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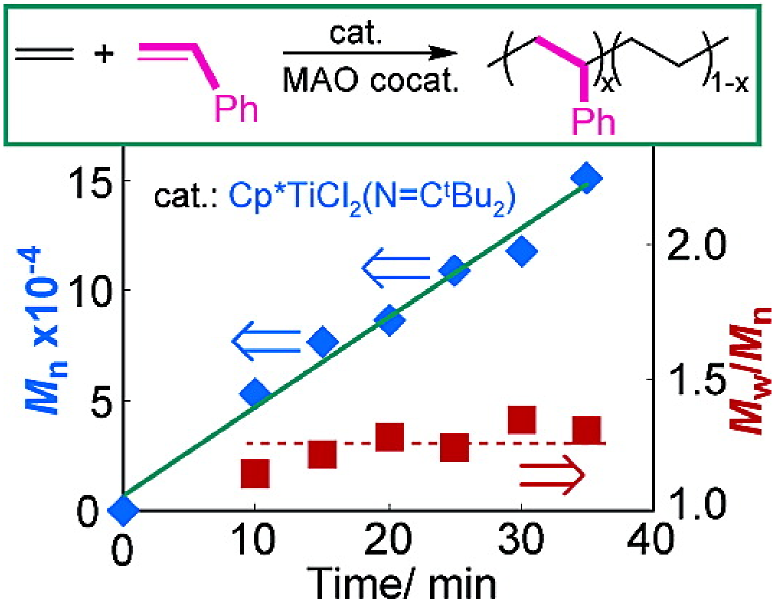

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Living Copolymerization of Ethylene with Styrene Catalyzed by (Cyclopentadienyl)(ketimide)titanium(IV) Complex−MAO Catalyst System

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Precise control over macromolecular structure and the resulting material properties is a central goal in synthetic polymer chemistry, and copolymerization is an important process that usually allows the alteration of the (physical, mechanical, and electronic) properties of a material through adjustment of the ratio of individual components. New synthetic methods for precise placement of the chemical functionality thus attract considerable attention, and transition metal catalyzed living polymerization[1] is one of the best methods to prepare polymers with controlled monomer repeating units.[1−3] Although many efforts for the living polymerization of ethylene, α-olefin, and others[1−6] are known, examples for living copolymerization with the exception of block copolymerization are limited.[2b,c,3f,h,5,6] Ethylene/styrene copolymers,[7−9]which cannot be prepared by free radical or ordinary Zigler−Natta processes,[10] attract great attention due to their promising properties;[11] however, no examples are reported for the successful living copolymerization. In this paper, we present the first example of the efficient living copolymerization by a half-titanocene containing a ketimide ligand,[12,13] $Cp^*TiCl_2(N{=}^tBu_2)$ (**1**, $Cp^* = C_5Me_5$)−MAO (methylaluminoxane) catalyst (Scheme 1).

Scheme 1

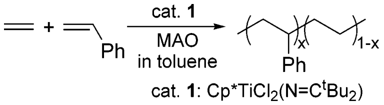

Table 1 summarizes the results for the copolymerization by **1** in toluene.[14,15] The reaction proceeded efficiently without decrease in the activity (runs 1−6), and the activity increased at higher ethylene pressure and temperature. Poly(ethylene-*co*-styrene)s were obtained exclusively,[16] and the resultant polymers possessed low PDI values ($M_w/M_n = 1.14{-}1.36$), and the styrene distributions were uniform as confirmed by GPC/FT-IR spectra.[14,17] Time-course plots of the number average molecular weights (M_n) and the M_w/M_n values (4 atm of ethylene, 25 °C) are shown in Figure 1. The M_n values increased with longer reaction times with consistently low PDI values. The same first-order relationship between the M_n values and the yields was observed under these conditions. The polymerizations at higher ethylene pressure (6 atm) also afforded copolymers with low PDI values, and the M_n values increased upon increasing the polymer yields. Note that the two-step polymerization under ethylene pressure of 4 and then 6 atm (run 13) afforded the copolymer with a low PDI value, and the polymer yield, styrene content, and the M_n value were identical to the estimated value, based on the independent runs (runs 1 and 8).[14,18] These results indicate that the copolymerization proceeded in a living manner. Relatively low PDI values were also observed for the copolymers prepared at 40 and 55 °C, suggesting the possibility of a living polymerization.

