Efficient Ethylene/Norbornene Copolymerization by (Aryloxo)(indenyl)titanium(IV) Complexes−MAO Catalyst System

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Introduction. The design and synthesis for efficient transition metal complex catalyst toward controlled olefin polymerization has attracted considerable attention in the fields of catalysis, organometallic chemistry, and polymer chemistry.[1] It has been well-known that poly(ethylene-*co*-norbornene)s prepared by so-called single-site catalysts are amorphous materials with a promising combination of a high glass transition temperature (T_g), transparency in the UV−vis region, and heat resistance.[2,3] In particular, it has also been reported that a linked half-titanocene complex like [$Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**5**) showed remarkable catalytic activity with efficient norbornene (NBE) incorporation for ethylene/NBE copolymerization.[4−6] However, the microstructure possesses few NBE repeat units and contained alternating E−N sequences as well as isolated NBE units.[5,6]

We have demonstrated that *nonbridged* (aryloxo)(cyclopentadienyl)titanium(IV) complexes displayed unique characteristics, especially not only for ethylene/α-olefin copolymerization but also for ethylene/styrene copolymerization.[7] We have also reported that the efficient catalyst for ethylene polymerization can be modified to an efficient catalyst for syndiospecific styrene polymerization only by replacing the substituent on the cyclopentadienyl group (Cp′) of the half-titanocene complexes containing aryloxy,[7] anilide,[8] and amide ligands.[9] Since our original catalyst incorporates bulky monomers such as 1-octene[7b,d] and styrene[7c,e] efficiently, also since the effect of substituents on Cp′ plays an essential role for monomer reactivities as well as for monomer sequence distributions in ethylene/α-olefin copolymerization,[7b,d] we thus have an interest to explore a possibility of using this type of complex as catalyst precursors for ethylene/norbornene copolymerization (Scheme 1).[10]

Results and Discussion. On the basis of our previous results,[7b,d] (indenyl)$TiCl_2$(OAr) (**1**) and Cp′$TiCl_2$(OAr) [Cp′ = C_5Me_5 (Cp*, **2**), $^tBuC_5H_4$ (**3**), 1,3-$^tBu_2C_5H_3$ (**4**), OAr = O-2,6-$^iPr_2C_6H_3$] (Chart 1) were chosen for the copolymerization because the substituent on Cp′ should directly affect both the catalytic activity and the comonomer incorporation.[11] The complex containing the indenyl ligand was chosen for this study because we assumed that electronic nature of Cp′ should play an important role for the copolymerization. This is also due to the fact that the same level of NBE incorporation could be seen between [$Me_2Si(indenyl)_2]ZrCl_2$ and [$Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**5**).[12] The results are summarized in Table 1.[13,14]

Scheme 1

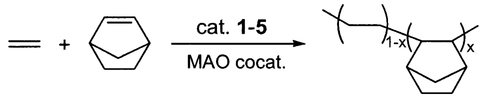

Chart 1

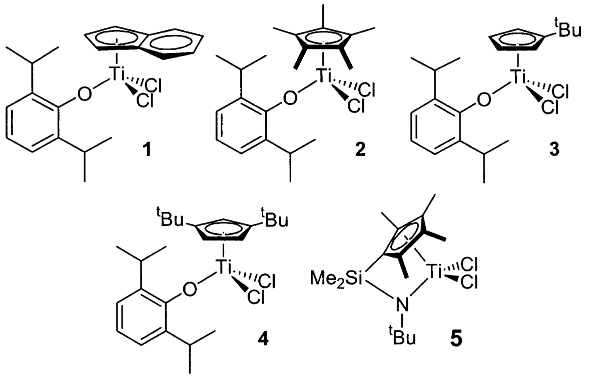

Table 1. Ethylene/Norbornene Copolymerization by Cp′$TiCl_2(O$-2,6-$^iPr_2C_6H_3)$ [Cp′ = Indenyl (1), C_5Me_5 (2), $^tBuC_5H_4$ (3), 1,3-$^tBu_2C_5H_3$ (4)], or [$Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (5)−MAO Catalyst Systems[a]

