Direct Precise Functional Group Introduction into Polyolefins: Efficient Incorporation of Vinyltrialkylsilanes in Ethylene Copolymerizations by Nonbridged Half-Titanocenes

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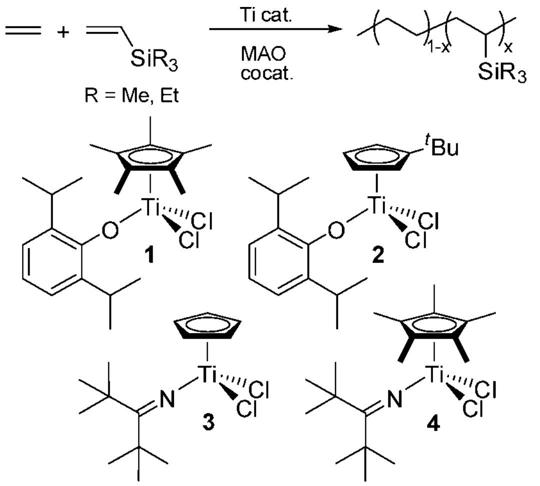
Introduction. Precise, efficient functionalization of polyolefins under mild conditions is an attractive, challenging subject from both academic and industrial viewpoints, and the approach by an efficient introduction of a reactive group using metal catalyzed copolymerization attracts considerable attention.[1] Controlled incorporation of the desired functionalities by the direct copolymerization has been considered as one of the promising approaches;[1a,b,e,2−6] however, the introduction by the copolymerization of ethylene or propylene with (protected) polar monomer(s) faces difficulties because of the catalyst poisoning and interaction of centered metal with the functional groups in coordination polymerization. The approach by metal-catalyzed atom transfer radical copolymerization has also been considered as another promising approach, but an unfavorable equilibrium for generating active radicals exists in the copolymerization and obtainment of the copolymers with relatively high olefin contents seems impossible at this stage.[1e,4]

The approach using alkenylsilane has also been known as a promising route in the coordination polymerization,[7−9] but both the activity and the molecular weight(s) in the (co)polymers generally decreased upon increasing the comonomer content(s).[7a,8,9] We recently achieved an efficient copolymerization of ethylene with allyltrialkylsilanes by using *nonbridged* half-titanocenes containing anionic ancillary donor ligands,[7b] whereas both the activities and M_w values in the copolymers in the copolymerization using Cp_2ZrCl_2, $[(CH_2)_2(indenyl)_2]ZrCl_2$, decreased upon increasing the content(s) of allyltrimethylsilane ($M_w = 1200−2900$) due to the subsequent β-hydrogen elimination after the insertion.[7a] Vinyltrialkylsilanes should be considered as better comonomer in terms of the direct functional group introduction into polyethylene (or polypropylene) backbone as well of its use as cross-linking reagents to improve thermal properties.[10] These sterically encumbered olefins are, however, very difficult to coordinate into the metal center in ordinary metallocenes,[11] and no reports for the copolymerization with vinyltrialkylsilane (or *tert*-butylethylene) have thus been known until now.[11] In this paper, we thus herein present that the efficient incorporation of vinyltrialkylsilanes, $CH_2{=}CHSiR_3$ [R = Me (VTMS), Et (VTES)], in the ethylene copolymerization has been achieved for the first time (Scheme 1), whereas the incorporation of *tert*-butylethylene was very low under the same conditions.[12]

Results and Discussion. $Cp'TiCl_2(X)$ [X = O-2,6-$^iPr_2C_6H_3$, Cp′ = C_5Me_5 (Cp*, **1**), *tert*-BuC_5H_4 (**2**); X = N=C^tBu_2, Cp′ = Cp (**3**), Cp* (**4**)] have been chosen because these complexes display unique characteristics for certain ethylene copolymerizations,[13,14] and both Cp′ and X are demonstrated to affect the catalytic activity and the comonomer incorporation.[13] The results are summarized in Table 1.[15]

Scheme 1



It turned out that **1** incorporated VTMS into polyethylene with moderate catalytic activities, and the resultant copolymers possessed high molecular weights with uniform molecular weight distributions (runs 1−4). Both the catalytic activity (estimated based on polymer yield) and the M_n value (measured by GPC) decreased upon increasing the VTMS contents in the copolymer (estimated by ^1H NMR spectra).[15] The copolymers also possess uniform VTMS compositions (distributions in the copolymers) confirmed by DSC thermograms,[15] and the melting temperature in the copolymer decreased upon increasing the VTMS content(s).[15] The *tert*-BuC_5H_4 analogue (**2**) showed better VTMS incorporation under the same conditions, but the M_n value was low (run 5) as seen in the copolymerization of ethylene with 1-hexene.[14a]

The Cp−ketimide analogue (**3**) exhibited both higher catalytic activities and better VTMS incorporations than **1**, whereas the Cp* analogue (**4**) exhibited low catalytic activity under the same conditions (run 10). Efficient synthesis of high molecular weight poly(ethylene-*co*-VTMS)s with uniform compositions could be achieved by adopting **3**, although both the activity and the M_n values seemed decreasing upon increasing the VTMS contents. As seen in the copolymerization by **1**, both the catalytic activity and the M_n value decreased upon increasing the VTMS contents in the copolymer.[15] This would be probably due to that certain degree of chain transfer (probably β-H elimination) after incorporation of VTMS would be accompanied (and insertion/coordination of subsequent monomer after the VTMS incorporation seems not easy due to the steric bulk).[7a] The copolymerization with vinyltriethylsilane (VTES) by **3**−MAO catalyst also took place under the same conditions, affording the copolymer containing VTES with uniform molecular weight distribution (run 9).