In contrast, the polymerization by $Cp^*TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**2**) under the same conditions (as in run 8) afforded the copolymer with a high styrene content (31.9 mol %, run 18). The polymer possessed a unimodal, rather large PDI value (1.62), suggesting that some extents of chain transfer reaction occurred. Negligible catalytic activities were observed if $CpTiCl_2(N{=}C^tBu_2)$ ($Cp = C_5H_5$), which showed both high activity and efficient 1-hexene incorporation in ethylene/1-hexene copolymerization,[13b] was used in place of **1** under the same conditions.[19] These results clearly indicate that the nature of both cyclopentadienyl and the anionic donor ligands *directly affects* the polymerization behavior.

Table 1. Ethylene/Styrene Copolymerization Catalyzed by **1**[a]

run	ethylene (atm)	temp (°C)	time (min)	polymer yield[b] (mg)	activity[c]	styrene content[d]	M_n[e] (×10⁻⁴)	M_w/M_n[e]
1	4	25	10	68	200	11.2	5.30	1.14
2	4	25	15	100	200		7.61	1.21
3	4	25	20	108	160	11.1	8.57	1.28
4	4	25	25	154	180		10.9	1.24
5	4	25	30	173	170	10.9	11.7	1.34
6	4	25	35	236	200		15.1	1.30
7	6	25	5	53	320		5.28	1.19
8	6	25	10	132	400	7.4	9.50	1.18
9	6	25	20	270	410	7.2	17.3	1.36
10	6	40	10	262	790	9.3	14.4	1.28
11	6	55	10	373	1110	10.4	19.7	1.31
12	6	70	10	432	1290	12.2	16.3	1.57
13	4+6[f]	25	10+10[f]	199	300	8.1	12.3	1.31
14		25	10	21	63	100	7.84	2.34
15		40	10	27	81	100	9.22	2.27
16[g]	6	25	2	51	30600		58.3	74.4
17[g,h]	4	40	10	552	16600		47.3	2.20
18[i]	6	25	10	168	500	31.9	5.73	1.62

[a] Conditions: 2.0 μmol complex **1** (run 16, 0.05 μmol), 3.0 mmol MAO, 10 mL of styrene, 30 mL of styrene + toluene total. [b] Polymer yield based on acetone insoluble, THF soluble fraction.[14,16] [c] Activity in kg·polymer/mol·Ti·h. [d] Styrene content (mol %) estimated by ^1H NMR spectra. [e] GPC data in *o*-dichlorobenzene versus polystyrene standards. [f] First, 4 atm of ethylene (10 min) and then 6 atm (10 min). [g] Ethylene homopolymerization results. [h] Complex **1** (0.20 μmol), 40 mL of toluene.[13b] [i] $Cp^*TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**2**) in place of **1**.

Figure 2 shows the ^{13}C NMR spectra for the copolymers.[7d] A trace amount of resonances due to so-called pseudo random [$S_{\alpha\beta}$, SS by tail-to-tail and/or SES (S = styrene, E = ethylene)] sequences

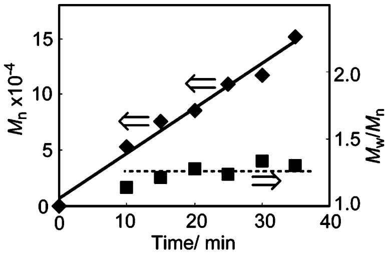

Figure 1. Time-course plots of M_n and M_w/M_n for copolymers prepared by ethylene/styrene copolymerization catalyzed by the $[Cp^*TiCl_2(N{=}C^t\text{-}Bu_2)]$ (**1**)−MAO system (in toluene at 25 °C, 4 atm of ethylene).