run no.	Cat. (μmol)	Al/Ti[b]	NBE concn[c] × 10^1	polymer yield/mg	activity[d]	NBE content[e]/mol %	M_n[f] × 10^{-4}	M_w/M_n[f]	T_g (T_m)[g]/°C
1	**2** (1.5)	2000	1.0	1010	4030	4.7	70.0	1.8	−6.4 (85.7)
2	**2** (1.5)	2000	2.0	576	2300	7.6	26.1	2.0	−4.4 (61.9)
3	**2** (2.5)	1200	5.0	746	1790	12.9	28.7	1.4	14.9
4	**2** (2.5)	1200	10.0	354	850	26.2	14.6	1.4	44.8
5	**3** (2.5)	1200	0.5	612	1470		18.0	2.5	(92.7)
6	**3** (2.5)	1200	1.0	877	1060		12.9	2.2	−5.7 (65.9)
7	**3** (5.0)	600	2.0	585	702	14.1	4.4	1.6	1.2
8	**3** (5.0)	600	5.0	146	176	27.5	0.6	4.1	54.8
9	**4** (2.5)	1200	1.0	24	58		1.3	2.6	−5.0 (76.4)
10	**4** (2.5)	1200	2.0	19	45		0.7	2.1	0.4 (39.2)
11	**1** (1.5)	2000		283	1130		44.7	1.8	
12	**1** (1.5)	2000	0.5	790	3160	6.0	24.9	2.0	−2.4 (99.2)
13	**1** (1.5)	2000	2.0	1210	4840		11.6	1.4	
14	**1** (1.5)	2000	3.0	1510	6040	16.0	17.8	1.6	9.4
15	**1** (1.5)	2000	4.0	989	3960	20.4	6.5	1.4	30.9
16	**1** (1.5)	2000	5.0	1130	4520	25.9	6.0	2.0	56.4
17	**1** (2.0)	2500	10.0	1170	3510	39.7[h]	7.3	2.1	87.3
18	**1** (5.0)	1400	20.0	1270	1520	48.9[h]	4.2	2.1	113.4
19	**5** (2.5)	1200	1.0	1030	2470	9.2	26.9	1.8	−5.3 (57)
20	**5** (5.0)	600	5.0	1610	1930	29.6	27.1	1.6	63.0
21	**5** (5.0)	600	10.0	1800	2160	32.4	11.9	1.8	73.4

[a] Conditions: toluene 50 mL, d-MAO (prepared by removing $AlMe_3$ and toluene from PMAO), ethylene 4 atm, 25 °C, 10 min. [b] Molar ratio of Al/Ti. [c] Norbornene (NBE) concentration charged (mol/L). [d] Activity in kg of polymer/(mol of Ti h). [e] NBE content (mol %) estimated by ^{13}C NMR spectra. [f] GPC data in *o*-dichlorobenzene vs polystyrene standards. [g] By DSC measurement. [h] Norbornene (NBE) content (mol %) estimated by DSC (T_g).[18,19]

Remarkable catalytic activity was observed when **2** was chosen as the catalyst precursor, but the activity significantly decreased upon increasing the initial NBE concentration. Resultant polymers prepared by **2** were poly(ethylene-*co*-norbornene)s with high molecular weights (M_n = (14.6−70.0) × 10^4) as well as with narrow molecular weight distributions (M_w/M_n = 1.4−1.9). DSC thermograms showed a sole glass transition tempera-

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ture (T_g) in all cases, and the copolymers also exhibit melting temperatures for low NBE incorporation indicating substantial crystalline poly(ethylene), suggesting that the resultant copolymers possess uniform NBE incorporation. The observed activities by **2** were comparable to those by **5**, especially at low NBE concentration region, but showed less NBE incorporation.[15]

NBE incorporation could be improved when **3** was used as the catalyst precursor,[15,16] and the observed activity by **4** was extremely low probably due to the steric bulk of two *tert*-Bu groups. The resultant copolymer possessed low molecular weight with a relatively broad polydispersity when the copolymerization by **3** was performed under high NBE concentrations (run 8).

