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Polymerization of 1,5-Hexadiene by Half-Titanocenes−MAO Catalyst Systems: Factors Affecting the Selectivity for the Favored Repeated 1,2-Insertion

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ABSTRACT: Polymerization of 1,5-hexadiene (HD) by Cp*TiCl$_2$(OAr) (**1**, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$), [Me$_2$Si(C$_5$Me$_4$)(N^t-Bu)]TiCl$_2$ (**2**), [Me$_2$Si(Ind)$_2$]ZrCl$_2$ (**3**), and Cp$_2$ZrCl$_2$ (**4**) was explored in the presence of methylaluminoxane (MAO). Both **1** and **3** exhibited the remarkable catalytic activities, and the resultant poly(HD)s were insoluble and possessed a sole glass transition temperature. On the basis of the DSC thermograms, ^{13}C CPMAS spectra, and the dynamic mechanical analysis (DMA) results, it turned out that **1** favored repeated 1,2-insertion rather than cyclization, affording a polymer-containing olefinic double bond (butenyl group) in the side chain with uniform distribution, whereas the polymerization by metallocenes (**3**, **4**) favored cyclization. Linked half-titanocene **2** showed lower catalytic activities with favored repeated insertion, affording high molecular weight poly(HD)s which possessed internal olefinic double bonds. (^{t}BuC$_5$H$_4$)TiCl$_2$(OAr) (**5**) exhibited lower catalytic activities and favored the repeated insertion; the Cp*-ketimide analogue, Cp*TiCl$_2$(N=C^{t}Bu$_2$) (**6**), also favored the repeated insertion, but the degree of the subsequent cross-linking was significantly higher than that by **1**. Both cross-linking and cyclization occurred in the polymerization by CpTiCl$_2$(N=C^{t}Bu$_2$) (**7**), and the distribution was not uniform. These results strongly suggest that nature of both cyclopentadienyl and anionic ancillary donor ligands directly affects selectivity for the repeated insertion as well as the microstructure in the resultant poly(HD)s.

Introduction

The design of efficient transition metal catalysts for precise olefin polymerization has been one of the most attractive subjects, especially because the evolution of new polyolefins with specified functions that cannot be prepared by the conventional catalyst can be expected.[1] Precise, efficient syntheses of functionalized polyolefins by controlled polymerization using transition metal catalysts have attracted considerable attention.[1−3] Two known strategies commonly employed toward this purpose are (1) direct copolymerization with functionalized monomers and (2) postpolymerization modification.[3] However, these approaches would face difficulties because the radical copolymerization generally required both ultrahigh pressure (ca. 1000 atm) and temperature, affording branched random copolymers,[3,4] as well as because of the catalyst poisoning and interaction of centered metal with functionalized monomers in transition metal catalyzed coordination copolymerization,[5−7] although recent rapid progresses in copper[8]/transition metal[9] mediated radical or free radical[10] copolymerization as well as in transition metal catalyzed coordination/insertion copolymerization with polar monomers[1e,2,3,5−7] offered new promising possibilities for this purpose. This is also because only very limited chemistry like a free radical grafting reaction is available to activate the completely saturated aliphatic molecular structure[3] as well as because transition metal catalyzed direct functionalization via catalytic C−H activation still requires harsh conditions, and the functionalizations were inefficient at this moment.[11]

Recently, considerable attention has been focused on the controlled incorporation of a reactive moiety that introduces functionalities through chemical modification,[2b] which has begun to be considered as the third approach. To propose the new environmentally benign synthetic route, we thus had focused on polymerization of nonconjugated diene (1,5-hexadiene, HD) to prepare functionalized polyolefin via the third approach by repeated insertion of HD, although most of the reported examples using ordinary catalysts such as zirconocene,[12,13] titanocene,[12c] half-zirconocene,[14a] and others[14b] favor cyclopolymerization incorporating the methylene−1,3-cyclopentane unit (Scheme 1, route A). This is because the promising possibilities like (i) incorporation of terminal olefinic double bond (route B) that would introduce a polar functionality in a controlled manner by chemical modification under mild conditions and/or (ii) controlled incorporation of cross-linking (route C) that improves chemical or heat resistance can be highly expected, if selectivity of the repeated insertion (route B and C) against cyclization can be improved by designing the complex catalyst employed.[15,16]

