

# Copolymerization of ethylene with $\alpha$ -olefin catalyzed by [1,8-C<sub>10</sub>H<sub>6</sub>(NSi<sup>t</sup>BuMe<sub>2</sub>)<sub>2</sub>]TiCl<sub>2</sub> and [ArN(CH<sub>2</sub>)<sub>3</sub>NAr]TiCl<sub>2</sub> (Ar = 2, 6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)–MMAO catalyst systems

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## Abstract

Copolymerization of ethylene with 1-hexene, 1-octene and 1-decene catalyzed by [1,8-C<sub>10</sub>H<sub>6</sub>(NR)<sub>2</sub>]TiCl<sub>2</sub> [R = Si<sup>t</sup>BuMe<sub>2</sub> (**1**)] and [ArN(CH<sub>2</sub>)<sub>3</sub>NAr]TiCl<sub>2</sub> [Ar = 2, 6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**2**)] complexes–MMAO (MMAO = methyl isobutyl aluminoxane) catalyst systems have been explored. It was revealed that  $\alpha$ -olefin contents in the resultant copolymer are highly dependent upon catalyst complex used. The resultant copolymer with **1** gave relatively broad molecular weight distributions, consisting of high and low molecular weight copolymers. On the other hand, it was difficult to prepare high molecular weight ( $M_w > 100,000$ ) copolymer with low  $\alpha$ -olefin content if complex **2** was employed as the catalyst component. The resultant copolymers prepared by both **1** and **2** have been analyzed by DSC, <sup>13</sup>C NMR, and CFC (cross-fractionation chromatography). The design of catalyst structure as well as ligands is thus necessary to prepare the desired ethylene/ $\alpha$ -olefin copolymers by non-metallocene type catalyst. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** Copolymerization; Ethylene;  $\alpha$ -Olefin

## 1. Introduction

Group 4 transition metal complexes that contain bidentate bis(amide) ligand are promising systems for application in olefin polymerization catalysis because of their relationship to the well-studied metallocene analogs [1,2], bridged cyclopentadienyl-amide complexes such as [Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)(N<sup>t</sup>Bu)]TiCl<sub>2</sub> [3–13], non-bridged cyclopentadienyl-aryloxy complexes [14,15], bis(amide) complexes of the type (R<sub>2</sub>N)<sub>2</sub>MX<sub>2</sub> [16–20], or chelate bis(amide) complexes [21–43], and others (examples for catalytic alkene polymerization using Group 4 complexes that contain aryloxy ligands) [44–54]. We believe that these studies should be very important for designing a highly efficient catalyst-complex with/without cyclopentadienyl group, and for understanding the scope and the limitation of these types of transition metal complexes as olefin polymerization catalysts.

We have recently reported that [1,8-C<sub>10</sub>H<sub>6</sub>(NSi<sup>t</sup>BuMe<sub>2</sub>)<sub>2</sub>]TiCl<sub>2</sub> (**1**)–MMAO (methyl isobutyl aluminoxane) catalyst showed remarkable catalytic activities for ethylene

homopolymerization, and that the effect of cocatalyst as well as solvent was found to be important for high activity in these catalyst systems [55,56].<sup>1</sup> We also reported that 1-butene content as well as the monomer sequence in the resultant poly(ethylene-*co*-1-butene)s, which were prepared by **1**–MMAO, by (TBP)TiCl<sub>2</sub> [TBP = 2,2'-thiobis-(4-methyl-6-*tert*-butyl-phenolato)]–MAO [44,46], and by [Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)(N<sup>t</sup>Bu)]TiCl<sub>2</sub>–Al<sup>i</sup>Bu<sub>3</sub>/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> catalyst systems [4], were highly dependent upon the catalyst used [56].

In this paper, we wish to show a remarkable difference of reactivity among **1**– and [ArN(CH<sub>2</sub>)<sub>3</sub>NAr]TiCl<sub>2</sub> (**2**, Ar = 2, 6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) [30,31]–MMAO catalyst systems on copolymerization of ethylene with  $\alpha$ -olefin such as 1-hexene, 1-octene and 1-decene (Chart 1).<sup>2</sup>

<sup>1</sup> Similar paper, concerning the preparation of [1,8-C<sub>10</sub>H<sub>6</sub>(NR)<sub>2</sub>]MCl<sub>2</sub> [R = SiMe<sub>3</sub>, Si<sup>i</sup>Pr<sub>3</sub>, M = Ti, Zr] complexes and ethylene homopolymerization in the presence of cocatalyst, has also been reported [57], after our communication [55] has appeared.

<sup>2</sup> Similar results concerning some parts of copolymerization of ethylene with 1-hexene by **2**–MMAO catalyst was presented in the annual meeting in the Society of Polymer Science, Japan [58].

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Table 1  
Copolymerization of ethylene with 1-hexene by **1**-MMAO catalyst system<sup>a</sup> (effect of ethylene pressure)

Run no.	1-Hexene (ml)	Ethylene (bar)	Polymer (yield/g)	Activity <sup>b</sup>	$M_w^c (\times 10^{-4})$	$M_w/M_n^c$	SCB (Me/1000C) <sup>d</sup>	$T_m$ (°C)
1	5	4	0.80	80.0	18.2 <sup>e</sup>	5.2		116.9, 60.4
2	5	5	0.96	76.8	24.4 <sup>e</sup>	6.4	26.6	118.9
3	5	6	1.02	68.0	43.3	6.6		
					0.16 <sup>e</sup>	3.6		
4	5	7	1.14	65.1	24.9	4.4	20.1	121.0
					0.23 <sup>e</sup>	1.6		
5	5	8	1.18	59.0	58.7	9.3		
					0.21	11.9		
6	10	6	1.02	68.0	63.3	7.7	25.5	117.5
					0.24	1.4		
7	10	7	1.09	62.3	57.4	8.7	23.8	118.1, 108.1
					0.19	1.7		
8	10	8	1.12	56.0	62.3	10.9		
					0.18	1.9		

<sup>a</sup> Reaction conditions: [1,8-C<sub>10</sub>H<sub>6</sub>(NSi<sup>t</sup>BuMe<sub>2</sub>)<sub>2</sub>]TiCl<sub>2</sub> (**1**) 10 μmol, *n*-heptane 30 ml, 50°C, 15 min, MMAO (5.8 wt% (Al) in hexane), Al/Ti (molar ratio) = 1000.

