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Efficient Functional Group Introduction into Polyolefins by Copolymerization of Ethylene with Allyltrialkylsilane Using Nonbridged Half-Titanocenes

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Introduction. Precise, efficient introduction of reactive functionality into polyolefins via metal-catalyzed coordination polymerization attracts considerable attention for obtainment of desirable properties, such as increased melt-fracture resistance, paintability, and adhesion and such as compatibility with other materials.[1] One of the approaches to simultaneously control reactive functionalities were achieved by manipulating specific polymerization chain transfer pathways.[1a,2−5] The introduction by the copolymerization has also been considered as the other promising approaches,[6−9] although the *direct* copolymerization of ethylene or propylene with (protected) polar monomers would face difficulties because of the catalyst poisoning and interaction of centered metal with functionalized monomers.[6] The copolymerizations of ethylene with certain alkenylsilanes [$CH_2{=}CH(CH_2)_nSiH_3$], $n = 1, 2, 4, 6$, etc.] using (dinuclear) linked half-titanocenes have been known as a promising route;[8] however, the activity generally decreased upon increasing the comonomer content(s).[8b] These silane(s) also play a role as the chain transfer reagent(s) accompanied.[8b] The copolymerization of ethylene with allyltrimethylsilane (ATMS) by certain metallocenes was also known,[3c] but both the catalytic activities and the M_n values in the copolymers decreased upon the ATMS contents. This is because that ATMS also play a role as the chain transfer reagent due to the favored β-hydrogen elimination after bulky ATMS insertion.[10] In this paper, we thus present that highly efficient synthesis of high molecular weight copolymers containing SiR_3 (R = Me, ^{i}Pr) group has been achieved by copolymerization of ethylene with allyltrialkylsilanes by half-titanocenes containing anionic ancillary donor ligands (Scheme 1).

Results and Discussion. $Cp'TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ [Cp′ = C_5Me_5 (**1**), $^tBuC_5H_4$ (**2**)] were chosen, because the complexes demonstrate unique characteristics for some ethylene copolymerizations.[11,12] $Cp'TiCl_2(N{=}C^tBu_2)$ [Cp′ = C_5Me_5 (**3**), Cp (**4**)] were also chosen, especially because **4** were effective for the copolymerization with 1-hexene[13a] as well as norbornene.[13b] The results are summarized in Table 1.[14]

The catalytic activity (calculated based on the polymer yield) in the copolymerization of ethylene with ATMS by the Cp*−aryloxo analogue (**1**) increased upon increasing the initial ATMS concentration and/or ethylene pressure (runs 1−6). The resultant polymers were poly(ethylene-*co*-ATMS)s identified by both ^1H and ^{13}C (dept) NMR spectra,[14] and the copolymers possessed high molecular weights with uniform molecular weight distributions (M_n = (2.23−2.87) × 10^4. M_w/M_n = 2.27−2.79). The ATMS contents in the copolymer, estimated by integration ratios in the ^1H NMR spectra,[14] increased by increasing the ATMS concentration and/or at low ethylene pressure. Note that the ATMS content (43.4 mol %, ATMS 1.05 M, run 1) was relatively close to 1-pentene content in poly(ethylene-*co*-1-pentene) (48.5 mol %, 1-pentene 1.52 M) prepared under the similar conditions.[15] The fact thus clearly demonstrates that **1** efficiently incorporates ATMS without decrease in the M_n values. This should be a unique contrast to that in the copolymerization by ordinary metallocenes,[3c] in which the M_n values decreased upon increasing the ATMS contents due to the favored β-H elimination after ATMS insertion.[3c]