We communicated recently that Cp*TiCl$_2$(OAr) (**1**, OAr = O-2,6-^{i}Pr$_2$C$_6$H$_3$) exhibited remarkable catalytic activity for 1,5-hexadiene (HD) polymerization and favored the repeated 1,2-insertion (route B) rather than the cyclization (route A), affording a poly(HD)-containing olefinic double bond (butenyl group) in the side chain,[17] although the polymerization with ordinary metallocenes favored cyclopolymerization. Since a series of the nonbridged half-titanocenes containing anionic donor ligand (aryloxo, ketimide, etc.) displayed unique characteristics,[18] especially for copolymerization of ethylene with α-olefin,[18a−c,f] styrene,[18d,j] cyclic olefins,[18e,g,h] and 1,1-disubstituted-α-olefin,[18i] we thus explored the effect of cyclopentadienyl and anionic ancillary donor ligand in the HD polymerization using Cp′TiCl$_2$-

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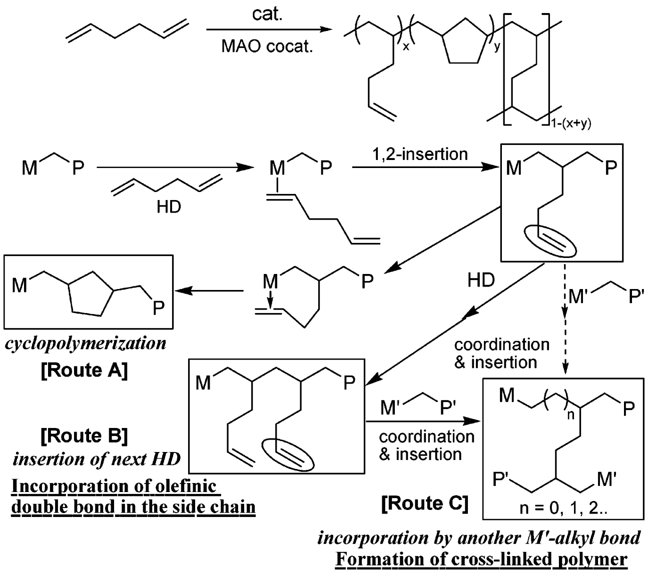
Scheme 1



(X) (Cp′ = Cp*, *tert*-BuC_5H_4, Cp, X = OAr, $N{=}C^tBu_2$) in the presence of MAO. In this paper, we wish to present our explored results for 1,5-hexadiene (HD) polymerization using linked half-titanocene, $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**2**), selected metallocenes, $[Me_2Si(indenyl)_2]ZrCl_2$ (**3**), Cp_2ZrCl_2 (**4**), and nonbridged half-titanocenes, such as $Cp'TiCl_2(OAr)$ [Cp′ = Cp* (**1**), *tert*-BuC_5H_4 (**5**)], and $Cp'TiCl_2(N{=}C^tBu_2)$ [Cp′ = Cp* (**6**), Cp (**7**)] in the presence of MAO (Chart 1), and explored factors to control the selectivity for the favored repeated insertion (route B, Scheme 1) in the HD polymerization based on full analysis of the resultant poly(HD)s (microstructures, thermal properties) by NMR spectra, DSC thermograms, and dynamic mechanical analyses (DMA).

Results and Discussion

1. Polymerization of 1,5-Hexadiene (HD) by Metallocenes and Half-Titanocenes−MAO Catalyst Systems: Remarkable Difference in the Selectivity of Repeated 1,2-Insertion. 1.1. HD Polymerization by 1−4−MAO Catalyst Systems. $Cp^*TiCl_2(OAr)$ (**1**) was chosen because **1** efficiently incorporates 1-hexene in ethylene/1-hexene copolymerization,[18b,c] and $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**2**), $[Me_2Si(indenyl)_2]ZrCl_2$ (**3**) and Cp_2ZrCl_2 (**4**) were also chosen for comparison.[12,19] MAO was prepared as white solids by removing toluene and $AlMe_3$ from the commercially available MAO (PMAO, Tosoh Finechem Co.) and was chosen as the cocatalyst because it was quite effective in the preparation of high molecular weight poly(ethylene-*co*-1-butene)s with narrow molecular weight distributions when **1** and **2** were employed as the catalyst precursors.[18a] The polymerization results by the **1**−MAO catalyst system are summarized in Table 1, and the results by **2**−**4**−MAO catalyst systems are summarized in Table 2.