<sup>b</sup> Polymerization activity: kg-polymer/(mol-Ti h bar).

<sup>c</sup> GPC data in *o*-dichlorobenzene vs. polystyrene standard.

<sup>d</sup> Side chain branching (SCB) = methyl/1000 carbon determined by FT-IR.

<sup>e</sup> A small amount of low  $M_w$  (ca. 150–500) peak was also observed on GPC trace.

## 2. Experimental

### 2.1. General procedure

All 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 the standard purification procedures. *n*-Heptane purchased from Wako Chemicals was distilled under nitrogen in the presence of Na and benzophenone, and stored in the presence of molecular sieves (mixture of 3A and 4A 1/16, and 13X) under nitrogen atmosphere. MMAO was used as received (Tosoh Akzo, MMAO-3A, 5.8 wt% (Al) in hexane). Ethylene for polymerization was of polymerization grade (purity >99%, Sumitomo

Seika), and used as received without further purification procedures. [1,8-C<sub>10</sub>H<sub>6</sub>(NSi<sup>t</sup>BuMe<sub>2</sub>)<sub>2</sub>]TiCl<sub>2</sub> (**1**) and [ArN(CH<sub>2</sub>)<sub>3</sub>NAr]TiCl<sub>2</sub> (**2**, Ar = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) were prepared according to the previous reports [30,31,56].

All <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, <sup>1</sup>H). All chemical shifts are given in ppm and are referenced to tetramethylsilane. Obvious multiplicities and routine coupling constants are usually not listed. All spectra were obtained in the solvent indicated at 25°C unless otherwise noted. All deuterated NMR solvents were stored over molecular sieves in a drybox. All <sup>13</sup>C NMR spectra for the ethylene/α-olefin copolymer were performed by using JEOL LA400 spectrometer (100.40 MHz; <sup>13</sup>C, *o*-dichlorobenzene-*d*<sub>4</sub>) with proton decoupling at 135°C. The pulse interval was 5.2 s, the acquisition time was 0.8 s, the pulse angle was

Table 2  
Copolymerization of ethylene with 1-hexene by **1**-MMAO catalyst system<sup>a</sup> (effect of polymerization temperature)

Run no.	Temperature (°C)	Polymer (yield/g)	Activity <sup>b</sup>	$M_w^c (\times 10^4)$	$M_w/M_n^c$
9	0	0.066	3.8		
10	24	0.552	31.5	285	16.5
11	40	1.02	58.3	58.9	8.1
				0.32	2.6
4	50	1.14	65.1	24.9	4.4
				0.23	1.6 <sup>d</sup>
12	60	1.06	60.6	39.5	10.3
				0.15	1.7

<sup>a</sup> Reaction conditions: **1** 10 μmol, *n*-heptane 30 ml, 1-hexene 5 ml, ethylene 7 bar, 15 min, MMAO (5.8 wt% (Al) in hexane), Al/Ti (molar ratio) = 1000.

<sup>b</sup> Polymerization activity: kg-polymer/(mol-Ti h bar).

<sup>c</sup> GPC data in *o*-dichlorobenzene vs. polystyrene standard.

<sup>d</sup> A small amount of low  $M_w$  ( $M_w$  333,  $M_w/M_n$  = 1.05) peak was also observed on GPC trace.

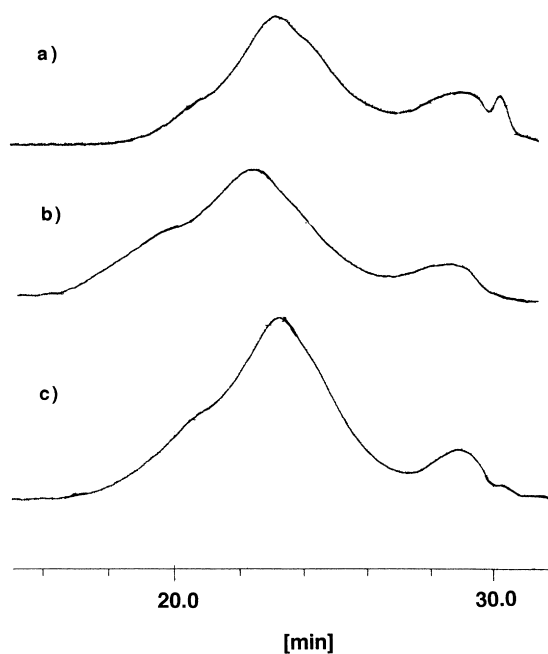


Fig. 1. GPC traces of poly(ethylene-co-1-hexene)s prepared by 1-MMAO catalyst system (see Table 1): (a) run 4 (ethylene 7 bar, 1-hexene 5 ml); (b) run 5 (ethylene 8 bar, 1-hexene 5 ml); and (c) run 7 (ethylene 7 bar, 1-hexene 10 ml).

90°, and the number of transients accumulated was ca. 8000. The polymer solutions were prepared by dissolving polymers in *o*-dichlorobenzene-*d*<sub>4</sub>.

