Macromolecules **2002,** *35,* 5388−5395

Ethylene/Styrene Copolymerization by Various (Cyclopentadienyl)(aryloxy)titanium(IV) Complexes−MAO Catalyst Systems

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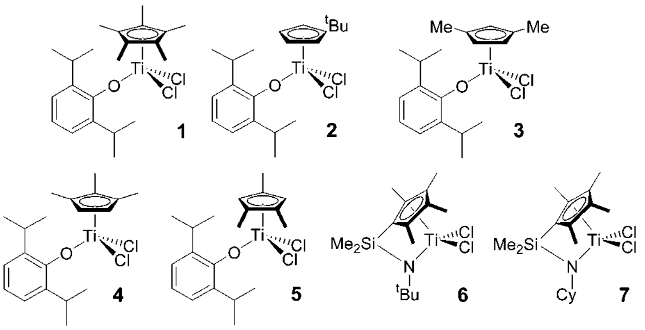
Received January 16, 2002; Revised Manuscript Received May 6, 2002

ABSTRACT: Copolymerizations of ethylene with styrene by various (cyclopentadienyl)(aryloxy)titanium(IV) complexes of the type Cp′TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) [Cp′ = ^{t}BuC$_5$H$_4$ (**2**), 1,3-Me$_2$C$_5$H$_3$ (**3**), 1,2,3-Me$_3$C$_5$H$_3$ (**4**), 1,2,4-Me$_3$C$_5$H$_3$ (**5**)] have been explored in the presence of methylaluminoxane (MAO) as the cocatalyst. Effect of cyclopentadienyl fragment was explored and the catalytic activity increased in the order **3**, **4** > **2** > **5**, suggesting that effects of both electronic and steric bulk play an essential role for the copolymerization. Resultant polymers by these catalyst systems were poly(ethylene-*co*-styrene)s exclusively in all cases, and the use of **4** was quite effective for preparing relatively high molecular weight polymer with unimodal molecular weight distribution as well as with efficient styrene incorporation. The styrene incorporation efficiency did not strongly depend upon the cyclopentadienyl fragment used, and this is somewhat different from those obtained by the linked cyclopentadienyl−amide titanium catalyst [Me$_2$Si(C$_5$Me$_4$)(NR)]TiCl$_2$ [R = *tert*-Bu (**6**), cyclohexyl (**7**)]. The resultant copolymers possessed unimodal comonomer distributions (single composition) confirmed by both cross-fractionation chromatography (CFC) and GPC/FT-IR. The microstructure for the resultant copolymer by **2**−**5** was different from those prepared by a linked type catalyst (**6**) and was fairly dependent upon the cyclopentadienyl fragment used.

Introduction

Olefin polymerization by homogeneous transition metal complex catalysts attracts particular attention in the fields of organometallic chemistry and catalysis, as well as the field of polymer chemistry. Many reports have been reported concerning this topic, in particular those using group 4 transition metal complexes.[1] We have recently reported that Cp*TiCl$_2$(OAr) (**1**, OAr = O-2,6-^{i}Pr$_2$C$_6$H$_3$) showed an exceptionally high catalytic activity not only for ethylene polymerization but also for ethylene/α-olefin copolymerization in the presence of MAO (methylaluminoxane).[2−4] We have also shown that the effect of substituents on both cyclopentadienyl and aryloxy groups plays an essential role not only for the catalytic activity[2,3] but also for monomer reactivities as well as for monomer sequence distributions in ethylene/α-olefin copolymerization.[4] Since the ordinary half-sandwich titanium complexes such as Cp*TiCl$_3$, Cp*Ti(OMe)$_3$, and (indenyl)TiCl$_3$ are known to be efficient catalyst precursors for syndiospecific styrene polymerization[5,6] and also since the copolymerization of ethylene/styrene attracted considerable attention in this research field,[7,8] we examined the possibility of expanding the utility of our original catalyst to these polymerizations.[9]

Chart 1



We reported our preliminary results recently that Cp′TiCl$_2$(OAr) complexes [in particular, Cp′ = ^{t}BuC$_5$H$_4$ (**2**), 1,3-Me$_2$C$_5$H$_3$ (**3**), Chart 1] are effective catalyst precursors for both styrene polymerization and ethylene/styrene copolymerization in the presence of MAO.[10] In particular, **3** should be the most useful catalyst precursor for preparing poly(ethylene-*co*-styrene)s with relatively high styrene contents, and the microstructure for the resultant copolymer possessed was completely different from that prepared by [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (**6**).[10] However, we do not have a clear reason why the polystyrene structure in the copolymer by **1**−**3** was atactic, although styrene homopolymerization by **3** afforded *perfect* syndiotactic polystyrene efficiently. This should also be a very important question to consider for the catalytically active species for both styrene polymerization and ethylene/styrene copolymerization, in particular, the use of half-titanocene catalysts.[7,8,11] Moreover, precise control of monomer sequence as well as stereospecificity by ligand modification in ethylene/styrene copolymerization has been one of the most challenging subjects in this research field, because the electronic and/or steric nature of the ligand moiety should affect both the insertion mode (2,1- or 1,2-insertion) of styrene and the comonomer incorporation. In fact, as in the related example, we recently have shown that *substituent on amide ligand* in [Me$_2$Si(C$_5$Me$_4$)(NR)]TiCl$_2$ [R = ^{t}Bu (**6**), Cy (**7**)] *directly affects both the styrene incorporation and the monomer se-*

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10.1021/ma0200773 CCC: $22.00

Table 1. Copolymerization of Ethylene with Styrene by Cp′TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) [Cp′ = ^{t}Bu (2), 1,3-Me$_2$C$_5$H$_3$ (3), 1,2,3-Me$_3$C$_5$H$_2$ (4), 1,2,4-Me$_3$C$_5$H$_2$ (5)] and [Me$_2$Si(C$_5$Me$_4$)(NR)]TiCl$_2$ [R = ^{t}Bu (6), Cy (7)] Complexes−MAO Catalyst Systems[a]