It turned out that **1** showed notable catalytic activity (after an induction period at the beginning), affording insoluble gel polymer that possesses a weak glass transition temperature (T_g) measured by DSC thermograms shown below (Table 1). The activity decreased at lower HD concentrations, and a $CHCl_3$-soluble polymer that possesses high molecular weight with unimodal distribution ($M_n = 2.83 \times 10^5$, $M_w/M_n = 2.3$, run 14) was obtained. The activity was affected by the Al/Ti molar ratios, and the ratio of 30 000 (MAO 3.0 mmol) seemed to exhibit the remarkable activity under these conditions, and no significant changes in the T_g values were seen in the resultant poly(HD)s by varying the ratios.[20] In contrast, the observed catalytic activities by the **2**−MAO catalyst system were low, and the resultant poly(HD)s were soluble in THF and $CHCl_3$ and possessed rather high molecular weights ($M_n = (3.3-10.9) \times 10^4$, Table 2, runs 16−20). The activity decreased at lower HD concentrations.

The observed catalytic activities by **3** under the same conditions were remarkable, and both the activities and the thermal properties for the resultant polymers measured by DSC were affected by the HD concentration. The resultant poly(HD)s prepared at low HD concentrations (2.0−6.0 M) and/or prepared for short reaction time (5 min) were soluble in THF but became insoluble upon increasing the catalyst concentration and/or longer polymerization time due to the subsequent cross-linking accompanied partially (Table 2, runs 21−29). In contrast, the activities by **4** were low under the same conditions, and the resultant polymers were insoluble in $CHCl_3$ and THF due to the cross-linking accompanied partially.

1.2. Microstructure and Thermal Property Analyses for Poly(HD)s Prepared by 1−4−MAO Catalysts. Figure 1 shows selected DSC thermograms for poly(HD)s prepared by **1**,**3**,**4**−MAO catalysts under various initial HD concentrations. The resultant poly(HD)s prepared by **1** possessed a weak single glass transition temperature (T_g) in all cases, and the T_g values increased when the polymerizations were conducted at lower HD concentrations, probably due to the increased extent of cyclization. The T_g values for resultant poly(HD)s were independent of the polymerization time (Figure 2) and the Al/Ti molar ratios.[20] Both T_g and melting temperature (T_m) were observed for the poly(HD)s by **3**, and the intensity for the T_m values (ca. 101−103 °C) increased when the polymerizations were performed at lower HD concentrations due to the increased degree of cyclization. The resultant poly(HD)s prepared by **4** possessed typical T_g and T_m ascribed to *trans*-atactic methylene−1,3-cyclopentane (MCP) microstructure.[12e] These facts especially by **3** and **4** are almost similar to those reported previously.[12a,e,f,18] These DSC thermograms clearly indicate that the microstructure in resultant poly(HD) was highly affected by the nature of catalyst employed (**1**, **3**, **4**).

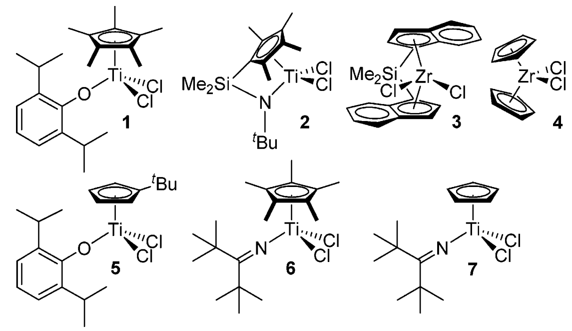
Figure 3 shows the ^1H NMR spectrum (in $CDCl_3$) for poly(HD) prepared by **1**−MAO catalyst under low HD concentration conditions (run 14). The spectrum suggests that the resultant polymer possessed a certain extent of terminal olefinic double bond (butenyl group) in the polymer side chain by repeated insertion (25 mol % of butenyl group remained based on HD inserted), although the polymerization by **3** and **4** favored cyclization. In contrast, it should be noted that the spectra for poly(HD)s prepared by **2**−MAO catalyst possessed both terminal and internal olefinic double bonds (Figure 4), and the ratio of internal/terminal olefins was dependent upon the HD concentration employed [Figure 4a,b; molar ratios for terminal/internal were (a) 36/1 (HD 8.0 M, run 16) and (b) 8.2/1 (HD 2.0 M, run 20)].[21] The observed difference in the ^1H NMR spectra for the poly(HD)s prepared by between **1** and **2** might be closely related to the observed difference in the molecular weights as well as the polymerization behavior, although it is clear that these catalyst precursors favored the repeated insertion. It is assumed that the formation of internal olefin is due to the β-hydrogen elimination after 2,1-insertion of HD (Scheme 2a) and/or isomerization of the terminal olefins (Scheme 2b). Since the extents of internal olefin were higher than those estimated by the M_n values (estimated by the integration ratio from the internal olefin as the chain end) and the ratio of internal olefin increased upon decreasing the HD concentration employed,

