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Efficient Incorporation of 2-Methyl-1-pentene in Copolymerization of Ethylene with 2-Methyl-1-pentene Catalyzed by Nonbridged Half-Titanocenes

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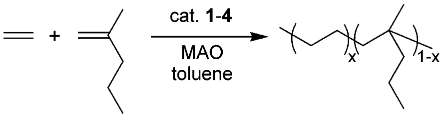
Introduction. The design of efficient transition-metal catalysts for precise olefin polymerization has been one of the most attractive subjects in the field of organometallic chemistry, catalysis, and polymer chemistry, especially because the evolution of new polyolefins with specified functions that have never been prepared by the conventional catalyst can be expected.[1] Although it had been described that 1,1-disubstituted α-olefins neither homo- nor copolymerize with other monoolefins in transition-metal-catalyzed olefin coordination and insertion polymerization,[2] only a few examples were reported for copolymerization of ethylene with isobutene (IB) using linked (amide)(cyclopentedienyl)titanium complex catalysts called constrained geometry catalysts,[3,4] whereas the IB content was low (<2.8 mol %) in the copolymerization by [Et(indenyl)$_2$]ZrCl$_2$−methylaluminoxane (MAO) catalyst under large IB stoichiometric excess conditions (IB:ethylene = 4000:1).[5] Cyclopolymerization of 2-methyl-1,5-hexadiene has also been known as a related example.[6] However, examples for synthesis of high-molecular-weight (co)polymers with unimodal molecular weight distributions, in particular, examples for copolymerization of ethylene with 1,1-disubstituted α-olefin except IB, have never been reported so far. In this paper, we wish to introduce our unique results for copolymerization of ethylene with so-called traditionally unreactive 2-methyl-1-pentene (2M1P) catalyzed by our original nonbridged half-titanocenes containing aryloxide ligands[7] (Scheme 1) under the moderate 2M1P/ethylene feed ratios in the presence of methylaluminoxane (MAO).[8]

Results and Discussion. Two complexes, Cp′TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) [Cp′ = Cp* (**1**), ^{t}BuC$_5$H$_4$ (**2**)] have been chosen as the catalyst precursor because these complexes showed the better comonomer incorporation (lower r_E values) than ordinary metallocenes and linked half-titanocenes in ethylene/1-hexene copolymerization.[7,9] This is also because that both monomer reactivities and microstructures were tuned by modifying the Cp′ in copolymerization of ethylene with α-olefin,[7] styrene,[10] and norbornene.[11] Half-titanocenes containing ketimide ligand, Cp′TiCl$_2$(N=C^{t}Bu$_2$) [Cp′ = Cp* (**3**), Cp (**4**)], have also been chosen for comparison[12,13] because the **4**−MAO catalyst exhibited remarkable catalytic activity for both 1-hexene polymerization and ethylene/1-hexene copolymerization.[13] The copolymerization results under the optimized conditions are summarized in Table 1.[14,15]

Scheme 1



cat. Cp'TiCl$_2$(X)
X = O-2,6-^{i}Pr$_2$C$_6$H$_3$; Cp' = Cp* (**1**), ^{t}BuC$_5$H$_4$ (**2**),
X = N=C^{t}Bu$_2$; Cp' = Cp* (**3**), Cp (**4**).

It was revealed that the copolymerization by the **1**−MAO catalyst took place, and the observed activity calculated on the basis of the polymer yield was higher than ethylene polymerization under low 2M1P concentration conditions (runs 1 and 2). The activity by **1** decreased upon increasing the 2M1P concentration and/or upon decreasing ethylene pressure (runs 3−7). The resultant polymers were poly(ethylene-*co*-2M1P)s confirmed by ^{13}C NMR spectra (Figure 1) and DSC thermograms (T_m values),[14] and the copolymer possessed high molecular weight with unimodal molecular weight distributions (M_n = (3.3−13) × 10^4, M_w/M_n = 1.7−1.9) as well as with uniform 2M1P distributions. These results thus strongly suggest that the copolymerization took place with single catalytically active species. The both M_n and meting temperature (T_m) values decreased upon increasing the 2M1P contents in the copolymer, and the contents were lower than 1-hexene contents under similar conditions.[14] The linear relationship between T_m values and the 2M1P contents was observed, and the 2M1P contents increased linearly upon increasing the 2M1P/ethylene initial feed molar ratios under these conditions.[16]