							THF soluble fraction				
run no.	catal	ethylene/atm	styrene/mL	[S]/[E][b]	acetone soluble content[c]	activity[d]	content[e]/wt %	M_w[f]/$\times 10^{-4}$	M_w/M_n[f]	styrene/mol %[g]	THF insoluble content[e]/wt %
1	**2**	4	3	1.80	0.4	2040	99.4	9.7	1.6	34.0	0.2
2	**2**	4	5	3.00	0.4	2180	99.6	5.9	1.7	37.6	tr.
3	**2**	4	10	6.01	1.0	1840	98.7	3.5	2.2	51.2	0.3
4	**2**	6	3	1.20	0.3	4600	99.6	8.2	1.6	25.2	0.1
5	**2**	6	10	4.00	0.6	1740	99.3	2.4	1.6	50.0	0.1
6	**3**	4	3	1.80	tr.	3670	97.1	6.4	1.8	32.3	2.9
7	**3**	4	5	3.00	1.5	4280	97.8	6.0	2.1	38.5	0.7
8	**3**	4	10	6.01	1.1	4140	98.2	3.7	1.6	49.0	0.7
9	**3**	6	3	1.20	0.1	4140	94.2	9.4	1.6	25.8	5.7
10	**3**	6	5	1.99	0.9	5210	96.4	7.4	1.7	33.1	2.7
12	**4**	4	3	1.80	tr.	4100	99.1	17	1.6	26.0	0.8
13	**4**	4	3	1.80	tr.	4140	99.9	16	1.6	24.2	tr.
14	**4**	4	5	3.00	tr.	3070	98.3	11	1.7	38.8	1.6
15	**4**	4	5	3.00	0.3	2950	98.9	10	1.6	33.1	0.9
16	**4**	4	10	6.01	tr.	2720	97.8	6.6	1.6	51.2	2.1
17	**4**	2	15	18.0	9.5	1850	90.4	3.6	2.1	73.6	tr.
18	**5**	4	3	1.80	0.1	1810	99.8	7.9	1.5	31.7	0.1
19	**5**	4	5	3.00	2.2	1100	97.4	6.0	1.6	41.1	0.4
20	**5**	4	10	6.01	4.0	740	95.0	2.6	2.0	54.8	1.0
21[h]	**6**	4	5	3.00	0.3	5110	1.5	- - -	- - -	- - -	89.1[i]
22[h]	**6**	4	10	6.01	0.3	5630	99.6	18	1.8	32.7	tr.
23[h]	**7**	4	3	1.80	tr.	1370	99.8	4.8	1.7	40.9	tr.
24[h]	**7**	6	3	1.20	tr.	1140	99.4	4.2	1.5	37.0	0.5
25[h]	**7**	8	3	0.90	tr.	1030	99.7	7.5	1.5	36.0	0.2
26[h]	**7**	4	5	3.00	0.3	1640	99.6	5.0	1.9	44.6	tr.
27[h]	**7**	6	5	1.99	tr.	1430	99.7	3.0	2.3	42.0	0.2
28[h]	**7**	4	10	6.01	tr.	1980	99.8	4.5	1.8	45.7	tr.

[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, and 100 mL scale autoclave. [b] Initial molar ratio in the reaction solution (mmol/mL). [c] Polymer yield of acetone soluble fraction. [d] Polymerization activity (kg of polymer/mol of Ti·h), polymer yield in acetone insoluble fraction. [e] Percentage of content in acetone insoluble fraction. [f] GPC data in *o*-dichlorobenzene vs polystyrene standard. [g] Styrene content (mol %) in copolymer by ^{1}H NMR (C$_2$D$_2$Cl$_4$). [h] These results were cited from our previous report (ref 12). [i] Poly(ethylene-*co*-styrene) was obtained as THF insoluble fraction ($M_w = 2.52 \times 10^5$, $M_w/M_n = 2.0$, styrene 12.2 mol %).

quence in the ethylene/styrene copolymerization.[12] In this paper, we wish to introduce our detailed results for ethylene/styrene copolymerization with a series of Cp′TiCl$_2$(OAr) in the presence of MAO.[13]

Results and Discussion

1. Synthesis of Complexes and Copolymerization of Ethylene with Styrene by Various (Cyclopentadienyl)(aryloxy)titanium Complexes−MAO Catalyst Systems. Since **3** was found to be the better catalyst precursor than **1** for the ethylene/styrene copolymerization in the presence of MAO as the cocatalyst, two kinds of trimethylcyclopentadienyl analogues, (1,2,3-Me$_3$C$_5$H$_2$)TiCl$_2$(OAr) (**4**) and (1,2,4-Me$_3$C$_5$H$_2$)TiCl$_2$(OAr) (**5**) complexes were prepared in order to explore the effect of ligand in the ethylene/styrene copolymerization. These complexes could be prepared by the analogous procedure for **3** and were identified by ^{1}H NMR, ^{13}C NMR, and elemental analysis.

Copolymerization of ethylene with styrene was conducted in toluene by using a 100 mL scale autoclave in the presence of MAO (white solid), which was prepared by removing toluene and AlMe$_3$ from the commercially available MAO (PMAO-S, Tosoh Finechem Co.). Results for the copolymerization with a series of Cp′TiCl$_2$(OAr) (**2**−**5**) complexes are summarized in Table 1.[14] Linked cyclopentadienylamide titanium (IV) complexes of types **6** and **7** were also chosen as the reference.[15]

It turned out that the copolymerizations took place efficiently in all cases, affording poly(ethylene-*co*-styrene)s exclusively without by-producing polyethylene and/or polystyrene. As pointed out in our preliminary communication,[10] this should be *an especially interesting example of efficient copolymerization of ethylene with styrene by half-sandwich titanium complex catalyst*. The catalytic activity with a series of Cp′TiCl$_2$(OAr) complexes increased in the following order: **3**, **4** > **2** > **5**. In addition, these results are reproducible (Table 1, runs 12−15). It should also be noted that a remarkable difference in the catalytic activity was observed between **4** and **5**, clearly suggesting that steric bulk directly affects the catalytic activity. This would be explained clearly if the internal rotation of cyclopentadienyl group was considered, because the decrease in the catalytic activity by **5** was remarkable, in particular in a relatively high styrene concentration region (runs 19 and 20, Table 1).