Table 1. 1,5-Hexadiene Polymerization by $Cp^*TiCl_2((O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (1)−MAO Catalyst[a]

run no.	cat./μmol	Al/M[b] × 10^{-3}	HD concn[c]	time/min	polymer yield/mg	activity[d] × 10^{-3}	TON[e] × 10^{-3}	T_g (T_m)[f]/°C	M_n[g] × 10^{-4}	M_w/M_n[g]
1	**1** (0.05)	60.0	8.0[h]	10	132	15.8	32.1	−3		–[i]
2	**1** (0.05)	60.0	8.0[h]	15	584	46.7	142	−1		–[i]
3	**1** (0.05)	40.0	8.0[h]	20	390	23.4	95	−2		–[i]
4	**1** (0.10)	30.0	8.0[h]	5	285	34.2	34.7	−5		–[i]
5	**1** (0.10)	30.0	8.0[h]	10	973	58.4	118	0		–[i]
6	**1** (0.10)	30.0	8.0[h]	20	1240	37.2	151	2		–[i]
7	**1** (0.10)	30.0	8.0[h]	20	1250	37.5	152	2		–[i]
8	**1** (0.10)	30.0	8.0[h]	30	1570	31.4	191	5		–[i]
9	**1** (0.10)	50.0	8.0[h]	20	1354	40.6	165	0		–[i]
7	**1** (0.10)	30.0	8.0[h]	20	1250	37.5	152	2		–[i]
10	**1** (0.10)	10.0	8.0[h]	20	1023	30.7	125	4		–[i]
11	**1** (0.10)	5.0	8.0[h]	20	634	19	77.2	2		–[i]
7	**1** (0.10)	30.0	8.0[h]	20	1250	37.5	152	2		–[i]
12	**1** (0.10)	30.0	6.0	20	890	26.7	108	5		–[i]
13	**1** (0.10)	30.0	4.0	20	401	12	48.8	11		–[i]
14	**1** (0.10)	30.0	2.0	20	167	5	20.3	23	28.3	2.3
15	**1** (0.10)	30.0	2.0	40	325	4.9	39.6	29		–[i]

[a] Conditions: 1,5-hexadiene (HD) + *n*-hexane total 20 mL, catalyst solution (toluene) 1.0 mL, MAO 3.0 mmol, at 25 °C. [b] Molar ratio of Al/Ti. [c] HD concentration charged (mol/L). [d] Activity in kg of polymer/(mol of Ti h). [e] HD consumed (mmol)/catalyst (mmol). [f] By DSC. [g] GPC data in THF vs polystyrene standards. [h] Under bulk polymerization conditions. [i] Insoluble gel polymer.

Chart 1



therefore, formation of the internal olefin should not be due to only the β-hydrogen elimination after 2,1-insertion but be due to the presence of two possibilities (β-hydrogen elimination and isomerization shown in Scheme 2). In both cases (polymerizations by **1** and **2**), 1-vinyltetramethylene unit formed by 2,1-insertion and cyclization followed by β-alkyl elimination (Scheme 3) were not observed in the resultant poly(HD)s, suggesting that these polymerizations especially by **1** take place with 1,2-insertion.[18a,22]

