out that the ethylene/VCHen copolymerizations by **1**−**3** afforded high molecular weight copolymers with unimodal molecular weight distributions (M_w/M_n = ca. 2). The resultant polymers were soluble in hot *o*-dichlorobenzene and possessed single melting points (T_m) or glass transition temperatures (T_g), suggesting that the resultant polymers possessed uniform compositions and the polymerization proceeded without cross-linking under these conditions (terminated with low VCHen conversion).

Figures 1 and 2 show typical ^{13}C NMR and the DEPT spectra of the resultant polymers.[26] Their resonances were identified by comparison of the spectra (with different VCHen contents) as well as the spectra reported previously,[18] and by comparison with the spectra of copolymers after hydrogenation (Figure 1b) as well as with poly(ethylene-*co*-VCH) (Figure 1c).[23] Resonances ascribed to the pendent cyclohexenyl group (C_6 branch), which were derived from insertion of the monoolefin in VCHen (vinyl addition)

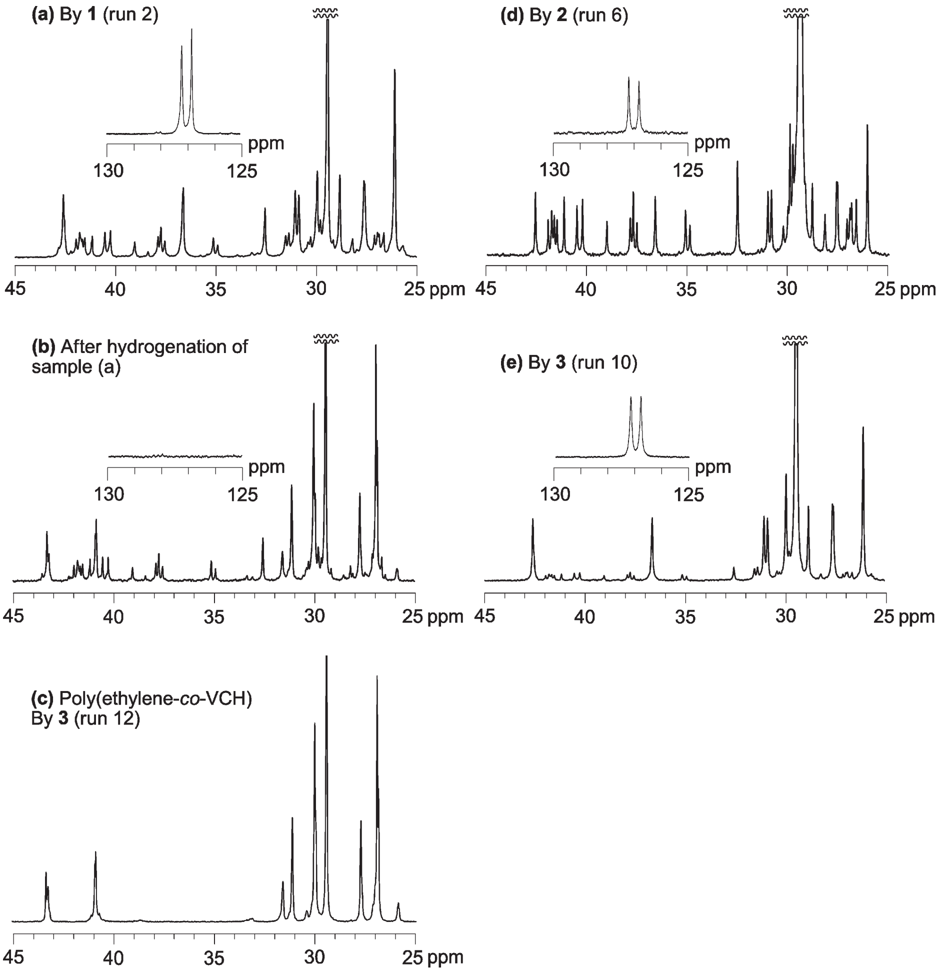


Figure 1. ^{13}C NMR spectra (in tetrachloroethane-d_2 at 110 °C) for poly(ethylene-*co*-VCHen)s prepared by (**1**−**3**)−MAO catalyst systems. Sample: (a) run 2 by **1**, (d) run 6 by **2**, (e) run 10 by **3**; (b) hydrogenated samples of poly(ethylene-*co*-VCHen) (run 2); (c) poly(ethylene-*co*-VCH) (run 12).

