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Syndiospecific Styrene Polymerization and Efficient Ethylene/Styrene Copolymerization Catalyzed by (Cyclopentadienyl)(aryloxy)titanium(IV) Complexes−MAO System

Kotohiro Nomura,* Takashi Komatsu, and Yukio Imanishi

Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST), 8916-5 Takayama, Ikoma, Nara 630-0101, Japan

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Introduction. We have recently reported that $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**5a**) showed an exceptionally high catalytic activity not only for ethylene polymerization but also for ethylene/α-olefin copolymerization in the presence of MAO (methylaluminoxane) or $Al^iBu_3/Ph_3CB(C_6F_5)_4$.[1−3] In addition, effect of substituents on both cyclopentadienyl and aryloxy groups plays an essential role not only for the catalytic activity[1,2] but also for monomer reactivities and monomer sequence distributions in ethylene/α-olefin copolymerization.[3]

Since the ordinary half-sandwich titaninum complexes such as Cp^*TiCl_3, $Cp^*Ti(OMe)_3$, and $(Ind)TiCl_3$ are known to be an efficient catalyst precursor for syndiospecific styrene polymerization,[4,5] also since the copolymerization of ethylene/styrene attracted considerable attention in this research field,[6,7] we concentrate on exploring the possibility to expand the utility of our original catalyst to these polymerizations. In this paper, we wish to introduce our explored results for styrene polymerization with $Cp'TiCl_2(OAr)$ [Cp' = Cp (**1a**), ${}^tBuC_5H_4$ (**2a**), $1,3\text{-}Me_2C_5H_3$ (**3a**), $1,3\text{-}{}^tBu_2C_5H_3$ (**4a**), and C_5Me_5 (**5a**), OAr = $O\text{-}2,6\text{-}{}^iPr_2C_6H_3$; Cp' = C_5Me_5, and OAr = $O\text{-}2,6\text{-}{}^iPr_2C_6H_3$ (**3a**), $O\text{-}2,6\text{-}Me_2C_6H_3$ (**3b**), $3,5\text{-}Me_2C_6H_3$ (**3c**)] complexes−MAO catalyst systems (see Chart 1). We also wish to report our results for copolymerization of ethylene with styrene by **3a**−MAO catalyst.

Results and Discussion. Since **5a** has been an efficient catalyst precursor for alkene polymerization,[1,2] we examined a possibility as a catalyst for styrene polymerization in the presence of MAO (Table 1, run 1).[8] The resultant polymer consisted of two compositions: MEK (2-butanone) insoluble fraction which has a relatively high molecular weight ($M_w = 39.7 \times 10^4$, $M_w/M_n = 2.47$) and MEK soluble fraction which has a low molecular weight ($M_w = 3.5 \times 10^4$).[9] The polymer yield of the MEK soluble fraction (112 mg) was lower than that only by MAO without a titanium compound (150−170 mg, runs 6 and 7), and the M_w value was also the same as those in the comparative experiments, strongly suggesting that the polymer prepared by **5a** should be ascribed to that of MEK insoluble fraction. However, the catalytic activity calculated from the polymer yield of MEK insoluble fraction was much lower than those by ethylene and 1-hexene polymerization.

To improve the activity, we explored the effect of substituents on cyclopentadienyl group, and the results are summarized in Table 1. It was revealed that the activity with a series of $Cp'TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ increased in the order **3a** (4270 kg of polymer/(mol of Ti h)) > **2a** (3900) > **1a** (470) > **4a** (260) > **5a** (92), and this is quite different from those observed on ethylene and 1-hexene polymerizations.[10] The probable reason for higher activity by **3a** or **2a** than **1a** should be due to the fact that the electron-donating substituent on Cp' stabilizes the active species and thus leads to the higher activity,[1,4f,5] and the low activity by **4a** should be due to the steric bulk of two *tert*-butyl group as observed in the same reaction with a series of $Cp'Ti(OMe)_3$−MAO catalyst.[4k,5c] The low activity by **5a**, which is completely different from the result with $Cp'Ti(OMe)_3$, might also be due to the steric bulk of both Cp* and aryloxy group for this type of polymerization, especially for 2,1-type insertion, or low efficiency for generating catalytically active species. Another probable reason for this difference among the series of $Cp'TiCl_2(OAr)$ would be due to the efficiency for generating active species [Ti(IV) for ethylene vs Ti(III) for styrene], although the *exact* reason for this difference is not clear at this moment. The resultant polymer by **3a** has a relatively high molecular weight ($M_w = 28.3 \times 10^4$) with narrow molecular weight distribution ($M_w/M_n = 1.83$)[11] and possesses exclusive syndiotacticity from the ^{13}C NMR spectrum.