Microstructural Analysis by ^{13}C CPMAS and DDMAS Spectra. The ^{13}C CPMAS spectrum[23] for the poly(HD) prepared by **1** under the bulk (without solvent, neat) polymerization conditions (Figure 5a,g) showed that repeated 1,2-insertion (incorporation of olefinic double bond in the polymer side chain and subsequent cross-linking) was favored rather than cyclization (37 mol % of butenyl group remained based on inserted HD, estimated by the ^{13}C DDMAS spectrum for the same sample in run 6). In addition, the ^{1}H NMR spectrum for poly(HD) prepared by **1**−MAO catalyst at low HD concentration (run 14, Figure 3) showed 25 mol % of butenyl group remained based on HD inserted, and this value is the same as that estimated from the ^{13}C DDMAS spectrum (25 mol %, CPMAS: Figure 5d). Moreover, no resonances due to internal olefin or vinyl group were observed, clearly indicating that isomerization and/or β-hydrogen elimination after 2,1-insertion (and/or vinyltetramethylene unit after 2,1-insertion[15]) shown in Schemes 2 and 3 did not take place. A certain degree of cross-linking by insertion of the butenyl group with another Ti−alkyl bond was found to be accompanied because the content of the butenyl group decreased gradually for longer reaction hours (13 mol % after 40 min under the same conditions of runs 14 and 15 in Table 1), and the resultant poly(HD) became insoluble in THF.

In contrast, no olefinic resonances were seen in ^{13}C CPMAS spectra for polymers prepared by **4**, and a typical MCP microstructure was observed (Figure 5c,f,I,j).[12a] The content of butenyl group in the poly(HD) by **3** under bulk conditions was 24 mol % (run 23, Figure 5b), and the content decreased for the polymer prepared at lower HD concentration (9.1 mol %, run 29, Figure 5e). These are similar to the fact that cyclization took place (96.8%) predominantly under lower HD conditions (HD 0.84 M).[12f,19]

*Dynamic Mechanical Analysis for Poly(HD)s Prepared by **1**−**4**−MAO Catalysts.* Dynamic mechanical analyses (DMA) were explored to observe differences in both the microstructure and the thermal properties for resultant poly(HD)s prepared by **1**−**4**−MAO catalysts (Figure 6). Poly(HD) prepared by **4** (run 30) showed a similar property to that reported previously,[12e] indicating that cyclopolymerization took place predominantly accompanied by the partial cross-linking with low extent. In contrast, poly(HD) prepared by **1** possessed high tan δ value (at ca. 20 °C) with narrow peak width, and the observed E' value (storage module) at 60 °C was the lowest among these samples. Moreover, the $\Delta E'$ ($E'_{-40°\mathrm{C}} - E'_{60°\mathrm{C}}$) was relatively large, and E' reached to a rubbery plateau modulus (constant value). These results indicate that repeated insertion of HD took place preferably and also strongly suggest that the distribution of cross-linking formed by the subsequent insertion of the butenyl group with other Ti species is uniform. The DMA result for poly(HD) by **2** was similar to that by **1**, strongly suggesting that **2** favored repeated insertion and the cross-linking distribution in the resultant polymer was uniform. The polymer by **3** possessed a lower tan δ value (at ca. −10 °C) with a rather broad peak width, suggesting the copresence of both cyclization and cross-linking. The result also suggests that the cross-linking distribution was not uniform like **1**. On the basis of these results, it is clear that the degree of cyclization increased in the order **4** ≫ **3** > **1**, **2**, and the cross-linking distribution was influenced by the nature of catalyst.

Taking into account the above facts, the HD polymerization results by **1**−**4**−MAO catalysts are summarized as follows:

(1) $Cp^*TiCl_2(OAr)$ (**1**) favored the repeated HD 1,2-insertion rather than cyclization, affording polymer with olefinic double bond (butenyl group) in the side chain, and a certain extent of cross-linking accompanied after the repeated insertion. The resultant poly(HD)s by **1** possessed uniform compositions (cross-linking distribution is uniform).