In contrast, the 2M1P contents for the copolymer prepared by **2** were lower than those by **1** under the same conditions, although **2** incorporates 1-hexene more efficiently than **1** under the same conditions in ethylene/1-hexene copolymerization.[7] This may be due to the steric hindrance of the *tert*-butyl group on Cp′ against the Me group in inserted 2M1P. In addition, the 2M1P contents in the resultant polymer prepared by half-titanocenes containing the ketimide ligand (**3**, **4**) were negligible (0.27, 0.30 mol %) under the same conditions, strongly indicating that the nature of the anionic ancillary donor ligand also affects the 2M1P incorporation as proposed previously in ethylene/1-hexene copolymerization.[7b,13,17] The result by **4** should be an interesting contrast with those observed both in 1-hexene polymerization.[13]

Figure 1 shows the typical ^{13}C NMR spectra in poly(ethylene-*co*-2M1P) (run 7, in benzene-d_6/1,2,4-trichlorobenzene at 110 °C), and all resonances were identified by the dept analysis as well as by comparison with poly(ethylene-*co*-isobutene)s reported previously.[4] The resultant copolymer possessed the isolated 2M1P inserted unit among repeated ethylene insertions, and the alternating sequence (assigned as k ($\beta\beta$) and j ($\alpha\gamma$), Scheme 2) was also present with low extent.[14,18] No resonances ascribed to repeated 2M1P insertion were observed, and the fact may clearly explain that negligible or no catalytic activity was observed in an attempted homopolymerization of 2M1P by the **1**−MAO catalyst. These also indicate that the 2M1P incorporation was not so efficient as the 1-hexene incorporation.

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Table 1. Copolymerization of Ethylene with 2-Methyl-1-pentene by $Cp'TiCl_2(X)$ [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)]−MAO Catalysts[a]

run no.	cat. (μmol)	MAO/mmol (Al/Ti × 10^{-3})[b]	ethylene/atm	2M1P conc[c]	yield/mg	activity[d]	2M1P[e]/mol %	M_n[f] × 10^{-4}	M_w/M_n[f]
1	**1** (0.5)	3.0 (6.0)	6		530	63 600		49	2.1
2	**1** (0.5)	3.0 (6.0)	6	1.35	582	69 800		13	1.7
3	**1** (0.5)	4.5 (9.0)	6	1.35	672	80 600	3.2	13	1.7
4	**1** (0.5)	4.5 (9.0)	6	1.35	705	84 600	3.3	12	2.1
5	**1** (0.5)	4.5 (9.0)	6	2.70	480	57 600	5.7	7.2	1.8
6	**1** (0.5)	4.5 (9.0)	4	1.35	353	42 400	5.0	6.5	2.0
7	**1** (0.5)	4.5 (9.0)	4	2.70	223	26 800	9.4	4.9	1.6
8	**2** (2.0)	4.0 (2.0)	6	1.35	270	8 100	2.3	5.5	1.9
9	**2** (2.0)	4.0 (2.0)	6	2.70	226	6 800	3.2	4.3	2.0
10	**2** (2.0)	4.0 (2.0)	4	1.35	156	4 700	3.2	3.1	2.1
11	**2** (2.0)	4.0 (2.0)	4	2.70	108	3 200	5.1	1.8	2.3
12	**4** (0.2)	3.0 (15.0)	6		638	19 100		53	2.1
13	**4** (0.2)	3.0 (15.0)	6	2.70	232	69 600	0.27	34	1.8
14	**3** (0.2)	3.0 (15.0)	6	2.70	259	77 700	0.30	63	1.9

[a] Conditions: 2-methyl-1-pentene (2M1P) + toluene total 30 mL, 2M1P 5.0 or 10.0 mL, d-MAO (prepared by removing toluene and $AlMe_3$ from ordinary PMAO), 25 °C, 10 min. [b] Molar ratio based on Al/Ti. [c] 2M1P concentrated charged (mol/L). [d] Activity in kg of polymer/(mol of Ti h). [e] 2M1P in copolymer (mol %) estimated by ^{13}C NMR. [f] GPC data in *o*-dichlorobenzene vs polystyrene standards.