The resultant poly(ethylene-*co*-styrene)s possessed relatively high molecular weights with unimodal and narrow molecular weight distributions (M_w/M_n = 1.6−2.2). The styrene content in the copolymer increased upon the increase in the initial styrene concentration in the reaction mixture. The M_w value increased if **4** was used in place of **3**. One plausible explanation for the observed difference is that the more electron-donating nature of **4** as compared with that of **3** increases the propagation rate rather than the chain-transfer rate, although the observed catalytic activity by **4** showed no difference under the same conditions. Taking into account these results, it is thus concluded that substituent on cyclopentadienyl group *affects* both

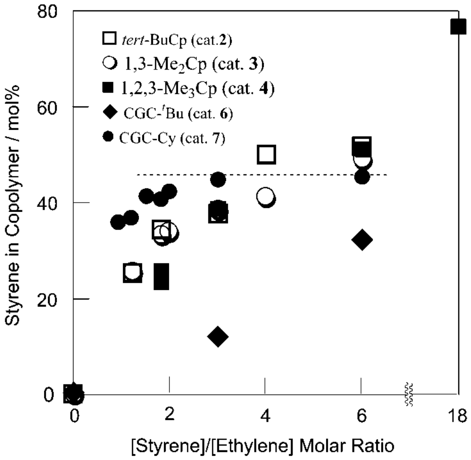


Figure 1. Plots of styrene (mol %) in copolymer vs [styrene]/[ethylene] molar ratio for copolymerization of ethylene with styrene by (**2**−**7**)−MAO catalyst systems (Table 1). Catalyst: $Cp'TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ [Cp′ = *tert*-Bu (**2**, □), 1,3-$Me_2C_5H_3$ (**3**, ○), 1,2,3-$Me_3C_5H_2$ (**4**, ■); $[Me_2Si(C_5Me_4)(NR)]TiCl_2$ [R = *tert*-Bu (**6**, ◆), cyclohexyl (**7**, ●). Data for **6** and **7** were cited from our previous report.[12]

the catalytic activity and the molecular weight for the resultant copolymer.

The selected results for **6** and **7** cited from our previous report,[12] performed under the same conditions, are also attached in Table 1 for comparison. The resultant polymers were poly(ethylene-*co*-styrene)s exclusively, and they possessed relatively high molecular weights with unimodal molecular weight distributions in all cases. Plots in styrene content (mol %) in poly(ethylene-*co*-styrene)s vs [styrene]/[ethylene] (molar ratio) in feed based on results in Table 1 are summarized in Figure 1.[16] It is clear that **2**−**5** showed more efficient styrene incorporation than **6**, although the observed catalytic activities by **6** were somewhat higher than those by **2**−**5**. It is also clear that **7** showed more efficient styrene incorporation, in particular more than **2**−**5** at low [styrene]/[ethylene] molar ratios, and the styrene content in **7** reached a constant value (ca. 46 mol %). As described in our previous report,[12] only trace (negligible) amounts of styrene repeat unit ($S_{\alpha\beta}$) was observed by the ^{13}C NMR spectrum for the copolymer prepared by **7**, despite the fact that the copolymer contains 44.6 mol % of styrene. This should be the clear reason for the difficulty in preparing the copolymer with a styrene content higher than ca. 50 mol % by this catalyst, because styrene should be incorporated into the copolymer after inserted ethylene even at an almost equal molar ratio if **7** was employed as the catalyst. On the other hand, the styrene content in the copolymer prepared in particular by **4** increased at higher [styrene]/[ethylene] molar ratios, and in one case, a styrene content up to 73.6 mol % could be thus attained (run 17).[17] DSC thermograms of these copolymers by **4**, **6**, and **7** showed broad traces, and the glass transition temperature measured by differential scanning calorimetry (DSC) increased upon the increase in the styrene content (Table 2).

2. Microstructure and Composition Dirstribution Analysis for Poly(ethylene-*co*-styrene)s. Figure 2 shows typical ^{13}C NMR spectra (methylene and methine region) of the copolymers (THF-soluble fraction) prepared by **3** (styrene content 38.5 mol %, run 7) and by **6** (styrene content 32.7 mol %, run 22). In addition to the resonances at δ = 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, SES), the resonances at δ = 40.7−41.0 ppm ($T_{\beta\beta}$, three styrene unit connected to head-to-tail coupling) and 43.1−45 ppm ($S_{\alpha\alpha}$ and $T_{\beta\delta}$, two styrene unit connected to head-to-tail coupling) were observed.[18] This is an especially interesting contrast with that prepared by $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$- (**6**-) based catalyst.

Table 2. Selected DSC Data for Poly(ethylene-*co*-styrene)s (THF-Soluble Fraction) Prepared by $(1,2,3\text{-}Me_3C_5H_2)TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (4) and $[Me_2Si(C_5Me_4)(NR)]TiCl_2$ [R = ᵗBu (6), Cy (7)] Complexes−MAO Catalyst Systems[a]

run no.	catal	M_w[b]/10^{-4}	M_w/M_n[b]	styrene/mol %[c]	T_g[d]/°C
12	**4**	17	1.6	26.0	−8.1
14	**4**	11	1.7	38.8	14.2
16	**4**	6.6	1.6	51.2	34.0
17	**4**	3.6	2.1	73.6	58.3
22	**6**	18	1.8	32.7	4.6
25	**7**	7.5	1.5	36.0	6.4
23	**7**	4.8	1.7	40.9	11.9

[a] Reaction conditions, see Table 1. [b] GPC data in *o*-dichlorobenzene vs polystyrene standard. [c] Styrene content (mol %) in copolymer by ^1H NMR ($C_2D_2Cl_4$). [d] Measured by DSC.