Molecular weight and the molecular weight distributions of the resultant polymers were measured at 145°C by means of gel-permeation chromatography (Waters 150 CV (with Shodex MS/80 column), or Tosoh 8121GPC/HT (with polystyrene gel column, TSK gel GMHHR-H(20)HT × 3)) using *o*-dichlorobenzene containing 0.05 % (w/v) 2,6-di-*tert*-butyl-*p*-cresol as solvent and the calibration with standard polystyrene samples.

Differential scanning calorimetric (DSC) data for the resultant copolymers were recorded by means of DSC6100 (Seiko Instruments) under nitrogen atmosphere (conditions: heating from 40 to 150°C (10°C/min), cooling from 150 to 40°C (5°C/min)).

The analysis data by cross-fractionation chromatography (CFC) were recorded by means of CFC T-150B (Dia Instruments) with *o*-dichlorobenzene as an extraction solvent. Approximately 30 mg/10 ml of sample (run 4, 20 mg/ml) was loaded onto a column of insert packing with slow cooling, followed by stepwise elution from the column at 0, 10, 20, 30, 40, 45, 49, 52, 55, 58, 61, 64, 67, 70, 73, 76, 79, 82, 85, 88, 91, 94, 97, 100, 102, 120, 140°C (samples, run 4) at a flow rate of 1.0 ml/min. Each eluted polymer solution was automatically sent to the GPC section (column AD806MS × 3, 140°C) of the CFC system equipped with an infrared detector.

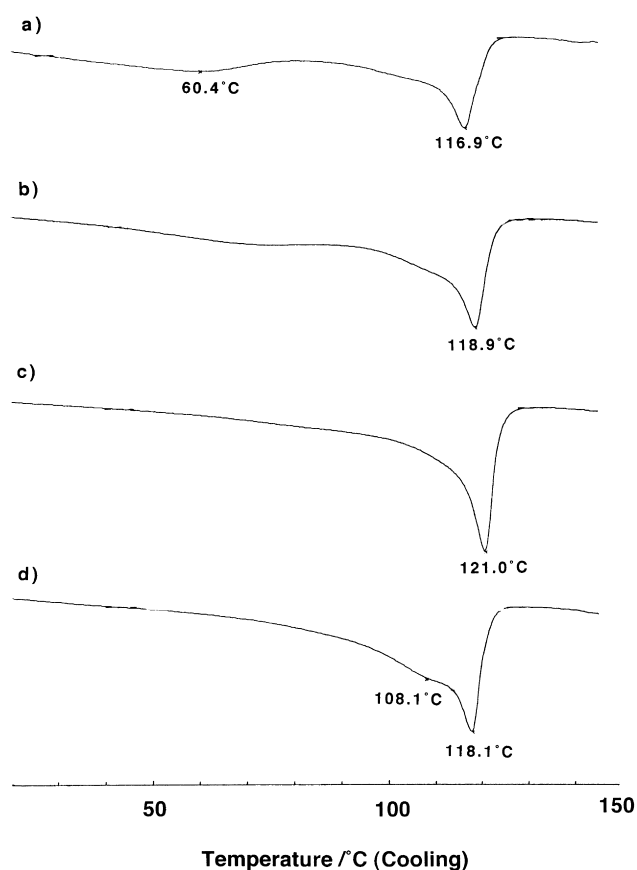


Fig. 2. DSC thermograms (offset scale) for poly(ethylene-co-1-hexene)s prepared by 1-MMAO catalyst system (see Table 1): (a) run 1 (ethylene 4 bar, 1-hexene 5 ml); (b) run 2 (ethylene 5 bar, 1-hexene 5 ml); (c) run 4 (ethylene 7 bar, 1-hexene 5 ml); (d) run 7 (ethylene 7 bar, 1-hexene 10 ml).

## 2.2. Copolymerization of ethylene with $\alpha$ -olefin

The catalytic ethylene/ $\alpha$ -olefin ( $\alpha$ -olefin = 1-hexene, 1-octene, and 1-decene) copolymerizations were performed by using a 100 ml scale autoclave. Typical reaction procedure (Table 1, run 2) is as follows: heptane (30 ml), MMAO (5.8 wt% (Al) in hexene, 10.0 mmol) and 1-hexene (5 ml) were added into the autoclave filled with nitrogen, and the reaction apparatus was then replaced with ethylene at 1 bar. The toluene solution of [1,8-C<sub>10</sub>H<sub>6</sub>(NSi<sup>t</sup>BuMe<sub>2</sub>)<sub>2</sub>]TiCl<sub>2</sub> **1** (10  $\mu$ mol) was then introduced into the autoclave, the autoclave was then pressurized with ethylene upto 4 bar. The reaction mixture was stirred for 10 min (50°C), and the polymerization was terminated with the addition of ethanol (15 ml). The solution was then poured into ethanol (100 ml) containing HCl, and the resultant white precipitate was adequately washed with ethanol and then with water dried in vacuo for several hours.