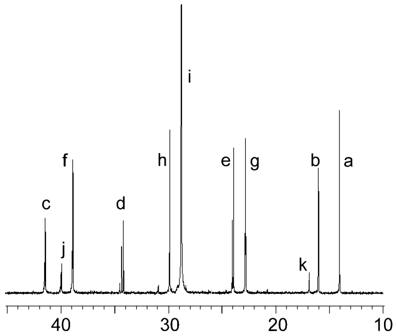
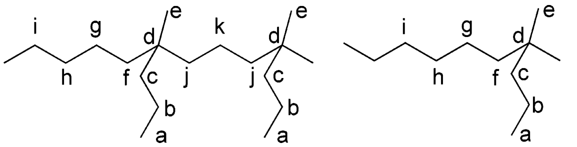


Figure 1. ^{13}C NMR spectrum for poly(ethylene-*co*-2-methyl-1-pentene) (in benzene-d_6/1,2,4-trichlorobenzene at 110 °C, sample run 7).

Scheme 2



We have shown that 1,1-disubstituted α-olefin, 2M1P, has been efficiently copolymerized with ethylene by using our original complex catalyst of nonbridged half-titanocenes containing aryloxo ligand (even under moderate 2M1P/ethylene feed molar ratios),[8] affording high-molecular-weight copolymer with uniform composition. It was also revealed that both the cyclopentadienyl fragment and anionic donor ligand directly affect the 2M1P incorporation. Since this copolymerization has not been achieved by ordinary transition-metal complexes such as metallocenes, linked half-titanocenes, we believe, this should be one of the most unique characteristics of using this type of complex as the catalyst precursor for precise olefin polymerization. The copolymerization with other 1,1-disubstituted olefins as well as 1,2-disubstituted olefins and property analysis for resultant new polyolefins are now under way.

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Supporting Information Available: General experimental details, additional polymerization results, ^{13}C NMR (dept) spectra for poly(ethylene-*co*-2M1P)s, and typical DSC thermograms for the copolymer; plots of T_m vs 2M1P contents and plots of 2M1P (1-hexene) contents vs initial 2M1P (1-hexene)/ethylene feed ratios. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) The initial feed molar ratios of 2M1P/ethylene in Table 1 were 1.86−5.57, and these values were lower than those in previous report for IB/ethylene feed ratios using metallocene (4000)[5] or binuclear linked half-titanocenes−borate catalysts (ca. 9.8).[4] For detailed results, see the Supporting Information.

(9) The r_E values in ethylene−1-hexene copolymerization (at 40 °C) by the **1**− and **2**−MAO catalysts are 2.70 and 2.46, respectively, and these values are lower than that by the [$Me_2Si(C_5Me_4)(N^tBu)$]$TiCl_2$−MAO catalyst (r_E = 3.42).[7b]

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(13) Effect of Cp′ fragment in ethylene/1-hexene copolymerization by various $Cp'TiCl_2(N{=}C^tBu_2)$–MAO catalysts. Nomura, K.; Fujita, K.; Fujiki, M. *J. Mol. Catal. A* **2004**, *220*, 133–144. The r_E values in the copolymerization by **3** and **4** (25 °C) were 5.1 and 4.5, respectively.

(14) For more details, see the Supporting Information.

(15) To control 2M1P conversion less than 10%, we performed the polymerization with low catalyst concentration, and we terminated the reaction at the initial stage (10 min). The polymerization for longer reaction hours increased polymer yields.

(16) Melting temperature (T_m) for resultant copolymer decreased upon increasing the 2M1P contents. T_m = 102.9, 93.8, 89.2, and 78.2 °C with 3.3, 5.0, 5.7, and with 9.4 mol % of 2M1P content, respectively (runs 4–7, Table 1, copolymer prepared by the **1**–MAO catalyst system).

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(18) Since the M_w values were not dependent upon the Al/Ti molar ratios employed, the dominant chain transfer pathway in the present polymerization may be β-hydrogen or β-methyl elimination. However, the attempted chain-end analysis for resultant copolymer (sample run 7 in *o*-dichlorobenzene-d_4 at 110 °C) revealed that no olefinic resonances were observed. The studies are now under way.

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