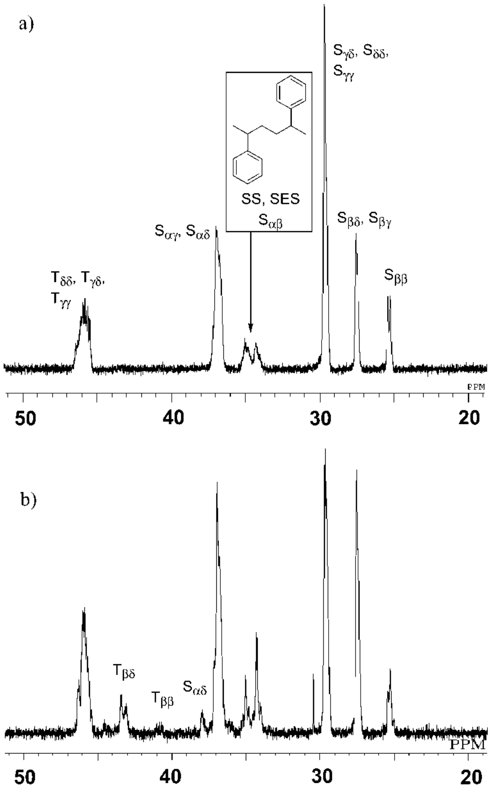


Figure 2. ^{13}C NMR spectra (in $CDCl_3$ at 60 °C) of poly(ethylene-*co*-styrene)s (methylene and methine region, THF-soluble fraction): (a) catalyst = $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**6**), styrene content 32.7 mol % (run 22); (b) catalyst = $(1,3\text{-}Me_2C_5H_3)TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**3**), styrene content 38.5 mol % (run 7). The peak at 30.5 ppm is due to the impurity (2,6-di-*tert*-butyl-*p*-cresol) as the added stabilizing agent.

Because of that the styrene repeat unit for the copolymer with high styrene content prepared by **4** possessed mixture of head-to-tail ($T_{\beta\beta}$, $T_{\beta\delta}$, etc.) and tail-to-tail (or SES, $S_{\alpha\beta}$) sequences, the dept spectrum was measured for identification of each resonances. Figure 3 shows the ^{13}C NMR spectrum with relatively high styrene content (51.2 mol %). On the basis of the dept spectrum and data reported previously,[7,8] chemical

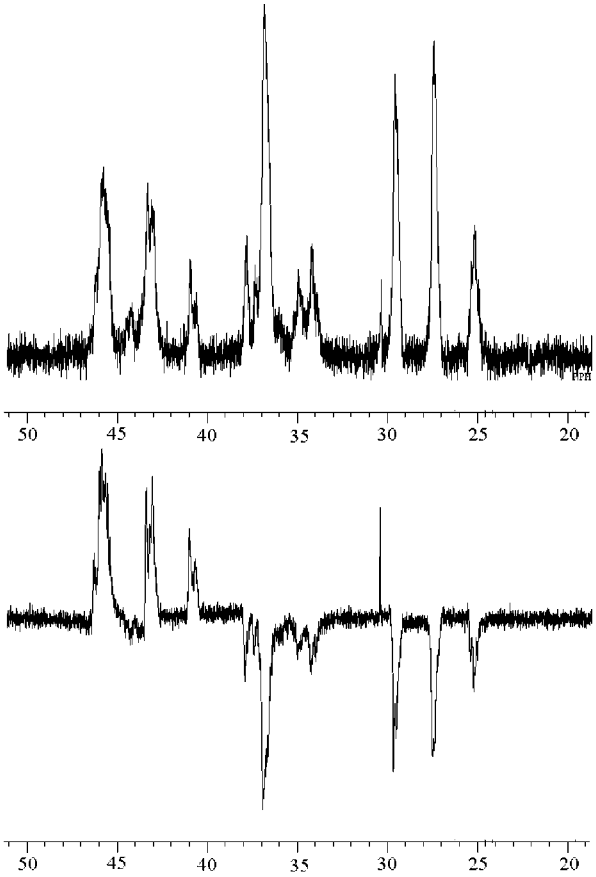


Figure 3. ^{13}C NMR spectra (with the dept spectrum) for poly(ethylene-*co*-styrene) prepared by the **4**−MAO catalyst system (styrene content, 51.2 mol %, run 16 in Table 1).

Table 3. ^{13}C NMR Chemical Shift for Poly(ethylene-*co*-styrene)

carbon	ppm		ppm
$S_{\alpha\alpha}$	43.6−45.2	E*S*SE	43.8
		S*S*SE	44.3
		S*S*SS	44.5
$S_{\alpha\beta}$		m	34.3
		r	35.0
		S**E*SSS	35.3−35.8
$S_{\alpha\gamma}$	36.6		
$S_{\alpha\delta}$		E*S*E	36.9
		*E*SSE	37.9
		SS*S*E	37.4
		S*E*S m	25.2
		S*E*S r	25.4
$S_{\beta\gamma}$	27.5		
$S_{\beta\delta}$	27.5		
$S_{\gamma\gamma}$	29.7		
$S_{\gamma\delta}$	29.7		
$S_{\delta\delta}$	29.7		
$T_{\beta\beta}$		S*S*SE	41.0
		S*S*SS	40.7
$T_{\beta\gamma}$			
$T_{\beta\delta}$		ES*S*EE	43.5
		SS*S*EE	43.2
$T_{\gamma\gamma}$	45.2−46.7		
$T_{\gamma\delta}$	45.2−46.7		
$T_{\delta\delta}$	45.2−46.7		

[a] Styrene insertion with regio irregularity (inversion).

shifts in the ^{13}C NMR spectrum for poly(ethylene-*co*-styrene) are summarized in Table 3.