The copolymerization using Cp_2ZrCl_2−MAO catalyst was conducted under the same conditions (as in runs 1, 5, 6, 10), but a negligible amount of polymer was collected from the reaction mixture. The polymer yield was thus low if the copolymerization was conducted in the presence of large amount of Cp_2ZrCl_2 (run11); the resultant polymer was a linear polyethylene (by ^{13}C NMR spectrum). Since the attempted

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Table 1. Copolymerizations of Ethylene with CH_2=CHX (X = $SiMe_3$, $SiEt_3$, ^{t}Bu) by Cp′$TiCl_2$(O-2,6-^{i}$Pr_2C_6H_3$) [Cp′ = C_5Me_5 (1), ^{t}Bu (2)] and Cp′$TiCl_2$(N=C^tBu_2) [Cp′ = Cp (3), C_5Me_5 (4)]−MAO Catalyst Systems[a]

			CH_2=CHX							
run	cat. (μmol)	ethylene(atm)	X	mL	yield (mg)	activity[b]	M_n[c] × 10^{-4}	M_w/M_n[c]	content[d] (mol %)	T_m (T_g)[e](°C)
1	**1** (0.5)	6	$SiMe_3$	5	156	1870	30.5	1.86	5.1	89 (−32)
2	**1** (0.5)	4	$SiMe_3$	5	76	910	19.1	1.92	7.2	75 (−34)
3	**1** (1.0)	6	$SiMe_3$	10	119	710	15.1	1.95	8.1	73 (−35)
4	**1** (2.0)	2	$SiMe_3$	5	50	150	4.28	1.85	18.6	
5	**2** (5.0)	6	$SiMe_3$	5	77	92	1.41	2.84	13.6	
6	**3** (1.0)	6	$SiMe_3$	5	622	3730	57.3	2.26	11.9	(−41)
7	**3** (1.0)	4	$SiMe_3$	5	260	1560	42.2	2.32	18.7	(−45)
8	**3** (1.0)	6	$SiMe_3$	10	137	820	30.4	2.44	21.4	(−46)
9	**3** (1.0)	6	$SiEt_3$	5	606	7270	55.8	2.10	4.9	
10	**4** (0.5)	6	$SiMe_3$	5	31	370	13.5	2.02	1.9	
11	**Zr**[f] (10)	6	$SiMe_3$	5	38	23	0.56	3.86	trace	
12	**1** (0.2)	6	^{t}Bu	10	422	12 700	43.3	2.11	0.8	
13	**3** (0.2)	4	^{t}Bu	5	153	4590	65.9	1.99	trace	
14	**3** (0.2)	6	^{t}Bu	10	200	6000	68.7	1.93	trace	

[a] Conditions: toluene and comonomer total 30 mL, dried MAO (prepared by removing toluene and $AlMe_3$ from the ordinary MAO) 3.0 mmol, 25 °C, 10 min. [b] Activity = kg of polymer/(mol of Ti h). [c] GPC data in *o*-dichlorobenzene vs polystyrene standards. [d] Comonomer contents estimated by ^1H NMR spectra.[15] [e] By DSC thermograms.[15] [f] Cp_2ZrCl_2 was used in place of **1**.

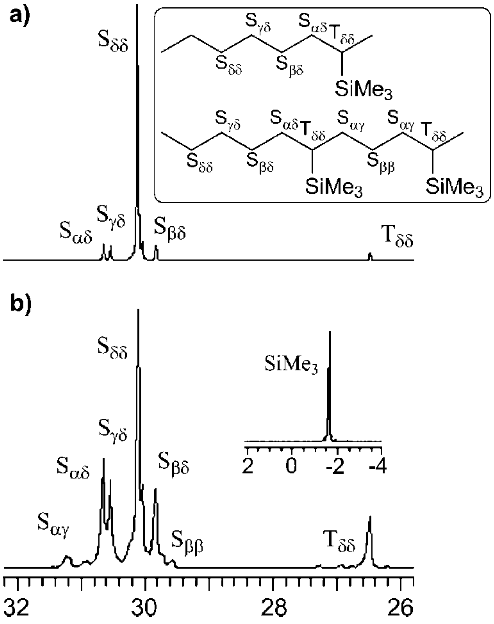
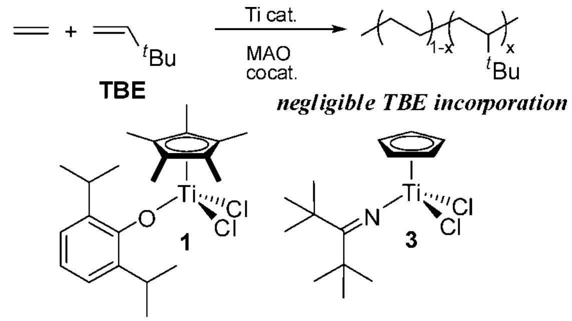