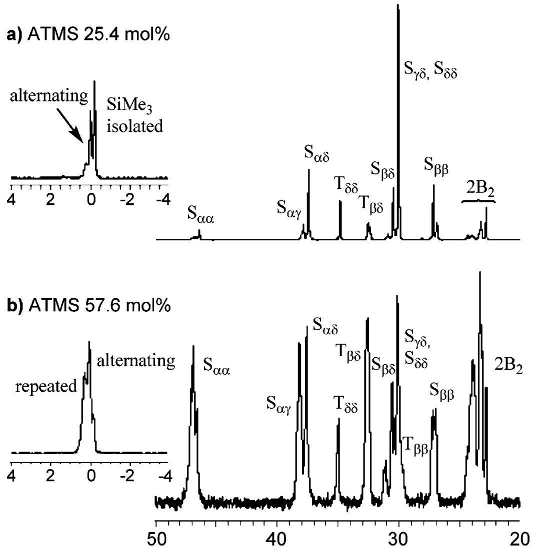
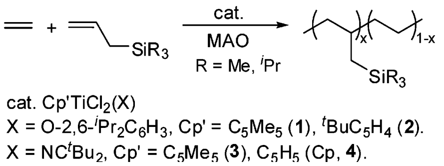
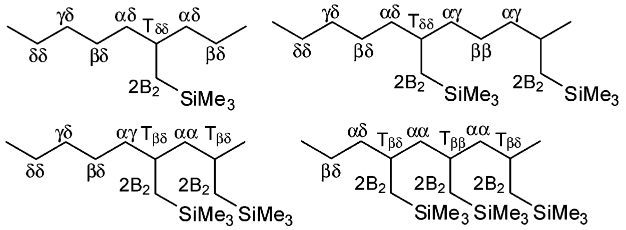


Figure 1. Selected ^{13}C NMR spectra (in benzene-d_6/1,2,4-trichlorobenzene at 110 °C) for poly(ethylene-*co*-allyltrimethylsilane)s prepared by **1**−MAO catalyst system. Sample: (a) run 5 and (b) run 2 (Table 1).

Scheme 1



Scheme 2



The *tert*-BuC_5H_4 analogue (**2**) which showed better 1-hexene incorporation than **1** in the ethylene/1-hexene copolymerization[16] exhibited moderate catalytic activities under the same conditions (runs 7−10). However, notable improvements in the ATMS incorporation compared to **1** were not seen, and the activity was lower than **1**, and the copolymers possessed rather low M_n values.

Both the Cp*−ketimide (**3**) and the Cp−ketimide (**4**) analogues exhibited higher catalytic activities than **1** under the same conditions (runs 11−15, runs 17−21, 24−25), although the ATMS contents in the copolymers were rather lower than

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Table 1. Copolymerization of Ethylene with Allyltrialkylsilane ($CH_2{=}CHCH_2SiR_3$) by $Cp'TiCl_2(X)$−MAO [X = O-2,6-$^iPr_2C_6H_3$, Cp′ = Cp* (1), $^tBuC_5H_4$ (2); X = N=C$^tBu_2$, Cp′ = Cp* (3), Cp (4)] Catalysts[a]

run	catal (amt (μmol))	ethylene (atm)	R (amt (mL))	activity[b]	cont[c] (mol %)	M_n[d] $\times 10^{-4}$	M_w/M_n[d]
1	**1** (1.0)	4	Me (2.5)	678	43.4	2.23	2.32
2	**1** (0.5)	4	Me (5.0)	1740	57.6	2.55	2.79
3	**1** (0.5)	6	Me (2.5)	1836	29.5	2.37	2.43
4	**1** (0.5)	6	Me (5.0)	3550	48.8	2.78	2.69
5	**1** (0.25)	8	Me (2.5)	4850	25.4	2.87	2.27
6	**1** (0.25)	8	Me (5.0)	3600	42.6	2.86	2.38
7	**2** (2.0)	4	Me (2.5)	369	43.3	1.30	2.56
8	**2** (2.0)	4	Me (5.0)	312	60.4	1.27	2.45
9	**2** (2.0)	6	Me (2.5)	840	34.6	1.42	2.49
10	**2** (1.0)	8	Me (2.5)	1722	25.9	1.55	2.38
11	**3** (0.2)	4	Me (2.5)	2280	30.1	14.5	2.00
12	**3** (0.2)	4	Me (5.0)	4350	51.2	11.6	2.02
13	**3** (0.2)	6	Me (2.5)	5070	20.1	28.2	2.09
14	**3** (0.2)	6	Me (5.0)	4980	35.6	21.5	2.18
15	**3** (0.2)	8	Me (2.5)	9000	13.6	35.1	2.38
16	**4** (0.1)	4	−	5800	−	45.2	2.30
17	**4** (0.1)	4	Me (1.0)	10 000	11.6	23.4	2.28
18	**4** (0.1)	4	Me (2.5)	16 500	26.2	24.6	2.30
19	**4** (0.1)	4	Me (5.0)	23 220	43.8	24.3	2.38
20	**4** (0.05)	6	Me (2.5)	45 000	16.6	31.3	2.35
21	**4** (0.05)	6	Me (5.0)	47 500	30.3	28.3	2.55
22	**4** (0.5)	6	*^iPr* (2.5)	3600	7.6	29.6	2.68
23	**4** (0.5)	6	*^iPr* (5.0)	3480	17.5	13.0	1.97
24	**4** (0.05)	8	Me (2.5)	41 600	11.9	37.0	2.46
25	**4** (0.05)	8	Me (5.0)	67 000	23.7	32.8	2.57
26	**4** (5.0)	−	Me (5.0)	318	100	4.50	2.16