Although the resultant copolymer prepared by **4** possessed a relatively high molecular weight ($M_w = 2.3-17 \times 10^4$), unimodal molecular weight distribution ($M_w/M_n = 1.6-2.1$), and sole T_g peaks (−8.1 to +58.3 °C) in the DSC thermograms, we further tried to confirm a conclusion that the resultant copolymer has a single composition. This should be potentially important for evaluating the effect of ligand for the microstructure in the copolymer, because, in one case, the copolymer prepared by the $CpTiCl_3$−MAO catalyst consisted of a mixture of separate polymer fractions.[19] Cross-fractionation chromatography (CFC) is known as one of the most powerful tools for analyzing comonomer distribution, in particular in ethylene/α-olefin copolymers, and the copolymer sample was studied under similar conditions. The syndiotactic polystyrene prepared by **3** was also chosen as the reference.[20] Figure 4 shows the contour maps for both poly(ethylene-*co*-styrene) (styrene content 51.2 mol %, run 16) and syndiotactic polystyrene. It is clear that the selected sample for the copolymer possessed unimodal styrene distribution without containing a certain amount of syndiotactic polystyrene and/or polyethylene. However, the confirmation whether atactic polystyrene would be still contaminated (remained) or not may not be clear enough with these procedures (^{1}H and ^{13}C NMR, DSC, GPC, CFC), because the present sample was eluted at low temperature in the CFC method. Since GPC attached to FT-IR (GPC/FT-IR) is also known as a powerful tool for analyzing comonomer distribution, in particular for ethylene/α-olefin copolymer,[21] the copolymer samples prepared by **3** (styrene content 41.2 mol %, run 11) and **4** (styrene content 51.2 mol %, run 16) were thus examined for styrene distribution at each molecular weight. The results are shown in Figure 5.[22] It is clear that the resultant copolymer possessed unimodal styrene incorporation at each molecular weight. On the basis of completely full analysis for the copolymer sample (run 16), it is thus concluded that the poly(ethylene-*co*-styrene) prepared by **3** and **4** should have an unimodal styrene distribution (single composition).

3. Effect of Ligand on Microstructure in the Copolymer. Since the confirmation that the copolymer possessed a single composition distribution was made, the effect of cyclopentadienyl fragment on monomer sequence in the copolymer prepared with a series of (cyclopentadienyl)(aryloxy)titanium complexes of the type $Cp'TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ was thus explored. Figure 6 summarizes selected ^{13}C NMR spectra for the polymer samples with styrene contents at 37.6−41.1 mol % prepared by **2**, **4**, and **5**. Although the remarkable differences were not seen in these spectra, the small difference for the integration ratio of $T_{\beta\delta}$, $T_{\beta\beta}$, and $S_{\alpha\beta}$ could be observed. Since the relative signal intensities for carbon atom attached to phenyl (tertiary) and hydrogen (secondary) were, however, different due to the NOE, the precise quantitative analysis for the detailed monomer sequence could not be done with these spectra. On the other hand, the ratios of $[T_{\beta\beta}]/[T_{total}]$ and $[S_{\alpha\beta}]/[S_{\alpha\alpha} + S_{\beta\beta}]$ were chosen to evaluate the frequency as well as the regioselectivity of styrene insertion (Table 4). If the insertion of styrene obeys the Bernoullian mode in a regioselective manner, $[T_{\beta\beta}]$ should be calculated as $[St]^3$, and the value of $[T_{\beta\beta}]/[T_{total}]$ should be thus indicated in Figure 7 (by ●). As easily found, the $[T_{\beta\beta}]/[T_{total}]$ value by the bridged cyclopentadienylamide titanium complex **6** should be zero, because the resultant copolymer does not contain a head-to-tail sequence (in particular $T_{\beta\beta}$) for a three styrene repeat unit. All copolymer samples prepared by using **2**−**5** showed lower values of $[T_{\beta\beta}]/[T_{total}]$ than those estimated by the

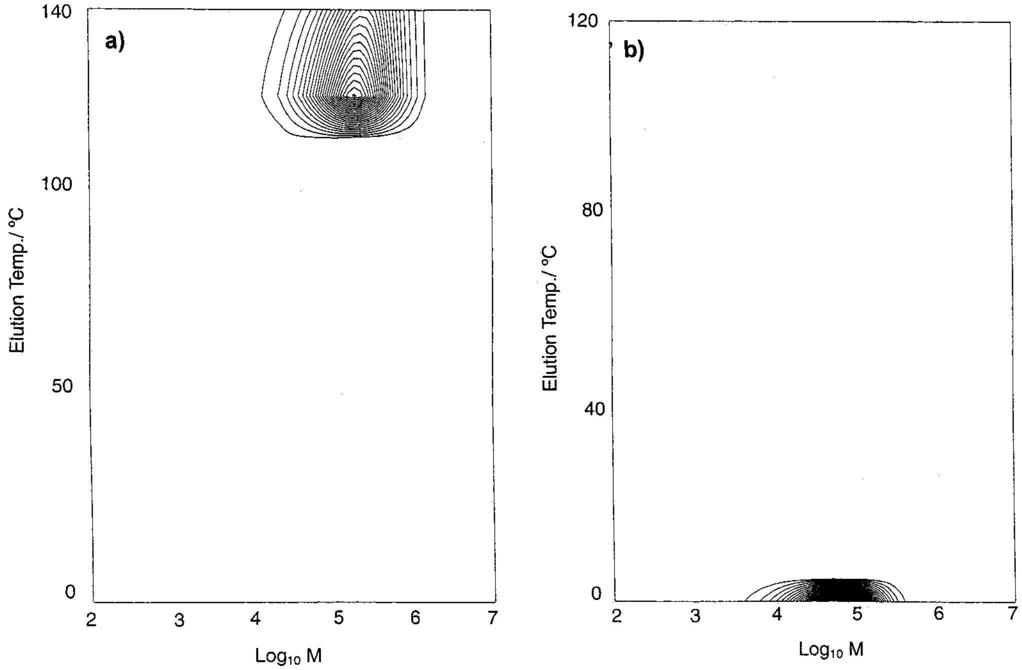


Figure 4. Contour maps of (a) syndiotactic polystyrene prepared by **3**−MAO catalyst system, and (b) poly(sthylene-*co*-styrene) prepared by **4**−MAO catalyst system (styrene content, 51.2 mol %, run 16 in Table 1) measured by cross-fractionation chromatography (CFC).