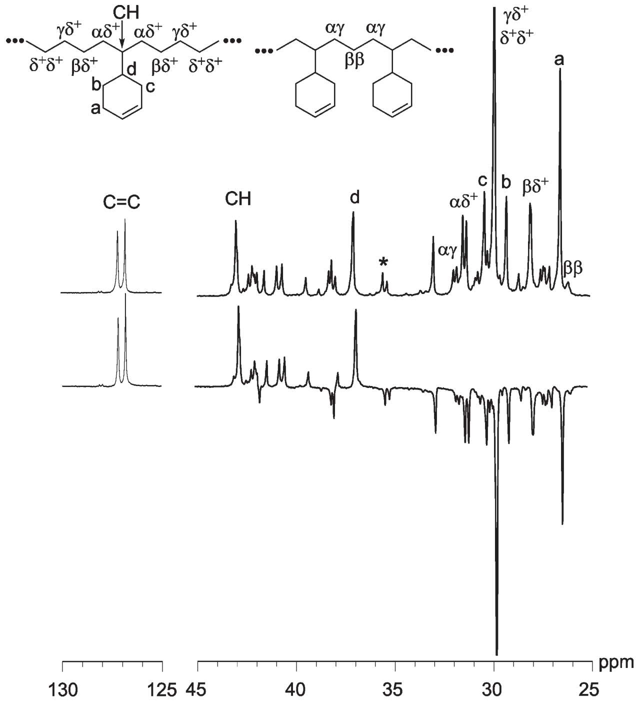


Figure 2. ^{13}C NMR and DEPT spectra (in tetrachloroethane-d_2 at 110 °C) for poly(ethylene-*co*-VCHen) by **1**−MAO catalyst system (sample run 2).

without insertion of the internal (disubstituted) olefin, could be assigned by comparison of the spectra after hydrogenation (Figure 1a,b), because their microstructures (monomer sequence etc.) were unchanged before/after hydrogenation and the peaks newly observed after hydrogenation were identical with these of the spectra of the ethylene/VCH copolymer (Figure 1c). Resonances ascribed to the vinyl group were not observed in the spectra, suggesting that selective incorporation of the cyclohexenyl unit did not occur under these conditions: this can also be assumed from the results in the ethylene/cyclohexene copolymerization by **1**−**3** that no or trace amount of cyclohexene units were incorporated in the copolymerization even under high cyclohexene concentrations (ethylene 2 atm, cyclohexene 5.0 M, incorporations).[24,25]

It also turned out that resonances which cannot be ascribed to the carbons by vinyl addition of VCHen were also observed (at ca.35−42 ppm),[26] and their degree was dependent upon the nature of the catalyst precursors employed (**1**−**3**, Figures 1a,d,e).[27] As described below, the degree was dependent upon the ethylene pressure (initial molar ratio of VCHen/ethylene) and the temperature, but the degree of these resonances was not affected by the Al/Ti molar ratios and the time course.[26] Taking into account these facts, these peaks would be thus assigned as resonances due to intramolecular cyclization of the pendent double bond after insertion of the vinyl group in VCHen (C_6 branch) unit.

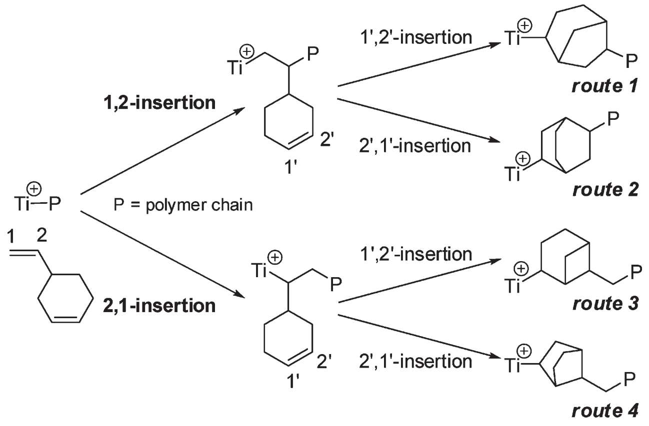
Four pathways shown in Scheme 2 can be considered as the intramolecular cyclization after the vinyl insertion of