It was revealed that **1** exhibited both remarkable catalytic activity and efficient NBE incorporation,[16] and the resultant copolymers possessed relatively high molecular weights ((4.2−24.9) × 10^4) with narrow polydispersities ($M_w/M_n = 1.4-2.1$). DSC thermograms for the copolymer also showed a sole glass transition temperature in all cases, and both GPC and DSC results thus suggest that the resultant copolymer possesses uniform NBE incorporation. The catalytic activity for the copolymerization was higher than that for ethylene homopolymerization, and extremely low activity was observed (activity < 1 kg of polymer/(mol of Ti)) when the polymerization was performed in the absence of ethylene.[17] The observed catalytic activities by **1** were higher than those by **5**, and the NBE incorporation was almost in the same level at the low NBE concentration region. The copolymers with relatively high NBE contents (48.9 mol % in run 18) with both relatively high molecular weights and unimodal polydispersities were obtained when the polymerization was performed under higher NBE concentration conditions.[18−20]

Figure 1 summarizes typical ^{13}C NMR spectra for poly(ethylene-*co*-norbornene)s (NBE contents: 25.9−27.5 mol %) prepared by **1**−**3**−MAO catalyst systems. The microstructure by **2** possesses few NBE repeat units and contained both *meso* and *racemo* alternating E−N sequences as well as isolated NBE units (33.0−33.5 ppm), and the result is similar to that by **5**. On the other hand, resonances ascribed to NBE dyads were observed (shown as an asterisk in Figure 1b, corresponding to C_5, C_6, and C_7 carbons) in the spectra for the copolymer by **3**,[6] and the result clearly indicates that the monomer sequences were dependent upon the substituent on Cp′. The observed results may be an appropriate explanation for difference in the observed NBE incorporation between **2** and **3**.

The microstructure by **1** estimated by ^{13}C NMR spectra possesses a mixture of NBE repeat units (including dyads) in addition to alternating and isolated NBE sequences.[20] Although detailed assignment for each resonances could not be accomplished for the spectrum at this moment, this should be a notable difference from those by **2**, **3**, **5**, and [$Me_2Si(indenyl)_2$]$ZrCl_2$. The present result thus clearly indicates the substituent on Cp′ *directly affects* both monomer reactivities and monomer sequence distributions in the copolymerization.[21]

We have shown that **1** is an effective catalyst precursor for ethylene/norbornene copolymerization. Since the efficient catalyst precursor can be tuned only by modifying the substituent on Cp′ in ethylene-based copolymerizations (with α-olefin, styrene, and norbornene), we believe this should be the unique characteristics for using this type of catalyst for precise olefin polymerization.

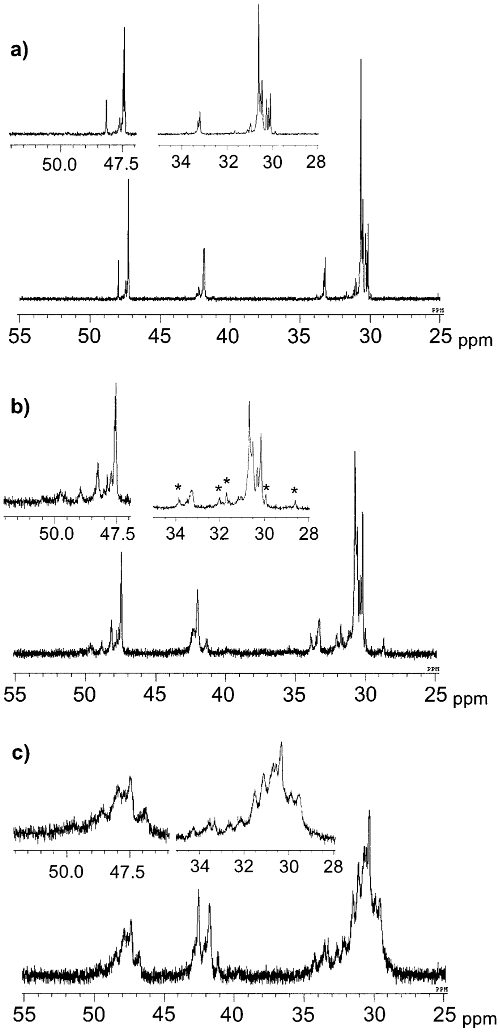

Figure 1. ^{13}C NMR spectra for poly(ethylene-*co*-norbornene)s by **1**−**3**−d-MAO catalyst systems (in 1,3,5-trichlorobenzene/benzene-d_6 at 130 °C): (a) copolymers by **2** (norbornene 26.2 mol %, run 4); (b) copolymer by **3** (norbornene 27.5 mol %, run 8); (c) copolymer by **1** (norbornene 25.9 mol %, run 16).