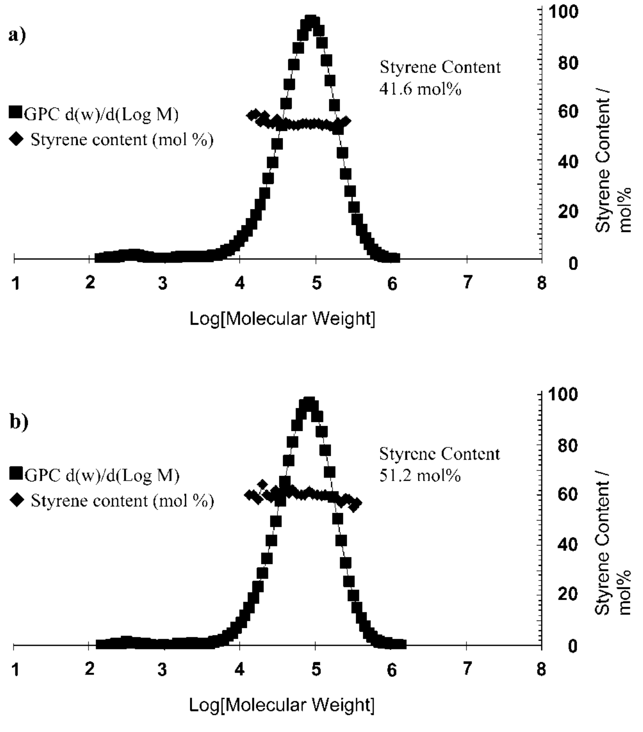


Figure 5. GPC/FT-IR spectra for poly(ethylene-*co*-styrene)s prepared by **3** (styrene content 41.6 mol %, run 11) or **4** (styrene content, 51.2 mol %, run 16). The styrene contents were somewhat different from those determined by ^{1}H NMR due to that different reference (standard) samples were used for calculating the contents in the FT-IR.

Table 4. Selected Data for $[T_{\beta\beta}]/[T_{total}]$ and $[S_{\alpha\beta}]/[S_{A\alpha} + S_{\beta\beta}]$ Determined by ^{13}C NMR Spectra[a]

run no.	catal	styrene/mol %	$([T_{\beta\beta}]/[T_{total}])/10^{-1}$	$[S_{\alpha\beta}]/[S_{\alpha\alpha} + S_{\beta\beta}]$
2	**2**	37.6	0.36	2.57
5	**2**	50.0	*b*	2.94
7	**3**	38.5	0.40	1.98
8	**3**	49.0	0.98	1.95
14	**4**	38.8	0.57	1.12
16	**4**	51.2	1.19	1.23
17	**4**	73.6	3.26	*b*
19	**5**	41.1	0.79	1.94
20	**5**	54.8	*b*	1.75
22	**6**	32.7	0.0	1.23

[a] These values were calculated from the intensity ratio based on ^{13}C NMR spectra for poly(ethylene-*co*-styrene)s. [b] Hard to determine.

Bernoullian mode, and these results assume that reactivity for styrene into the inserted propagating chain ends is less than that for ethylene. This would be easily considered because, in cases of ethylene/α-olefin copolymerization, not only by ordinary metallocene type and linked half-metallocene type catalyst but also by our (cyclopentadienyl)(aryloxy)titanium catalyst the copolymerization proceeds in a random manner and the monomer sequences obey not the Bernoulian model but the first-order Markov model.[4b,23] In addition, this is also because that structural features of the catalyst, in particular the steric bulk of ligand, bite angle, configuration, and conformation, do influence the coordination and/or insertion of monomers in transition-metal-catalyzed coordination polymerization reactions in most cases, and this is an distinct difference from conventional radical and ionic polymerization reactions.[23−24]

The values of $[S_{\alpha\beta}]/[S_{\alpha\alpha} + S_{\beta\beta}]$ vs styrene content in the copolymer (Table 4) are chosen to compare the regioselectivity among catalysts **2**−**6**. The secondary carbons of $S_{\alpha\alpha}$ and $S_{\beta\beta}$ are formed in the styrene−styrene and styrene−ethylene−styrene sequences with regioselective insertion of styrene, respectively (see also Charts 2 and 3). Among the series of (cyclopentadienyl)(aryloxy)titanium complexes, **4** showed relatively high regioselectivity which would be almost similar to **6**. On the other hand, **2** showed the highest $[S_{\alpha\beta}]/[S_{\alpha\alpha} + S_{\beta\beta}]$ value. Although the present comparison may lack the strongest quantitative preciseness, it is at least clear that the substituent on the cyclopentadienyl group directly affects the regioselectivity in the ethylene/

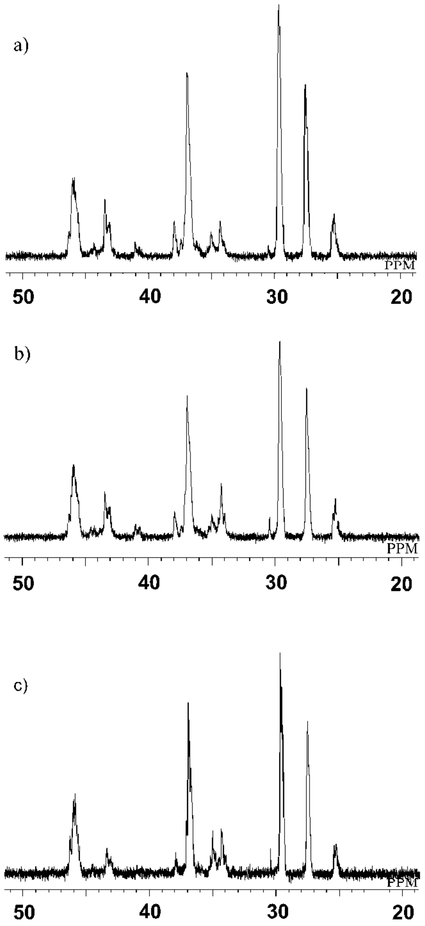


Figure 6. ^{13}C NMR spectra (in $CDCl_3$ at 60 °C) of poly(ethylene-*co*-styrene)s (methylene and methine region, THF-soluble fraction): (a) catalyst **4** ($Cp' = 1,2,3\text{-}Me_3C_5H_2$), styrene content 38.8 mol % (run 14); (b) catalyst **5** ($Cp' = 1,2,4\text{-}Me_3C_5H_2$), styrene content 41.1 mol % (run 19); (c) catalyst **2**, ($Cp' = {}^tBuC_5H_4$), styrene content 37.6 mol % (run 2).