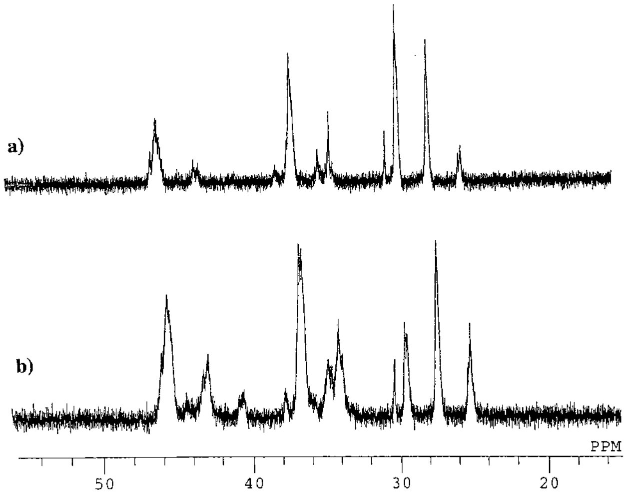

Figure 1. ^{13}C NMR spectra (in $CDCl_3$ at 60 °C) of poly(ethylene-*co*-styrene)s (methylene and methine region, THF soluble fraction): (a) run 8 and (b) run 10.

In addition, the catalytic activity is also dependent upon the aryloxy group, and the activity with a series of $(1,3\text{-}Me_2C_5H_3)TiCl_2(OAr)$ increased in the order **3a** (5150 kg of sPS/(mol of Ti h)) > **3b** (3900) > **3c** (3420).[12] The observed M_w value for the resultant polystyrene did not change significantly among these polymerizations ($M_w = (41.8−44.8) \times 10^4$), and the reduction in the steric bulk reflected M_w/M_n values, increasing the extent of low molecular weight shoulders (M_w/M_n = 2.31, 2.79, and 3.07 by **3a**, **3b**, and **3c**, respectively).[13]

It was also revealed that **3a** exhibited remarkable catalytic activity for copolymerization of ethylene with styrene in the presence of MAO.[14] The resultant polymer consisted of poly(ethylene-*co*-styrene) in high extent (94.8 to >99 wt %) as the THF soluble fraction and a small amount of both polyethylene and polystyrene

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* Corresponding author: Tel +81-743-72-6041; fax +81-743-72-6049; e-mail nomurak@ms.aist-nara.ac.jp.