Table 2. Copolymerization of Ethylene with 4-Vinylcyclohexene (VCHen) by $CpTiCl_2(N{=}C^tBu_2)$ (3)−MAO Catalyst System[a]

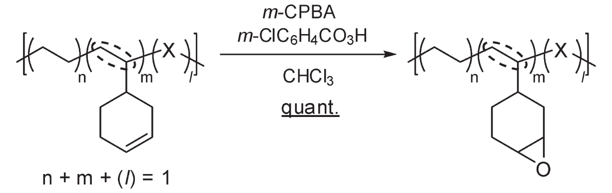
run	catalyst (μmol)	ethylene/ atm	MAO/ mmol	temp/ °C	time/ min	yield/ mg	activity[b]	M_n[c] × 10^{-4}	M_w/M_n[c]	C_6 branch[d]/mol %	S[e]	T_m (T_g)[f]/°C
13	**3** (0.05)	6	3	25	6	114	22800	50.4	2.0	10.1	0.12	57
10	**3** (0.1)	6	3	25	6	233	23300	50.8	2.0	10.0	0.13	57
14	**3** (0.1)	6	3	25	3	117	23400	41.9	2.0	10.3	0.14	60
15	**3** (0.1)	6	3	25	10	311[g]	18700	45.4	2.2	10.2	0.16	58
16	**3** (0.1)	6	1.5	25	6	210	21000	44.1	2.3	10.5	0.14	55
17	**3** (0.1)	6	4.5	25	6	246	24600	28.6	2.4	10.1	0.14	55
18	**3** (0.1)	4	3	25	6	74	7400	30.7	2.0	15.2	0.22	35
19	**3** (0.1)	8	3	25	6	456[g]	45600	53.5	2.0	7.6	0.13	70
20	**3** (0.1)	6	3	40	6	202	20200	38.4	2.2	8.2	0.21	65
21	**3** (0.1)	6	3	55	6	154	15400	29.6	2.2	7.0	0.34	72

[a] Conditions: VCHen + toluene total 30 mL (VCHen 2.43 M), MAO cocatalyst. [b] Activity in kg-polymer/mol-Ti·h. [c] GPC data in *o*-dichlorobenzene vs polystyrene standards. [d] Content of cyclohexenyl (C_6) branch unit in the copolymers by vinyl addition [m × 100; m in Scheme 1]. [e] Degree of side reaction (intramolecular cyclization), and the details are shown in the Supporting Information. [f] Measured by DSC thermograms. [g] The reaction was stopped due to a difficulty of stirring the mixture.

Scheme 2



Scheme 3

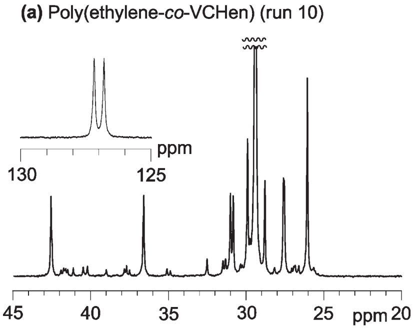


VCHen.[26] As described below,[27,28] the integration ratios of these (unidentified) resonances (on the basis of resonances at ca. 35 ppm) were not affected by the catalyst precursors employed and the polymerization conditions (ethylene pressure, the Al/Ti molar ratios, time course etc.) employed. Although the route 1 (1,2-insertion of VCHen and 1′,2′-insertion of the pendent double bond) seems dominant than route 2 on the basis of results in ethylene copolymerization with substituted monoolefins (1,2-insertion, and resonances observed between 37 and 42 ppm),[14,19i,23,26,28,29] however, the exact assignments of the observed resonances have not completed yet.[26,28]