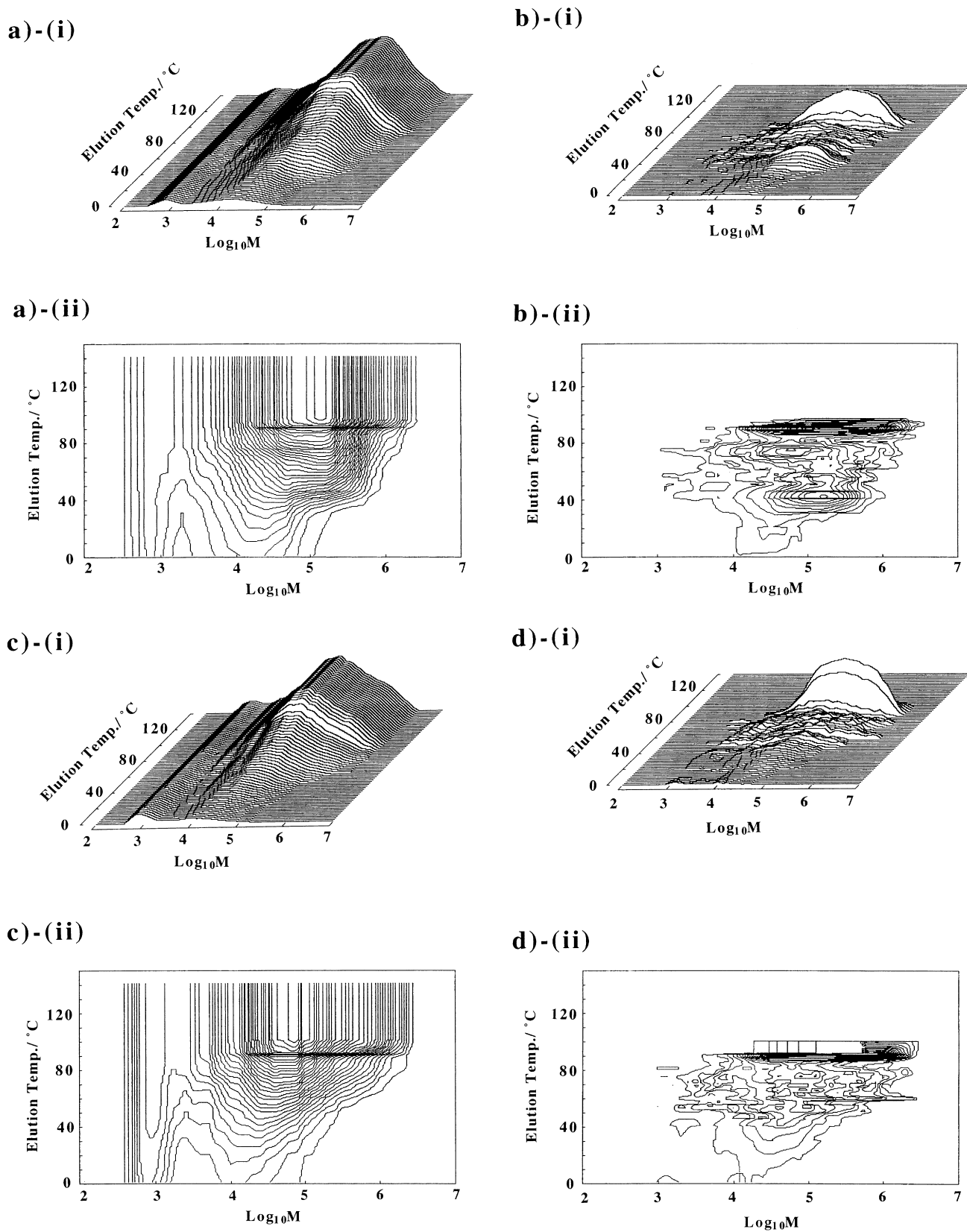


Fig. 3. (i) Bird's eye views and (ii) the corresponding contour maps of poly(ethylene-co-1-hexene)s prepared by 1-MMAO catalyst (see Table 1): (a) run 2 (integral-type); (b) run 2 (differential-type); (c) run 4 (integral-type); (d) run 4 (differential-type).

Table 3  
Selected GPC data of poly(ethylene-*co*-1-hexene)s by cross-fractionation chromatography

Sample run no.	Elution temperature (°C)	Relative extent in copolymer (wt%)	$M_w^a (\times 10^{-4})$	$M_w/M_n^a$
2	20–30	2.67	$7.72 \times 10^4$	3.04
	30–40	8.76	$1.46 \times 10^5$	5.92
	40–45	7.40	$1.64 \times 10^5$	7.18
	58–61	2.37	$1.65 \times 10^5$	6.27
	70–73	4.65	$1.85 \times 10^5$	8.72
	73–76	4.72	$1.73 \times 10^5$	10.47
	85–88	5.25	$3.16 \times 10^5$	4.72
	88–91	11.31	$3.69 \times 10^5$	4.74
	91–94	4.38	$6.31 \times 10^5$	4.20
	94–97	1.27	$6.24 \times 10^5$	3.37
4	20–30	3.47	$4.02 \times 10^4$	5.87
	30–40	4.09	$4.39 \times 10^4$	4.76
	40–45	2.89	$5.52 \times 10^4$	4.34
	58–61	3.88	$2.84 \times 10^5$	11.24
	70–73	4.10	$2.03 \times 10^5$	10.18
	73–76	4.30	$2.14 \times 10^5$	12.89
	85–88	5.16	$2.24 \times 10^5$	5.56
	88–91	15.94	$3.31 \times 10^5$	5.04
	91–100	10.71	$5.60 \times 10^5$	4.62

<sup>a</sup> Detailed conditions, see Section 2.

### 3. Results and discussion

#### 3.1. Copolymerization of ethylene with 1-hexene by [1,8- $C_{10}H_6(NSi^tBuMe_2)_2]TiCl_2$ -MMAO catalyst

It was revealed that **1** showed relatively high catalytic activity for copolymerization of ethylene with 1-hexene in the presence of MMAO (Tables 1 and 2). MMAO was chosen in this copolymerization, because the catalyst system in *n*-heptane showed the highest activity on the ethylene homopolymerization, and the use of toluene in place of *n*-heptane, or the use of MAO in place of MMAO showed the lower catalytic activity [56]. We speculated in the previous report [56] that this is probably due to that toluene coordinate to the catalytically active species as was previously postulated in 1-hexene polymerization by **2**-MMAO catalyst [31]. The results for copolymerization of ethylene with 1-hexene under various conditions are summarized in Tables 1 and 2.<sup>3</sup>

It was revealed that the observed catalytic activity was somewhat lower than that for ethylene homopolymerization (177 kg-PE/(mol-Ti h bar), ethylene 4 bar, 60°C, 1 h), or that for ethylene/1-butene copolymerization (150 kg-

polymer/(mol-Ti h bar), ethylene 6 bar, 1-butene 20 g, 70°C, 1 h) [56]. The reason for the lower activity might be due to the fact that rather bulky 1-hexene than 1-butene disturb olefin coordination or insertion by the steric hindrance in this catalysis under these polymerization conditions.