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Chart 1

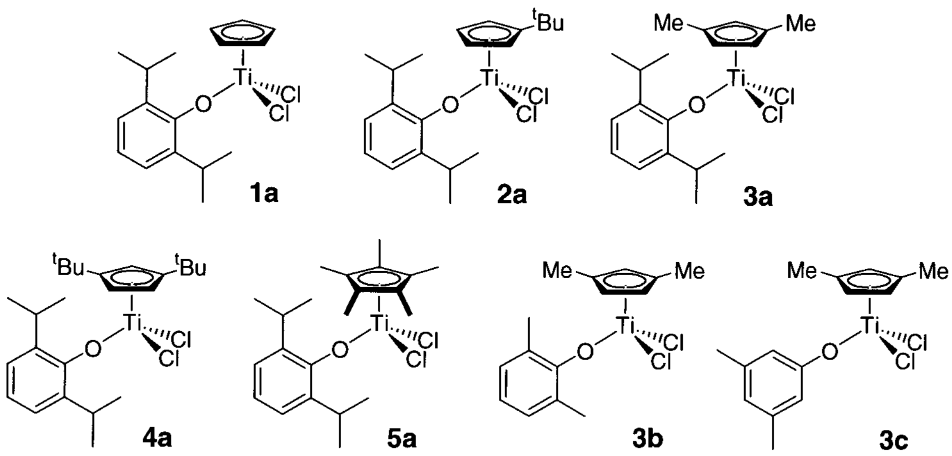

Table 1. Polymerization of Styrene by Cp′$TiCl_2$(O-2,6-$^iPr_2C_6H_3$)−Cocatalyst System[a]

run no.	catalyst	Al/Ti[b]	time	polymer yield[c]/mg	activity[d]	TON[e]	M_w[f]/$\times 10^{-4}$	M_w/M_n [f]
1	$Cp^*TiCl_2(OAr)$ (**5a**)	2000	30	38[g]	92	440	39.7	2.47
2	(1,3-$^tBu_2C_5H_3$)$TiCl_2(OAr)$ (**4a**)	2000	30	108	260	1250	7.7	2.07
3	(1,3-$Me_2C_5H_3$)$TiCl_2(OAr)$ (**3a**)	2000	10	590	4270	6840	28.3	1.83
4	($^tBuC_5H_4$)$TiCl_2(OAr)$ (**2a**)	2000	10	540	3900	6260	17.1	1.78
5	$CpTiCl_2(OAr)$ (**1a**)	2000	30	195	470	2260	20.7	1.81
6	MAO[h]		10	(150)[i]			3.4	2.09
7	MAO[h]		60	(170)[i]			3.6	2.00

[a] Reaction conditions: styrene, 4.58 mL; catalyst, 0.83 μmol (2 μmol/mL of toluene); MAO white solid (96 mg), 25 °C. [b] Molar ratio of Al/Ti. [c] Yield of MEK insoluble fraction. [d] Polymerization activity (kg of sPS/(mol of Ti h)). [e] TON (turnover number) = molar amount of sPS/mol of Ti). [f] GPC data in *o*-dichlorobenzene vs polystyrene standard. [g] Polymer yield of MEK soluble fraction was 112 mg. [h] Polymerization was employed with MAO (96 mg) in the absence of titanium complex. [i] Polymer yield of MEK soluble fraction.

Table 2. Copolymerization of Ethylene with Styrene Catalyzed by the 3a−MAO System[a]

					THF soluble fraction[d]					THF insoluble fraction[d]		
run no.	ethylene/ atm	styrene/ mL	polymer[b] yield/mg	activity[c]	content[e]/ wt %	M_w [f]/ $\times 10^{-4}$	M_w/M_n [f]	styrene[g] content	T_g [h]/ °C	content[e]/ wt %	M_w [f]/ $\times 10^{-4}$	M_w/M_n [f]
8	4	5	830	4980	94.8	22.7	1.76	33.1	18.0	5.2	bimodal[d]	
9	8	5	1041	6250	97.1	29.1	1.87	26.1	−2.1	2.9	bimodal[d]	
10	3	10	741	4450	>99	16.6	1.96	56.6	38.4	trace		

[a] Reaction conditions: catalyst, 1.0 μmol (2 μmol/mL of toluene), total volume of toluene and styrene, 30 mL; MAO white solid (Al/Ti = 2000, molar ratio), 25 °C, 10 min, 100 mL scale autoclave. [b] Polymer yield of acetone insoluble fraction. [c] Polymerization activity (kg of polymer/(mol of Ti h)). [d] Experimental procedure, see the Supporting Information. [e] Percentage of content in acetone insoluble fraction. [f] GPC data in *o*-dichlorobenzene vs polystyrene standard. [g] Styrene content (mol %) in copolymer by ^1H NMR ($C_2D_2Cl_4$). [h] Determined by DSC.