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Supporting Information Available: General experimental procedures, synthesis for (indenyl)$TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**1**), DSC charts, and ^{13}C NMR spectra including assignments for poly(ethylene-*co*-norbornene)s; some copolymerization results with **1**, **5**, and [$Me_2Si(indenyl)_2$]$ZrCl_2$ and plots of T_g vs NBE contents (based on copolymerization results with **2**−**5** and the above zirconium complex) for estimation of NBE contents in poly(ethylene-*co*-norbornene)s prepared by the **1**−MAO catalyst system. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Some of these results were introduced at the 1st Mitsui Chemicals International Symposium on Catalysis Science (MICS2003, Chiba, Japan, March 2003).

(11) During the course of this study, Shiono et al. reported living polymerization of norbornene by [Me_2Si(fluorenyl)(N^tBu)]-$TiMe_2$. This result may also support our initial assumption. Hasan, T.; Nishii, K.; Shiono, T.; Ikeda, T. *Macromolecules* **2002**, *35*, 8933.

(12) Nomura, K.; et al. Unpublished results and some results are shown in the Supporting Information.

(13) For experimental details, see the Supporting Information.

(14) To control NBE conversion less than 10%, we terminated the reaction at the initial stage.

(15) NBE contents (mol %) in the resultant poly(ethylene-*co*-norbornene)s were estimated by ^{13}C NMR spectra established previously by Tritto et al.[6]

(16) For more detailed results by **1**−**3**−MAO catalysts, see the Supporting Information.

(17) Polymerization conditions were the same as those in run 17, except that 10.0 μmol of **1**, 7.0 mmol of MAO (Al/Ti = 700), and the reaction was performed for 120 min. Yield: 8.6 mg (activity = 0.43 kg of polymer/(mol of Ti h)).

(18) Because the resonances around C_7 carbons in the copolymer prepared by **1**−MAO catalyst were broad probably due to the mixture of NBE repeat units (with *atactic* stereoselectivity) in addition to the alternating and isolated NBE sequences (shown in Figure 1c), we thus estimated the NBE content by using a calibration curve between T_g and NBE content prepared based on results by **2**−**5** and [Me_2Si-(indenyl)$_2$]$ZrCl_2$−d-MAO catalyst systems.[4c,6d] Detailed results and related references are introduced in the Supporting Information.

(19) As described in ref 18, we estimated some NBE contents by using DSC data,[4c,6d] although T_g values for the copolymer with high NBE contents were sometimes dependent upon the polymer microstructure (Forsyth, J.; et al. *Macromol. Chem. Phys.* **2001**, *202*, 614). We believe that this estimation should be appropriate because a linear relationship between T_g values and NBE contents was obtained for the copolymer by **1**−**5**−MAO catalysts, probably due to that the resultant copolymer (especially NBE repeat units) possessed no stereoregularity with random incorporation.

(20) The resultant copolymer possessed T_g of 157.4 °C (activity 126 kg of polymer/(mol of Ti h), $M_n = 1.1 \times 10^4$, $M_w/M_n = 2.4$), when the copolymerization was performed under the same conditions as in run 18 except that NBE concentration was 4.0 mol/L instead of 2.0 (**1**, 10.0 μmol; Al/Ti = 1000). The T_g value for the copolymer was 186.5 °C (activity 34 kg of polymer/(mol of Ti h), $M_n = 3.3 \times 10^4$, $M_w/M_n = 1.6$) when the polymerization was performed under the same conditions as in run 18, except that ethylene pressure was 1 atm (**1**, 10.0 μmol; Al/Ti = 500, time, 60 min).

(21) Results by brief molecular mechanics calculation [equilibrium geometry at ground state with semi-empirical PM3, geometry optimization, RHF/PM3D Spartan Pro ‘02 for Windows (Wavefunction Inc.)] indicate that differences between (indenyl)Ti(ethylene)(R)(OAr)$^+$ (**1a**, R = pentyl) and (indenyl)Ti(NBE)(R)(OAr)$^+$ (**1b**) were 7.69 and 9.16 kcal/mol, whereas the differences between Cp*Ti(ethylene)(R)-(OAr)$^+$ and Cp*Ti(NBE)(R)(OAr)$^+$ were 13.18 and 14.67 kcal/mol. In addition, the coordination mode of ethylene at the optimized structure by **1a** was perpendicular to both the indenyl ring and the alkyl chain that should require another barrier for insertion, whereas the coordination mode of norbornene by **1b** was parallel to both the indenyl ring and the alkyl chain. We assume that these may be the origin of the observed notable difference between **1** and **2**.

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