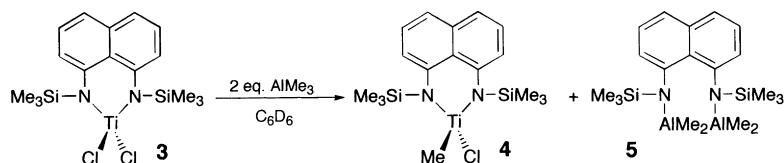
The polymer yields slightly increased under higher ethylene pressures (runs 1 and 2 → runs 4 and 5), with the decrease of 1-hexene contents in the resultant poly(ethylene-*co*-1-hexene)s. The observed catalytic activity, however, decreased at higher ethylene pressure (ex. 79.5 kg-polymer/(mol-Ti h bar), run 1 → 65.4 kg-polymer/(mol-Ti h bar), run 4) although the reason is not clear at this moment. The low catalytic activities were observed if the reactions were performed at low temperatures (0 and 24°C, Table 2), and the activities did not change between 40 and 60°C.

The molecular weight distributions for the resultant copolymers were, relatively broad as we can see from their GPC traces (Fig. 1), consisting of a mixture of high and low molecular weight copolymers. These results are different from those for poly(ethylene-*co*-1-butene)s prepared by the same catalyst [56], and the reason for the difference is somewhat not clear at this moment. The molecular weight for the resultant copolymer was relatively high ( $M_w = 285 \times 10^4$ ), if the reaction was carried out at low temperature (run 10, 24°C).

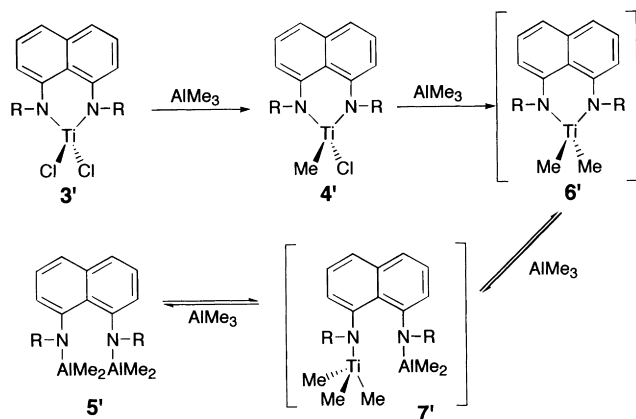
DSC thermograms of these copolymers (Fig. 2) showed relatively broad traces, suggesting that these copolymers consist of several copolymer compositions. The relative amount of low temperature peak (60.4°C, Fig. 2a) decreased under higher ethylene pressures (Fig. 2a, run 1 → Fig. 2c, run 4) accompanying the increase of  $T_m$  value (116.9 → 118.9 → 121.0°C). Only one  $T_m$  peak was thus apparently observed with the copolymer for lower 1-hexene content (Fig. 1c, run 4). These results indicate that the main composition of these copolymers consisted of copolymer with both high and low 1-hexene contents.

The above copolymers were also analyzed by CFC method, and the results are summarized in Fig. 3 (bird's eye views and the contour maps, differential and integral type). The selected GPC data for the fractionated copolymers are also summarized in Table 3. This result clearly indicates that the copolymer prepared by **1** (run 2) consisted of at least two compositions; copolymer fractionated at low elution temperature which would probably correspond to that with high 1-hexene content, and copolymer fractionated at relatively high temperature which would also correspond to that with low 1-hexene content (Table 3). The extent of copolymer fractionated at low temperature decreased if the polymerization was carried out at higher ethylene pressure (run 2, 5 bar → run 4, 7 bar) as shown in Fig. 3. These results are nicely corresponded to their DSC thermograms in which the extent of low  $T_m$  peaks decreased under higher ethylene pressure with the decrease of 1-hexene content (Fig. 2b → Fig. 2c). In addition, broad  $M_w/M_n$  values for

<sup>3</sup> We previously reported one experimental result concerning ethylene/1-hexene copolymerization with **1**-MMAO catalyst [55,56]. Polymerization activity 600 kg-polymer/mol-Ti h, SCB (side chain branching) 32.4/1000 carbons,  $T_m$  121.4°C,  $M_n = 7.35 \times 10^4$ ,  $M_w/M_n = 4.8$ : conditions, **1** 17.5 μmol, MMAO (Al/Ti = 1000), 1-hexene 10 ml, heptane 300 ml, ethylene 4 bar, 60°C, 1 h, 500 ml autoclave.



Scheme 1.



Scheme 2.

the copolymer at each elution temperature strongly suggest that these catalytic reactions did not proceed with a single-site nature.