The contents of cyclohexenyl (C_6) branch unit in the copolymers [$m \times 100$; m in Scheme 1] derived from the selective insertion of vinyl group in VCHen were estimated by both ^1H and ^{13}C NMR spectra,[26] and the results are summarized in Table 1. Degree of the side reaction (subsequent intramolecular cyclization) was assumed by the integration ratio on the basis of the peaks at ca. 35 ppm and the peak assigned as "CH" (Figure 2).[26] The catalytic activities by the Cp*-aryloxo analogue (**1**) for the ethylene/VCHen copolymerizations were lower than those in the ethylene/VCH copolymerization conducted under the same conditions (runs 1−4, Table 1); both the M_n values and the content of the C_6 pendent unit in the resultant copolymers were lower than these in the ethylene/VCH copolymerization. The trend in decrease in the activity was also seen in the copolymerization of ethylene with cyclohexene (CHE),[24] although **1** afforded negligible CHE incorporation; this would be speculated as due to weak coordination of CHE. The similar trend were observed in these copolymerizations by the Cp*-ketimide analogue (**2**) (runs 5−7). However, we do not have clear explanation (speculation) why the comonomer contents in the ethylene/VCHen copolymerizations were lower than those in the ethylene/VCH copolymerizations.

In contrast, it should be noted that both the catalytic activities and the M_n values in the resultant copolymers in the copolymerization with VCHen using the Cp−ketimide analogue (**3**) were higher than and those in the copolymerization with VCH under the same conditions (runs 10, 12). The contents of the C_6 units (VCHen contents by the vinyl addition) increased upon increasing the initial VCHen concentration without significant decrease in both the catalytic activity (calculated based on the polymer yield) and the M_n values in the resultant copolymers (runs 9−11). Although the VCHen incorporation by **3** was somewhat lower than that by **1**, **3** showed the highest catalytic activity among these complexes (**1**−**3**). Moreover, as seen in Figure 1, the resultant copolymers prepared by **3** possessed less contents by the subsequent intramolecular cyclization (resonances seen between ca. 35−42 ppm). Taking into account these facts, it is thus suggested that the **3**−MAO catalyst would be the most suited as the catalyst precursor for the copolymerization in terms of both the catalytic activity and the selectivity of the vinyl insertion of VCHen with minimizing the degree of the subsequent intramolecular cyclization.

Table 2 summarizes results in the copolymerization of ethylene with VCHen by **3**−MAO catalyst system under various conditions.[26] The copolymerizations proceeded without significant decrease in the catalytic activities affording high molecular weight copolymers with unimodal molecular weight distributions as well as with single compositions (confirmed as single melting temperature by DSC thermograms), if the copolymerizations were conducted at ethylene 6 atm, 25 °C (runs 10, 13−17). The catalytic activity increased at higher ethylene pressure along with decreasing the VCHen content in the resultant copolymer (runs 10, 18, 19); both the activity and the M_n value in the copolymer decreased upon increasing the polymerization temperature (25−55 °C, runs 10,20−21). Note that, as described above, degree of the subsequent intramolecular cyclization (as expressed as S in Table 2) was not affected by the



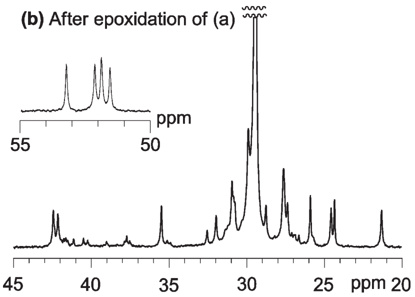


Figure 3. ^{13}C NMR spectra (in tetrachloroethane-d_2 at 110 °C) for (a) poly(ethylene-*co*-VCHen) prepared by **3**−MAO catalyst system (run 10) and (b) sample after epoxidation.

Al/Ti molar ratios, time course, and the catalyst concentration, but was affected by the polymerization temperature employed.[26] On the basis of these results, it is thus demonstrated that an efficient synthesis of unsaturated copolymers could be achieved by incorporation of VCHen in the ethylene copolymerization using **3**−MAO catalyst system.

Introduction of Polar Functionality into Poly(ethylene-*co*-VCHen). Epoxidation of the unsaturated side chain in poly (ethylene-*co*-VCHen) (run 10 in Table 1) was conducted by using *m*-chloroperbenzoic acid (*m*-CPBA) at room temperature in chloroform (Scheme 3).[30] The ^{13}C NMR spectra of the copolymer before and after the epoxidation are shown in Figure 3. The resonances of the olefinic carbons at 127 ppm (Figure 3a) were disappeared and four new signals at 51−54 ppm corresponding to the epoxy group were observed in the ^{13}C NMR spectrum (Figure 3b).[26] The result clearly demonstrates that a facile functionalization of the olefinic double bond (introduction of epoxy group) in polyolefin has been achieved under mild conditions in quantitative yield by adopting this approach. Although the conditions adopted here would not be very practical (in $CHCl_3$ and *m*-CPBA) and needed optimization, we believe that this would introduce a new powerful methodology for precise synthesis of polyolefins containing polar functionality under mild conditions.