(Table 2) as the THF insoluble fraction. This should be an especially interesting example of efficient copolymerization of ethylene with styrene by the half-sandwich titanium complex catalyst. The resultant copolymer has a relatively high molecular weight ($M_w = (16.6-29.1) \times 10^4$) with a narrow, unimodal molecular weight distribution ($M_w/M_n = 1.76-1.96$). The glass transition temperature measured by differential scanning calorimetry (DSC) increased upon the increase in the styrene content.

Figure 1 shows ^{13}C NMR spectra (methylene and methine region) of the copolymers (THF soluble fraction). In addition to the resonances at $\delta = 34.3$ and 35.1 ppm, which are attributed to $S_{\alpha\beta}$ (tail-to-tail coupling of styrene unit or head-to-head bridged by an intervening ethylene unit), the resonances at $\delta = 40.7$ ($T_{\beta\beta}$, three styrene units connected to head-to-tail coupling) and 43.1−5 ppm ($S_{\alpha\alpha}$ and $T_{\beta\delta}$, two styrene units connected to head-to-tail coupling) were observed.[15] This is an especially interesting contrast with that prepared by the [$Me_2Si(C_5Me_4)(N^tBu)$]$TiCl_2$-based catalyst.[7] We have shown that (cyclopentadienyl)(aryloxy)titanium(IV) complexes are effective catalyst precursors for both styrene polymerization and ethylene/styrene copolymerization. More detailed studies are now under way.

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Supporting Information Available: General experimental procedures containing synthesis and characterization of **3b**−**c**, polymerization, and analysis procedures; ^1H and ^{13}C NMR spectra of polystyrene prepared by **3a**−MAO catalyst and GPC traces for polystyrene prepared by **3a**−**c**−MAO catalyst; ^1H and ^{13}C NMR spectra of poly(ethylene-*co*-styrene)s prepared by **3a**−MAO catalyst and the DSC charts. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Effect of substituents on cyclopentadienyl group in ethylene polymerization[1a] ($Al^iBu_3/Ph_3CB(C_6F_5)_4$ cocatalyst): **5a** (2220 kg of PE/(mol of Ti h)) > **4a** (653) > **2a** (258), **3a** (215) > **1a** (77). The effect in 1-hexene polymerization (MAO cocatalyst):[2a] **5a** (970 kg of polymer/(mol of Ti h)) > **3a** (184) > **2a** (89) > **1a** (63) > **4a** (26).

(11) Molecular weight and molecular weight distribution of the resultant copolymers were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with polystyrene gel column (TSK gel GMH_{HR}-H HT × 2) at 140 °C using *o*-dichlorobenzene containing 0.05 w/v % 2,6-di-*tert*-butyl-*p*-cresol as solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

(12) Reaction conditions: styrene, 5.0 mL; catalyst, 0.5 μmol (2.0 μmol/mL in toluene); MAO, 2.0 mmol (Al/Ti = 2000), 25 °C, 10 min. For more details, see the Supporting Information.

(13) For a related example, $Cp^*TiCl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**5b**) exhibited a higher activity (139 kg of sPS/(mol of Ti h)) than **5a** under the same conditions in run 1. The resultant polymer has high molecular weight ($M_w = 131 \times 10^4$) with broad molecular weight distributions ($M_w/M_n = 4.81$). This result also suggests that the electronic and steric factors of both aryloxy and cyclopentadienyl groups play a role in this catalysis.

(14) To control the monomer conversion less than 10%, we terminated the reaction at the initial stage. The resultant polymer was separated by boiling acetone and then by boiling THF. For more details, see the Supporting Information.

(15) It seemed very difficult to calculate *r*-parameters from the triad sequence distribution only from these NMR spectra, since the signals for $S_{\alpha\delta}$ and $S_{\alpha\gamma}$ at $\delta = 36.8$ and 37.0 ppm as well as those for $S_{\gamma\gamma}$, $S_{\gamma\delta}$, and $S_{\delta\delta}$ at $\delta = 29.7$ ppm are difficult to separate.[7b]

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