The  $M_w/M_n$  value for the resultant poly(ethylene-*co*-1-hexene) did not improve even if the polymerization was stopped only at 3 min under the same conditions of run 4 (polymer yield 357 mg, polymerization activity 102 kg-polymer/(mol-Ti h bar),  $M_w = 77.7 \times 10^4$ ,  $M_w/M_n = 7.7$ , ethylene 7 bar, 1-hexene 5 ml), as we previously demonstrated the low  $M_w/M_n$  value on ethylene homopolymerization by the same catalyst [56]. This result suggests that broad  $M_w/M_n$  value for these copolymers would not be due to the catalyst deactivation under these reaction conditions, and thus suggest the existence of several catalytically active species. In addition, attempts for 1-hexene polymerization with 1-MMAO gave trace amounts of poly(1-hexene) under the same conditions.<sup>4</sup>

It has already been reported that the reaction of [1,8- $C_{10}H_6(NSiMe_3)_2$ ]TiCl<sub>2</sub> (**3**) with a prescribed amount of AlMe<sub>3</sub> gave [1,8- $C_{10}H_6(NSiMe_3)_2$ ](AlMe<sub>3</sub>)<sub>2</sub> (**5**, Scheme 1)<sup>1</sup> [57]. In this case, the expected dimethyl complex could not be observed, and [1,8- $C_{10}H_6(NSiMe_3)_2$ ]Ti(Me)Cl (**4**) was the major product after 24 h at room temperature. On the other hand, **5** could be formed almost exclusively if the reaction was performed at 55°C for several hours. However, only monomethyl complex was observed if [1,8- $C_{10}H_6(NSi^iPr_3)_2$ ]TiCl<sub>2</sub> was used in place of **3**.

We assume that the formation of **5** from **3** or **4** takes place with stepwise reaction mechanism, and dimethyl complex

(**6'**) and monodentate titanium-amide species (**7'**) would be thus considered as the possible reaction intermediates (Scheme 2)<sup>5</sup>. If the cationic species derived from **6'** and **7'** would be both active for olefin polymerization, it would be thus possible to explain the above polymerization results, i.e. there are at least two catalytically active species and the copolymer composition is highly dependent upon the reaction conditions. In addition, it might also be possible to speculate that the equilibrium between **6'** and **7'** would be dependent upon the kind of olefin used as well as the polymerization conditions, not only because the polymerization activities were significantly different between homopolymerization of ethylene and 1-hexene, but also because the resultant copolymer composition was highly dependent upon the reaction conditions such as ethylene pressure, reaction temperature.

### 3.2. Copolymerization of ethylene with 1-octene, 1-decene [1,8- $C_{10}H_6(NSi^iBuMe_2)_2$ ]TiCl<sub>2</sub>-MMAO catalyst

**1** also exhibited relatively high catalytic activity for copolymerization of ethylene with 1-octene and with 1-decene (Tables 4 and 5). It was revealed that 1-decene or 1-octene could be incorporated in the resultant copolymer under these reaction conditions. The polymer yields apparently increased with the increase of ethylene pressure (runs 13 and 14 → runs 15 and 16) in the case of copolymerization of ethylene with 1-octene. The relative amounts of low molecular weight copolymer in both poly(ethylene-*co*-1-octene)s and poly(ethylene-*co*-1-decene)s were lower than those in poly(ethylene-*co*-1-hexene)s, as we can see in their GPC traces (Figs. 4 and 5). The DSC thermograms of poly(ethylene-*co*-1-octene)s showed a relatively sharp  $T_m$  peak (Fig. 6a and b). On the other hand, those of poly(ethylene-*co*-1-decene)s showed relatively high and low  $T_m$  peaks (Fig. 6c and d), suggesting that the copolymer consisted of poly(ethylene-*co*-1-decene)s with relatively high and low 1-decene contents.

### 3.3. Copolymerization of ethylene with 1-hexene, 1-octene by [ArN(CH<sub>2</sub>)<sub>3</sub>NAr]TiCl<sub>2</sub> (**2**)-MMAO catalyst system

As shown in Table 6, **2**-MMAO catalyst showed

<sup>4</sup> Reaction conditions, **1** 10 μmol, 1-hexene 10 ml, 50°C, 15 min. Only a trace amount of polymer or oligomer was observed after an extraction procedure.

<sup>5</sup> Although dimethyl complexes (**6'**) could not be observed, we believe, this did not exclude the possibility for the formation under the polymerization conditions, because the reaction is highly dependent upon the reaction temperature and the kind of bis(amido) ligands used, as was mentioned in this paper [57].

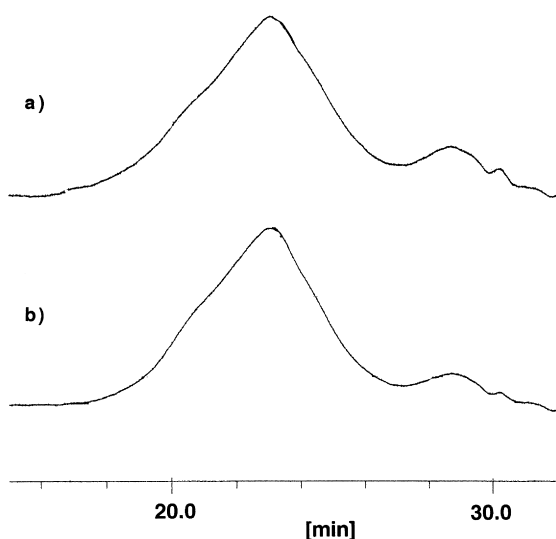


Fig. 4. GPC traces of poly(ethylene-*co*-1-octene)s prepared by 1-MMAO catalyst system (see Table 4): (a) run 15 (ethylene 7 bar, 1-octene 5 ml); (b) run 19 (ethylene 8 bar, 1-octene 10 ml).