[a] Conditions: toluene + allyltrialkylsilane total 30 mL, d-MAO (prepared by removing toluene and $AlMe_3$ from PMAO-S) 3.0 mmol, ethylene 4−8 atm, 25 °C, 10 min. [b] Activity in kg-polymer/mol-Ti•h. [c] Estimated by ^1H NMR spectra. [d] GPC data in *o*-dichlorobenzene vs polystyrene standards.

those prepared by **1**−MAO catalyst. The Cp−ketimide analogue (**4**) exhibited the highest activities among **1**−**4**, affording high molecular weight copolymers with unimodal molecular weight distributions ($M_n = (2.34-3.70) \times 10^5$. $M_w/M_n = 2.28-2.57$). Note that the activity increased upon increasing the ATMS concentration (runs 17−21, 24, and 25) as well as ethylene pressure, and that the M_n values in the copolymers were independent upon the ATMS contents. The M_n values also increased upon increasing the ethylene pressure.[17] The fact demonstrates a unique contrast to that observed in the copolymerization by ordinary metallocenes.[3c]

Allyltriisopropylsilane (R = ^{i}Pr) was also incorporated efficiently and the resultant copolymers possessed rather high molecular weights with uniform distributions. Polymerization of ATMS also proceeded by **4**−MAO catalyst, and the resultant polymer possessed rather high molecular weight with a uniform molecular weight distribution (run 26).[18]

Figure 1 shows typical ^{13}C NMR spectra for poly(ethylene-*co*-ATMS)s prepared by **1**−MAO catalyst. All resonances in the spectra were assigned based on the dept spectra (with different ATMS contents), and the ^{13}C NMR spectrum in poly(ATMS).[14] In addition to the resonances ascribed to carbons for both isolated and alternating ATMS inserted units, resonances ascribed to carbons for repeated inserted units were seen (Scheme 2). Poly(ATMS) structures were atactic (the polymer does not possess stereo regularity) based on the ^{13}C NMR spectrum.[14]

We have shown that an efficient introduction of reactive functionality (SiR_3 groups) into polyolefins has been achieved by half-titanocenes containing anionic ancillary donor ligands. The present fact should be, we believe, highly promising for precise synthesis of functionalized polyolefins under mild conditions.

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Supporting Information Available: Text giving general experimental procedures and figures showing selected ^1H and ^{13}C NMR (dept) spectra for the resultant (co)polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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

(15) Copolymerization of ethylene with 1-pentene was performed similarly as in run 1 (except **1** 0.01 μmol, 1-pentene 5.0 mL, toluene 25 mL). Activity = 48600 kg-polymer/mol-Ti·h, $M_n = 160000$, $M_w/M_n = 1.9$, and 1-pentene = 48.5 mol %. Nomura, K.; Kakinuki, K.; et al. Unpublished results (presented at Green Cat. Symposium, Kyoto, Japan, Nov 2007).

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(17) A reviewer commented that one reason that the high molecular weight copolymers were obtained might be due to the fact that these copolymerizations were conducted under rather high ethylene pressure. High ethylene pressure should be required to obtain the copolymer(s) with moderate comonomer content(s) with low comonomer conversion(s) (in order to obtain a copolymer with uniform composition); this point also might be considered.

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