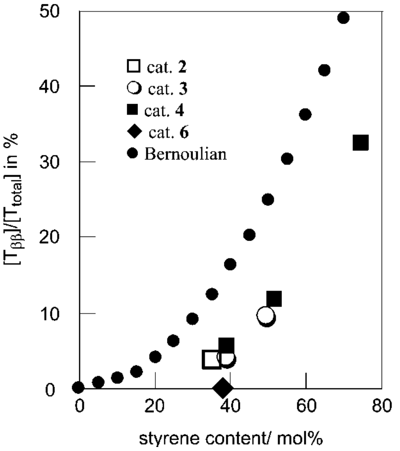


Figure 7. Plots of $[T_{\beta\beta}]/[T_{total}]$ ratio vs styrene in the copolymer determined by ^{13}C NMR spectra (in $CDCl_3$ at 60 °C, methylene and methine region, THF-soluble fraction). $[T_{\beta\beta}]/[T_{total}]$ value (in %) based on Bernoulian mode could be calculated as (styrene content)^2 × 100.

styrene copolymerization. Moreover, $S_{\alpha\alpha}$ as well as $S_{\alpha\beta}$ value were almost a trace amount if **7** was chosen as the catalyst, and it is also thus clear that the amide ligand in cyclopentadienylamide titanium complexes also directly affects both the monomer sequence and regioselectivity.

Chart 2

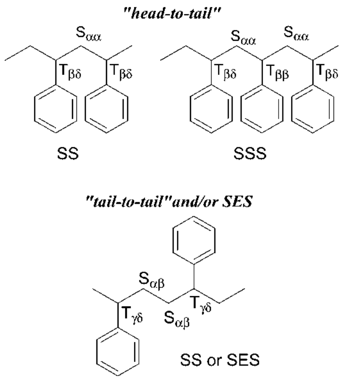
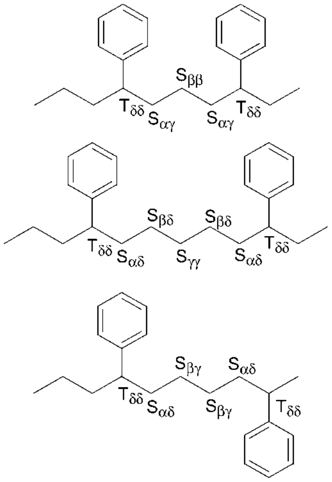


Chart 3



Summary

We have shown that our original catalyst, (cyclopentadienyl)(aryloxy)titanium complexes of the type $Cp'TiCl_2(OAr)$, exhibited unique characteristics for copolymerization of ethylene with styrene, affording poly(ethylene-*co*-styrene)s exclusively. Efficient styrene incorporation could be attained with these catalysts, and the copolymers possessed relatively high molecular weights with unimodal molecular weight distributions. On the basis of the full analysis for the resultant copolymers, it is thus concluded that the copolymer has a single composition distribution. In addition, substituent on cyclopentadienyl group directly affects the catalytic activity, styrene incorporation, and regioselectivity of styrene insertion. Although the *exact* catalytically active species could not be identified in this catalysis at this moment, these facts are very important and are effective for designing more powerful catalyst for precise polymerization.

Experimental Section

General Procedure. All synthetic experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques unless otherwise specified. All chemicals used were reagent grade and were purified by standard purification procedures. Toluene for the polymerization was distilled over sodium and benzophenone under nitrogen atmosphere and was stored in a Schlenk tube in the drybox in the presence of molecular sieves (mixture of 3A and 4A 1/16, and 13X). Reagent grade styrene was distilled under nitrogen in the presence of CaH_2 after the standard purification procedure, and was stored in a Schlenk tube under N_2 in the freezer. Ethylene for polymerization was of polymerization grade (purity >99.9%, Sumitomo Seika Co., Ltd.) and was used as received. (Cyclopentadienyl)(aryloxy)titanium(IV) complexes of the type $Cp'TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ [$Cp' = {}^tBuC_5H_4$ (**1**), 1,3-$Me_2C_5H_3$ (**2**)] were prepared according to our previous report.[2] $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**6**) was purchased from Kanto Chemical Co., Ltd., and synthesis of $[Me_2Si(C_5Me_4)(NCy)]TiCl_2$ (**7**) was described in our recent paper.[12] Toluene and $AlMe_3$ in the commercially available methylaluminoxane (PMAO-S, 9.5 wt % (Al) toluene solution, Tosoh Akzo Co.) were removed, the resulting material was dried in vacuo in the drybox and used as a white solid.

All ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, ^1H; 100.40 MHz, ^{13}C). All chemical shifts are given in ppm and are referenced to tetramethylsilane. Obvious multiplicities and routine coupling constants are usually not listed, and all spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. All deuterated NMR solvents were stored over molecular sieves. ^{13}C NMR spectra for the poly(ethylene-*co*-styrene)s were performed by using JEOL LA400 spectrometer ($CDCl_3$) with proton decoupling at 60 °C. The pulse interval was 5.2 s, the acquisition time was 0.8 s, the pulse angle was 90°, and the number of transients accumulated was ca. 10 000. ^1H NMR spectra for the copolymer (calculation of styrene content in the copolymer) were measured in the same manner (in tetrachloroethane-d_2) at 100 °C. The polymer solutions were prepared by dissolving polymers in solvent up to 10 wt %.

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 HTX2) 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. Differential scanning calorimetric (DSC) data for the copolymer were recorded by means of DSC6100 (Seiko Instruments Co.) under nitrogen atmosphere [conditions: heating from 25 to 300 °C (20 °C/min); cooling from +300 to −100 °C (10 °C/min)]. The analysis data by cross-fractionation chromatography (CFC) were recorded by means of CFC T-150C (Dia Instruments Co.) with *o*-dichlorobenzene as an extraction solvent. Approximately 20 mg/5 mL of polymer sample was loaded onto a column of insert packing with slow cooling (1.0 °C/min), followed by stepwise elution from the column at 0, 10, 20, 30, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 130, and 140 °C. Each eluted polymer solution was automatically sent to the GPC system, which was equipped with an infrared detector.