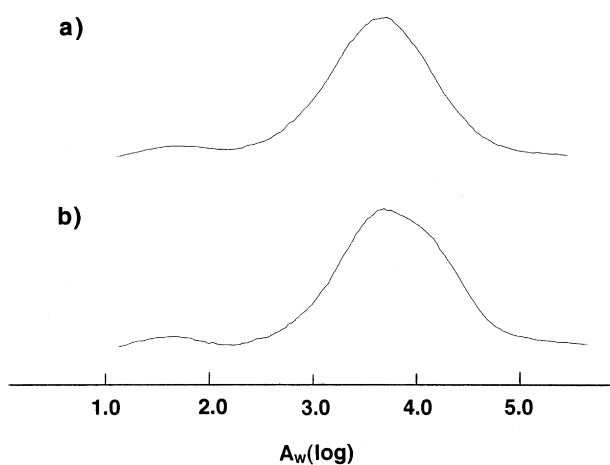


Fig. 5. GPC traces of poly(ethylene-*co*-1-decene)s prepared by 1-MMAO catalyst system (see Table 5): (a) run 21 (ethylene 6 bar, 1-decene 5 ml); (b) run 22 (ethylene 6 bar, 1-decene 10 ml).

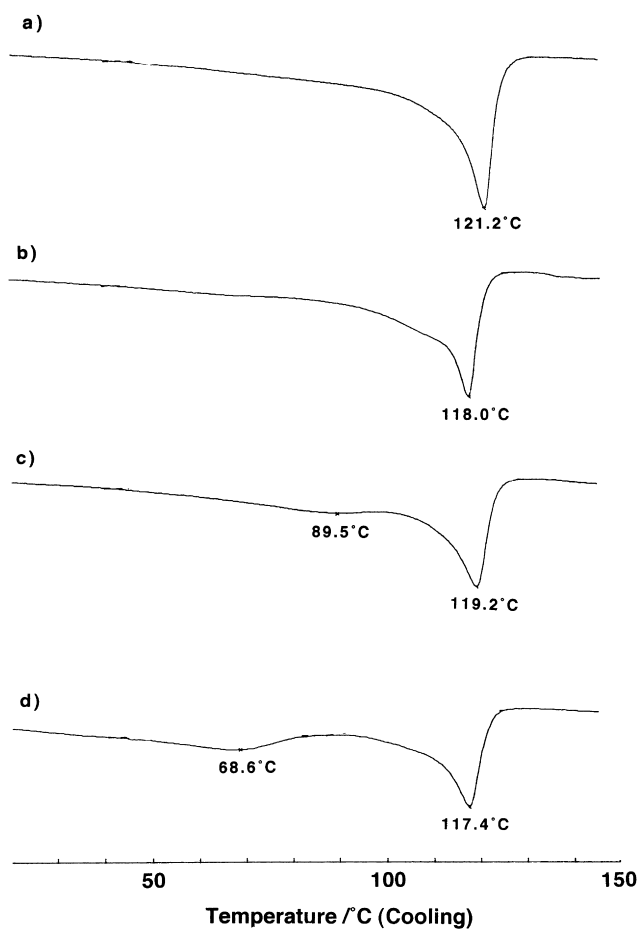


Fig. 6. DSC thermograms (offset scale) of (a), (b) poly(ethylene-*co*-1-octene)s, and (c), (d) poly(ethylene-*co*-1-decene)s prepared by 1-MMAO catalyst system (see Tables 4 and 5): (a) run 14 (ethylene 6 bar, 1-octene 5 ml); (b) run 18 (ethylene 7 bar, 1-octene 10 ml); (c) run 23 (ethylene 7 bar, 1-decene 5 ml); (d) run 24 (ethylene 7 bar, 1-decene 10 ml).

Table 4  
Copolymerization of ethylene with 1-octene with 1-MMAO catalyst system<sup>a</sup>

Run no.	Ethylene (bar)	1-Octene (ml)	Polymer (yield/g)	Activity <sup>b</sup>	$M_w^c (\times 10^{-4})$	$M_w/M_n^c$	SCB <sup>d</sup> (Me/1000C)	$T_m$ (°C)
13	5	5	0.67	53.6	32.2	7.4		120.7
14	6	5	0.76	50.7	63.9	8.1	14.5	121.2
15	7	5	1.18	67.4	59.9	8.2		
16	8	5	1.11	55.4	20.5	5.1		
17	6	10	1.05	70.0	72.3	8.5	23.5	118.3
18	7	10	1.06	60.6	27.2	6.3		118.0
19	8	10	1.29	64.5	47.7	5.9		

<sup>a</sup> Reaction conditions: 1 10  $\mu$ mol, *n*-heptane 30 ml, 50°C, 15 min, MMAO (5.8 wt% (Al) in hexane), Al/Ti (molar ratio) = 1000.

<sup>b</sup> Polymerization activity: kg-polymer/(mol-Ti h bar).

<sup>c</sup> GPC data in *o*-dichlorobenzene vs. polystyrene standard.

<sup>d</sup> Side chain branching (SCB) = methyl/total 1000 carbon determined by FT-IR.

Table 5  
Copolymerization of ethylene with 1-decene with 1-MMAO catalyst system<sup>a</sup>

Run no.	Ethylene (bar)	1-Decene (ml)	Polymer (yield/g)	Activity <sup>b</sup>	$M_w^c (\times 10^{-4})$	$M_w/M_n^c$	SCB <sup>d</sup>	$T_m$ (°C)
20	5	5	1.45	116				
21	6	5	1.04	69.3	14.6	3.7		118.1, 84.0
22	6	10	1.31	87.3	20.2	4.2	28.5	117.2, 58.5
23	7	5	1.02	58.3	19.9	4.6	18.7	119.2, 89.5
24	7	10	1.65	94.3	17.5	3.8	25.7	117.4, 68.6

<sup>a</sup> Reaction conditions: 1 10  $\mu$ mol, *n*-heptane 30 ml, 50°C, 15 min, MMAO (5.8 wt% (Al) in hexane), Al/Ti (molar ratio) = 1000.