Experimental Section

General Procedures. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques. Anhydrous grade toluene (Kanto Chemical Co., Inc.), 4-vinyl-1-cyclohexene (Merck & Co., Inc.) were stored in the drybox in the presence of molecular sieves (mixture of 3A 1/16 and 4A 1/8, and 13X 1/16) after passing through an alumina short column under nitrogen. *m*-Chloroperbenzoic acid, with water (*m*-CPBA·$x$$H_2O$, 69−75% purity, Wako Pure Chemical Ind., Ltd.) was used as received. Ethylene of polymerization grade (Sumitomo Seika Chemicals Co., Ltd.) was used as received without further purification procedures. Toluene and $AlMe_3$ in the commercially available methylaluminoxane [PMAO-S, 9.5 wt % (Al) toluene solution, Tosoh Finechem Co.] were removed under reduced pressure (at ca. 50 °C for removing toluene, $AlMe_3$, and then heated at > 100 °C for 1 h for completion) in the drybox to give white solids. $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1**)[31] and $Cp'TiCl_2(N{=}C^tBu_2)$ [Cp′ = Cp* (**2**)[32] and Cp (**3**)[32]], were prepared according to the previous reports.

All ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.78 MHz for ^1H and 100.53 MHz for ^{13}C). All spectra were obtained in the solvents indicated at room temperature unless otherwise noted. Chemical shifts are given in ppm and are referenced to $SiMe_4$ (δ 0.00, ^1H, ^{13}C). ^{13}C NMR spectra for polyethylenes and poly(ethylene-*co*-VCHen)s were measured at 110 °C in 1,1,2,2-tetrachloroethane-d_2. The relaxation delay was 5.2 s, the acquisition time was 1.3 s, the pulse angle was 90°, and the number of transients accumulated was ca. 6000.

Molecular weights and molecular weight distributions for the polyethylenes and poly(ethylene-*co*-VCHen)s were measured by a gel permeation chromatography (GPC, Tosoh HLC-8121GPC/HT) using a RI-8022 detector (for high temperature, Tosoh Co.) with polystyrene gel column (TSK gel GMH_{HR}-H HT × 2, 30 cm × 7.8 mm ϕ i.d.), ranging from $< 10^2$ to $< 2.8 \times 10^8$ MW at 140 °C using *o*-dichlorobenzene containing 0.05% w/v 2,6-di-*tert*-butyl-*p*-cresol as eluent. The molecular weights were calculated by a standard procedure based on the calibration with standard polystyrene samples.

Copolymerization of Ethylene with 4-Vinylcyclohexene (VCHen). A typical reaction procedure for copolymerization of ethylene with VCHen (run 1, Table 1) is as follows. Toluene (24.0 mL), VCHen (5.0 mL), and MAO solid (174 mg, 3.0 mmol) were added into the autoclave (100 mL scale, stainless steel) in the drybox, and the reaction apparatus was then replaced, filled with ethylene (1 atm) at 25 °C. A toluene solution (1.0 mL) containing **1** (2.0 μmol) was then added into the autoclave, and the reaction apparatus was then immediately pressurized to 5 atm (total ethylene pressure 6 atm). The mixture was magnetically stirred for 6 min, ethylene remained was then purged after the reaction upon cooling at 0 °C, and the mixture was then poured into MeOH (300 mL) containing HCl (5 mL). The resultant polymer was then collected on a filter paper by filtration, and was adequately washed with MeOH. The sample was then dried *in vacuo*.