Figure 1. ^{13}C NMR spectra (in C_6D_6/1,2,4-trichlorobenzene at 110 °C) of poly(ethylene-*co*-VTMS)s. Conditions (Table 1): (a) run 1 (VTMS 5.1 mol % by **1**) and (b) run 8 (VTMS 21.4 mol % by **3**).[14]

copolymerization with 2-methyl-1-pentene afforded polyethylene with high catalytic activity,[14f] the result should be an interesting contrast.[11]

Figure 1 shows selected ^{13}C NMR spectra for poly(ethylene-*co*-VTMS)s prepared by **1**,**3**−MAO catalysts.[15] All resonances in the spectra were assigned on the basis of dept spectra (in addition to the ^{13}C NMR spectra with different VTMS contents). In addition to the resonances ascribed to carbons for isolated VTMS inserted units, the resonances ascribed for alternating inserted units ($S_{\alpha\gamma}$, $S_{\beta\beta}$) were seen in small amount. No resonances ascribed to the repeated insertions were seen, suggesting that synthesis of the copolymer with high VTMS contents (>50 mol %) seems difficult.

Scheme 2



Note that the copolymerizations of ethylene with *tert*-butylethylene (TBE) by **1**,**3**−MAO catalyst systems under the same conditions afforded high molecular weight (co)polymers containing a trace amount of TBE with uniform molecular weight distributions (Table 1, runs 12−14, Scheme 2).[15] The results thus clearly indicate that *the efficient incorporation can be achieved by vinyltrialkylsilane (CH_2=CH$\underline{Si}$$R_3$), not by TBE ($CH_2$=CH$\underline{C}$$Me_3$).*

One appropriate, plausible speculation assumed on the basis of simple PM3 calculation results to explain the above facts would be that coordination energies [defined as difference in energy between the optimized π-complex and the cationic complex and the monomer] of VTMS are higher than those of TBE or ethylene, which may lead the better incorporation.[16] Although we are not sure about the exact reason why placement of Si plays an essential role for the efficient incorporation, the results here should be promising not only as the first successful example of efficient incorporation of sterically encumbered monomers but also as unique example observed in vinyltrialkylsilanes.[17]

We have shown that VTMS can be efficiently incorporated in the ethylene/VTMS copolymerization by transition-metal-catalyzed coordination polymerization. We also presented a unique reactivity between silicon (CH_2=CH$\underline{Si}$$Me_3$) and carbon ($CH_2$=CH$\underline{C}$$Me_3$). We believe that this should be a unique characteristic in this catalysis, and various modifications derived from the $SiMe_3$ group can also be considered. We are now exploring other possibilities for preparing new polyolefins by incorporation of other traditionally unreactive olefins.

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Supporting Information Available: Text giving general experimental procedures, ^1H and ^{13}C NMR spectra for poly(ethylene-*co*-VTMS)s and poly(ethylene-*co*-VTES), ^{13}C NMR spectrum of the polymer in the ethylene/TBE copolymerization, DSC thermograms for poly(ethylene-*co*-VTMS)s, GPC traces in the resultant (co)polymers, and the results for geometry optimizations for proposed catalytically active species and energy evaluations (by PM3). This material is available free of charge via Internet at http://pubs.acs.org.

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(15) Experimental procedures as well as selected ^1H and ^{13}C NMR (dept) spectra of the copolymers are shown in the Supporting Information.

(16) The results for geometry optimizations for proposed catalytically active species and energy evaluations [equilibrium geometry at ground state with semiempirical PM3, geometry optimization, RHF/PM3D Spartan '06 for Windows (Wavefunction Inc.)] are shown in the Supporting Information. Coordination energy (ΔE_{coord}) was calculated as the difference in energy between the optimized π-complex on one hand and the cationic complex and the monomer on the other, namely $\Delta E_{coord} = E_{cation} + E_{monomer} - E_{\pi\text{-complex}}$.

(17) A reviewer commented that a steric factor seems to be very important because $CH_2{=}CHSiMe_3$ is rather less crowded than $CH_2{=}CHCMe_3$, which would explain the poor incorporation of the latter monomer (this should also affect the coordination energy). Recently, Prof. Bochmann (University of East Anglia, UK) suggested a possibility of 2,1-insertion rather than 1,2-insertion. Therefore, we will explore the details in the forthcoming full article. K.N. expresses his thanks to the reviewer and Prof. Bochmann for helpful comments.

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