<sup>b</sup> Polymerization activity: kg-polymer/(mol-Ti h bar).

<sup>c</sup> GPC data in *o*-dichlorobenzene vs. polystyrene standard.

<sup>d</sup> Side chain branching (SCB) = methyl/1000 carbon.

Table 6  
Copolymerization of ethylene with  $\alpha$ -olefin with 2-MMAO catalyst system<sup>a</sup>

Run no.	Catalyst ( $\mu$ mol)	$\alpha$ -Olefin	$\alpha$ -Olefin (ml)	Ethylene (bar)	Polymer (yield/g)	Activity <sup>b</sup>	$M_w^c (\times 10^{-3})$	$M_w/M_n^c$
25	10	1-Hexene	5	7	5.51	315	9.76	1.98
26	2	1-Hexene	10	8	1.06	398	19.3	2.08
27	2	1-Hexene	10	9	1.22	407	22.5	1.87
28	2	1-Octene	10	8	1.29	484	22.4	1.67
29	2	1-Octene	10	9	1.18	393	20.1	1.71
30	2	1-Decene	10	8	0.47	176	18.5	1.78

<sup>a</sup> Reaction conditions: *n*-heptane 30 ml, 50°C, 10 min (run 25: 15 min), MMAO (5.8 wt% (Al) in hexane), Al/Ti (molar ratio) = 1000.

<sup>b</sup> Polymerization activity: kg-polymer/(mol-Ti h bar).

<sup>c</sup> GPC data in *o*-dichlorobenzene vs. polystyrene standard.

Table 7  
Monomer sequence distribution of ethylene/ $\alpha$ -olefin copolymers prepared by 2-MMAO catalyst system<sup>a</sup>

Run no.	$\alpha$ -Olefin	Triad sequence distributions <sup>b</sup> (%)						$\alpha$ -Olefin <sup>b</sup> (mol%)	$r_E \cdot r_X^c$
		EEE	EEX + XEE	XEX	EXE	XXE + EXX	XXX		
27	1-Hexene	11.06	27.70	15.22	17.40	9.69	18.93	46.0	0.90
28	1-Octene	22.43	17.24	17.11	18.72	–	24.50	43.2	1.54
29	1-Octene	21.90	26.10	15.39	19.37	–	17.24	36.6	1.05

<sup>a</sup> Detailed reaction conditions, see Table 6.

<sup>b</sup> Calculated based on <sup>13</sup>C NMR spectra, X =  $\alpha$ -olefin.

<sup>c</sup>  $r_E \cdot r_X = 4[EE][XX]/[EX]^2$ ,  $[EE] = [EEE] + [EEX + XEE]/2$ ,  $[EX] = [EEX + XEE]/2 + [XEX] + [EXE] + [XXE + EXX]/2$ ,  $[XX] = [XXX] + [XXE + EXX]/2$ .

higher catalytic activity than 1-MMAO catalyst for copolymerization of ethylene with 1-hexene, 1-octene in *n*-heptane. In addition, the molecular weight distributions for the resultant copolymers were relatively narrow in this catalysis, and these results strongly suggest that these polymerizations proceed with the nature of the single-site catalysis. It is also important to note that the resultant copolymers were high  $\alpha$ -olefin contents (36.6–46.0 mol%, Table 7). Attempts to prepare copolymer with low  $\alpha$ -olefin contents seemed difficult due to its higher relative rates for 1-hexene and 1-octene than that for ethylene.

These results should be an interesting contrast because the resultant copolymers are highly dependent upon the type

of ligand used among these 12e titanium(IV) complexes having 6-membered chelate bis(amide) structure. We believe at this stage that the remarkable difference observed here is probably due to its steric factors of the ligand, or the electronic nature of metal–alkyl bond. This information should be, we believe, potentially important for design of olefin polymerization catalyst complex for preparing precise copolymer (molecular weight, monomer sequence distributions, comonomer contents, etc.).

Triad sequence distribution for both poly(ethylene-*co*-1-hexene) and poly(ethylene-*co*-1-octene) prepared by 2 are summarized in Table 7 [59,60] (these calculations were made using <sup>13</sup>C NMR spectra of copolymers). The  $r_E \cdot r_H$



and  $r_E \cdot r_O$  values ( $r_E$ ,  $r_H$ , and  $r_O$  are relative monomer reactive ratios) were almost 1, which indicates that these copolymerization took place in a random manner.<sup>6</sup> This is very similar to poly(ethylene-co-1-butene)s prepared by 1-MMAO catalyst and by  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{TiCl}_2\text{-Al}(\text{i-Bu})_3/\text{Ph}_3\text{C}[\text{B}(\text{C}_6\text{F}_5)_4]$  catalyst, in which these polymerizations take place in a random manner. This is also a good agreement with our previous speculation [15] that monomer sequence distribution in copolymer would be dependent upon the catalyst structure. We are now exploring the more details concerning the polymerization mechanism in this catalysis, and these results will be introduced in the near future.

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<sup>6</sup> The observed  $r_E \cdot r_H$  and  $r_E \cdot r_O$  values in catalyst 2 were ca. 1.0 which show that the copolymerization proceeded in a random manner, and this is a good agreement with our previous speculation. However, as you can see, the sequence distributions were somewhat different: the contents in XXE + EXX sequence (in runs 28 and 29) were almost 0. This point is actually not so clear at this moment. Attempt for taking CFC (elution from room temperature) data was not successful due to its high 1-octene and 1-hexene content, although the  $M_w/M_n$  values in this catalysis were 1.67 and 1.71, respectively, which indicate that these copolymerizations take place in a single-site nature. This might be due to the electronic and steric nature of this catalysis.

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