Hydrogenation of Poly(ethylene-*co*-VCHen). A general procedure is as follow. Into a 10 mL scale stainless-steel autoclave, toluene (5 mL), $RhCl(PPh_3)_3$ (5 mg), and poly(ethylene-*co*-VCHen) (50 mg) were added. The reaction apparatus was pressurized to 4 atm by H_2, and was magnetically stirred overnight at 100 °C. The reaction mixture was then poured into MeOH, and the resultant polymer was collected on a filter paper by filtration. The polymer was purified again by reprecipitation, was collected, and then dried *in vacuo*.

Epoxidation of Poly(ethylene-*co*-VCHen). To a $CHCl_3$ solution containing poly(ethylene-*co*-VCHen) 1.154 g (run 10), *m*-CPBA·xH_2O 1.63 g was added. The reaction solution was stirred overnight at room temperature, and the mixture was then dropped into MeOH after passing through a cotton plug. The resultant polymer was collected on a filter paper and was then dried *in vacuo*. Yield: 1.17 g.

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Supporting Information Available: Text giving additional explanation, tables giving data for the copolymerization results, and figures showing selected ^1H and ^{13}C NMR spectra for poly(ethylene-*co*-VCHen)s before/after hydrogenation and after epoxidation. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) These copolymerization results by **1**,**3**−MAO catalysts were as follows [ethylene 2 atm, cyclohenexe (CHE) 5.0 mmol/mL in toluene at 25 °C for 10 min]. The activities by **1**,**3**−MAO catalysts were 1998 and 1944 kg-polymer/mol-Ti·h, respectively, and the CHE contents in the resultant polymers were negligible.[24] The activity by **2** was 1512 kg-polymer/mol-Ti·h, and the CHE content was negligible under the same conditions (Wang, W.; Nomura, K. et al. Unpublished results).

(26) Selected ^{13}C and ^{1}H NMR spectra of poly(ethylene-*co*-VCHen)s, assumed microstructure in the copolymer prepared by **3**, and basic equations for estimation of the composition (microstructure analysis) in the copolymers are shown in the Supporting Information.

(27) As a reviewer commented, three possibilities (i) vinyl addition (coordination/incorporation of vinyl group), (ii) coordination/incorporation of cyclohexene unit, and (iii) coordination of both (as seen in diene polymerization) should be considered. On the basis of independent experiments in the copolymerization of ethylene with vinylcyclohexane (VCH)[23] as well as with cyclohexene (CHE), these complexes (**1**-**3**) showed negligible CHE incorporation even under high CHE concentrations,[24,25] whereas the VCH incorporation by **1** was higher than those by **2** and **3**.[23] Since degree of the so-called side reaction (integration of resonances due to the subsequent cyclization) by **3** was low, also since the assignments of resonances, especially in the spectra of the copolymer by **1**, became too complicated, therefore, we did not argue the details concerning this matter. I personally believe that we may have to take into consideration of possibilities ii and iii in the copolymerization by **1**.

(28) As described in the text, the integration ratios of observed resonances on the basis of resonances at ca. 35 ppm were not dependent upon the catalyst precursors, polymerization conditions, time course, Al/Ti molar ratios. These facts would suggest that these resonances are due to the intramolecular cyclization after insertion of the pendant unit (C_6 branch), and the dominant pathway should be present in these catalysis. As described in the Supporting Information, route 1 (1,2-insertion of VCHen and 1′,2′-insertion of the pendant C_6 branch) seems to be a dominant pathway for the intra molecular cyclization, especially by comparison of route 1 and route 2 (resonances ascribed to methylene carbons at 37−42 ppm, these resonances would not be seen in the route 2) because vinylcyclohexane (VCH) incorporated with 1,2-insertion mode. However, we cannot delete the possibility of 2,1-insertion of the VCHen unit (route 3,4) at this moment.

(29) For additional examples, (a) Nomura, K.; Komatsu, T.; Imanishi, Y. *J. Mol. Catal. A* **2000**, *159*, 127−137 (1-hexene polymerization). (b) Khan, F. Z.; Kakinuki, K.; Nomura, K. *Macromolecules* **2009**, *42*, 3767–3773. Examples for ethylene copolymerizations with *tert*-butylethylene, vinyltrimethylsilane .

(30) Incorporation of olefinic double bonds in the ethylene/cyclopentadiene copolymerization and subsequent functionalization Pan, L.; Ye, W.; Liu, J.; Hong, M.; Li, Y. *Macromolecules* **2008**, *41*, 2981–2983.

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