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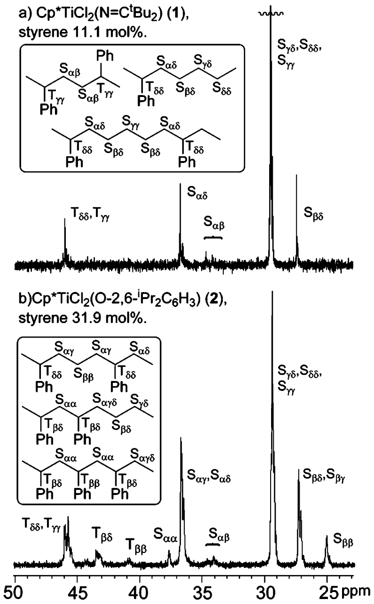

Figure 2. ^{13}C NMR spectra (in 1,1,2,2-tetrachloroethane-d_2 at 110 °C) of poly(ethylene-*co*-styrene)s (methylene and methine region): (a) 11.1 mol % of styrene (by **1**, run 3); (b) 31.9 mol % of styrene (by **2**, run 18).

were observed in both spectra. No resonances ascribed to a (head-to-tail) styrene repeating unit ($T_{\beta\delta}$, $T_{\beta\beta}$, $S_{\alpha\alpha}$) were seen in the copolymer prepared by **1**, whereas the peaks due to two and three styrene repeating units were seen for the polymer prepared by **2**.[7d]

1 exhibited a low activity for styrene polymerization even at 40 °C, affording a syndiotactic polymer with a large PDI value.[13a] In contrast, remarkable activity was observed for the ethylene polymerization (run 16), and the resultant polymer possessed a high molecular weight with a large PDI value, and the distribution became unimodal if the reaction was performed at 40 °C (M_w/M_n = 2.20),[13b] probably due to improved solubility. Since styrene repeating units were not seen in the ^{13}C NMR spectra for the copolymers by **1**,[14] it is thus assumed that some degree of styrene insertion may inhibit the chain transfer in this catalysis.

We have shown that a living copolymerization can be achieved for the first time by Cp*TiCl$_2$(N═C^{t}Bu$_2$) (**1**)−MAO catalyst. The nature of both the cyclopentadienyl and the anionic donor ligands affects the styrene incorporation and the polymerization behavior. Studies on the ligand effect toward the monomer reactivity, the polymerization mechanism, and their synthetic applications to various unique (block, graft) copolymers are now underway.

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Supporting Information Available: Experimental procedures, additional polymerization results, ^{13}C NMR spectra, GPC/FT-IR charts for copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Detailed results are shown in the Supporting Information.

(15) To obtain the copolymer with uniform compositions, the polymerization should be terminated at the initial stage. MAO white solid was prepared by removing toluene and AlMe$_3$ from the commercially available MAO (PMAO-S, Tosoh Finechem. Co.), and a certain excess amount of MAO was required for exhibiting high catalytic activity (results are shown in the Supporting Information).

(16) The resultant polymer consisted of poly(ethylene-*co*-styrene) and (acetone soluble) atactic polystyrene produced by MAO. The copolymer was isolated as the acetone insoluble and THF soluble fraction,[14] and amounts of THF insoluble fraction (polyethylene, syndiotactic polystyrene) were negligible.

(17) K.N. would like to express his thanks to Idemitsu Kosan Co. Ltd., for GPC/FT-IR measurement. The styrene contents in the copolymers by GPC/FT-IR are somewhat different from those estimated by ^{1}H NMR spectra due to the standard samples in the calibration curve for the analysis.

(18) Estimated yield = 200 mg (obtained 199 mg), the M_n value = 14.80 × 10^4 (obtained 12.3 × 10^4), the styrene content = 8.4 mol % (obtained 8.1 mol %).

(19) The copolymerizations by CpTiCl$_2$(N═C^{t}Bu$_2$)−MAO catalyst were attempted under the same conditions as run 8 (6 atm of ethylene, 10 mL of styrene). However, negligible amount of polymers were collected as the acetone insoluble fractions even if the reactions were performed with higher catalyst concentration for 30 min (<5 mg, 2.0 or 10.0 μmol of **3**).

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