Synthesis of $(1,2,3\text{-}Me_3C_5H_2)TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (4). LiO-2,6-$^iPr_2C_6H_3$ (189 mg, 1.03 mmol) was added in one portion to a Et_2O solution (30 mL) containing $(1,2,3\text{-}Me_3C_5H_2)TiCl_3$ (267 mg, 1.02 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature and was stirred for 10 h. The mixture was then filtered through Celite, and the filter cake and was washed with Et_2O. The combined filtrate and the wash were taken to dryness under reduced pressure to give an orange solid. The solid was then dissolved in a minimum amount of CH_2Cl_2 layered by a small amount of *n*-hexane. The chilled (−30 °C) solution gave orange microcrystals (222 mg, first crop). The microcrystals were pure enough by ^1H and ^{13}C NMR, and by elemental analysis. Yield: 54%. The second crop would increase the yield. ^1H NMR ($CDCl_3$): δ 7.09 (d, 2H, $J = 6.8$ Hz), 7.04 (t, 1H, $J = 6.9$ Hz), 6.02 (s, 2H), 3.21 (m, 2H, Me_2CH-), 2.28 (s, Me−Cp), 1.21 (d, 12H, $J = 6.8$ Hz). ^{13}C NMR ($CDCl_3$): δ 162.9, 138.5, 135.6, 133.9, 123.9, 123.3, 119.0, 26.9, 23.6, 15.3, 15.2, 12.4, 12.3. Anal. Calcd for $C_{20}H_{28}Cl_2OTi$, 403.19: C, 59.57; H, 7.00. Found: C, 59.46; H, 7.03; N, 0.14.

Synthesis of $(1,2,4\text{-}Me_3C_5H_2)TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (5). Synthetic procedure for **5** was the same as that for **4** except that LiO-2,6-$^iPr_2C_6H_3$ (275 mg, 1.49 mmol) was added in one portion to a Et_2O solution (30 mL) containing $(1,2,4\text{-}Me_3C_5H_2)TiCl_3$ (390 mg, 1.49 mmol) at −30 °C. Yield (first crop only): 370 mg (62%). ^1H NMR ($CDCl_3$): δ 7.10 (d, 2H, $J = 7.7$ Hz), 7.02 (t, 1H, $J = 7.5$ Hz), 6.17 (s, 2H), 3.22 (m, 2H, Me_2CH-), 2.25 (s, Me−Cp), 2.20 (s, Me−Cp), 1.21 (d, 12H, $J = 6.6$ Hz). ^{13}C NMR ($CDCl_3$): δ 161.8, 138.7, 134.8, 134.7, 123.8, 123.3, 123.2, 121.7, 121.0, 26.9, 24.0, 23.4, 16.4, 16.0, 15.2, 14.8, 14.4, 13.9. Anal. Calcd for $C_{20}H_{28}Cl_2OTi$, 403.19: C, 59.57; H, 7.00. Found: C, 59.44; H, 7.03; N, 0.19.

Typical Reaction Procedure for Copolymerization of Ethylene with Styrene by $(1,3\text{-}Me_2C_5H_3)TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (3) −MAO Catalyst. A typical example (run 7) is as follows: toluene (24.5 mL) and MAO (116 mg, 2.00 mmol) were added into the autoclave (100 mL, stainless steel) in the drybox, and the reaction apparatus was then replaced with ethylene. The reaction mixture was then pressurized to the prescribed ethylene pressure soon after the addition of styrene (5.0 mL) and a toluene solution containing **3** (0.5 mL, **3** 1.0 μmol). The mixture was stirred for 10 min, and the polymerization was terminated with the addition of EtOH (15 mL). The solution was then poured into EtOH (100 mL), and the resultant polymer was adequately washed with EtOH and then dried in vacuo for several hours.

According to the previous reports, the resultant polymer mixture was separated into three fractions, and atactic polystyrene (containing a trace amount of polyethylene observed by ^1H NMR) which was prepared only by MAO was extracted with acetone. Poly(ethylene-*co*-styrene) was then extracted with THF from the acetone-insoluble portion, and polyethylene and polystyrene, which were the byproducts in this reaction were separated as the THF-insoluble fraction. The basic experimental procedure is as follows.

The polymer sample obtained in the copolymerization experiment was added into a round-bottom flask containing acetone (100 mL) equipped with a reflux condenser, and the mixture was refluxed for 6 h to separate acetone-soluble and -insoluble fractions. Then the acetone-insoluble fraction was dried and added into a round-bottom flask containing tetrahydrofuran (THF, 100 mL) equipped with a reflux condenser, and the mixture was refluxed for 6 h to separate THF-soluble and -insoluble fractions. These fractions were analyzed by ^1H NMR, ^{13}C NMR, GPC, and DSC.

Acknowledgment. The present work is partly supported by a Grant-in-Aid from the Ministry of Education, Science, Sports, and Culture of Japan (No. 13555253). K.N. would like to express his heartfelt thanks to Idemitsu Petrochemicals Co., Ltd., for GPC/FT-IR analyses, and to Tosoh Finechem Co. for donating MAO (PMAO-S). K.N. also thanks Mr. H. Shirai (Asahi Chemical Co., Ltd.), and Dr. N. Tomotsu (Idemistu Petrochemical Co., Ltd.) for helpful discussions. The authors also acknowledge Prof. Y. Imanishi (Emeritus Prof. of NAIST) for comments on this project.

Supporting Information Available: Figures showing DSC thermograms for poly(ethylene-*co*-styrene)s in Table 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) As one attempt, the copolymer with the styrene content of 86.6 mol % could be obtained (under the same conditions as run 17 except that 20 mL of styrene was used in place of 15 mL, activity 1980 kg of polymer/mol of Ti·h). The resultant copolymer (THF-soluble fraction, 79.2 wt %) possessed relatively high molecular weight ($M_w = 2.3 \times 10^4$) and unimodal molecular weight distribution ($M_w/M_n = 2.0$), with no contamination of polyethylene and syndiotactic polystyrene confirmed by ^1H and ^{13}C NMR spectra and cross-fractionation chromatography. However, the result by GPC/FT-IR method suggests that the copolymer may contain trace amounts of atactic polystyrene in the low molecular weight region, although the precise measurement for the styrene content by FT-IR in this method, in particular at higher styrene content, may be difficult.

(18) 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.[8]

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