Table 2. Polymerization of 1,5-Hexadiene by [$Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (2), [$Me_2Si(indenyl)_2]ZrCl_2$ (3), and Cp_2ZrCl_2 (4)−MAO Catalysts[a]

run no.	cat./μmol	HD concn[b]	time/min	polymer yield/mg	activity[c] × 10^{-3}	TON[d] × 10^{-3}	T_g (T_m)[e]/°C	M_n[f] × 10^{-4}	M_w/M_n[f]
16	**2** (0.50)	8.0[g]	20	368	2.21	8.96	2	8	2.5
17	**2** (0.50)	8.0[g]	60	532	1.06	13.0	2	10.9	2.4
18	**2** (0.50)	6.0	20	287	1.72	6.99	8	6.1	2.4
19	**2** (0.50)	4.0	20	207	1.24	5.04	15	4.1	1.8
20	**2** (0.50)	2.0	20	102	0.61	2.48	33	3.3	1.6
21	**3** (0.05)	8.0[g]	5	218	52.3	53.1	−8[i]	14.5	2
22	**3** (0.05)	8.0[g]	5	218	52.3	53.1	−9[i]	12.1	1.9
23	**3** (0.05)	8.0[g]	10	876	105	213	−4[i]		−[h]
24	**3** (0.05)	8.0[g]	15	1148	91.8	280	−3[i]		−[h]
25	**3** (0.05)	6.0	10	300	36.0	73.0	0 (99)	8.7	1.8
26	**3** (0.05)	4.0	10	166	19.9	40.4	8 (103)	9.1	2.2
27	**3** (0.05)	2.0	10	56	6.7	14	33 (101)	4.1	1.4
28	**3** (0.05)	2.0	20	97	5.8	24	35 (101)	5.5	1.9
29	**3** (0.10)	2.0	20	313	9.4	38.1	6 (102)		−[h]
30	**4** (0.50)	8.0[g]	30	692	2.77	16.8	−4 (74)		−[h]
31	**4** (0.50)	6.0	30	538	2.15	13.1	−8 (79)		−[h]
32	**4** (0.50)	4.0	30	450	1.8	11	−8 (82)		−[h]
33	**4** (0.50)	2.0	30	248	0.99	6.04	−9 (85)		−[h]

[a] Conditions: 1,5-hexadiene (HD) + *n*-hexane total 20 mL, catalyst solution (toluene) 1.0 mL, MAO (prepared by removing toluene and $AlMe_3$ from PMAO-S) 3.0 mmol, at 25 °C. [b] HD concentration charged (mol/L). [c] Activity in kg of polymer/(mol of M h) (M = Ti, Zr). [d] HD consumed (mmol)/catalyst (mmol). [e] By DSC. [f] GPC data in THF vs polystyrene standards. [g] Under bulk polymerization conditions. [h] Contained insoluble gel polymer. [i] T_m peak was observed in small amount (T_m = 90−103 °C).

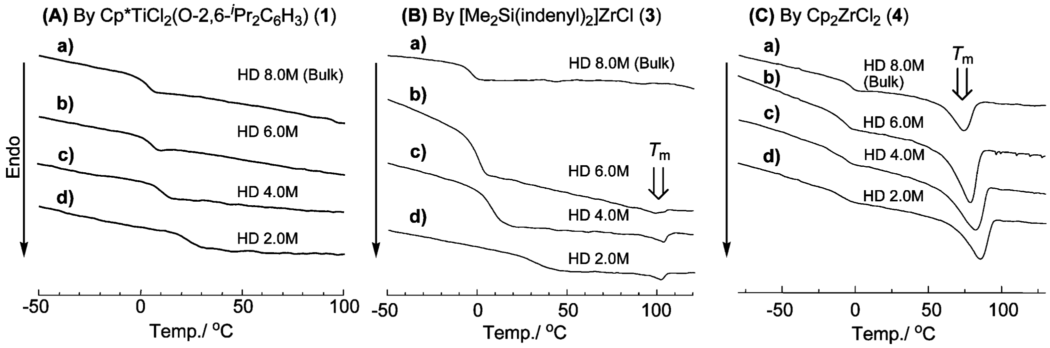


Figure 1. Selected DSC theromograms for poly(HD)s prepared by **1**,**3**,**4**−MAO catalyst systems. Polymerization conditions: (A) By **1**−MAO catalyst system (at 25 °C, 20 min): (a) HD 8.0 M (run 7), (b) 6.0 M (run 12), (c) 4.0 M (run 13), (d) 2.0 M (run 14). (B) By **3**−MAO catalyst system (at 25 °C, 10 min): (a) HD 8.0 M (run 23), (b) 6.0 M (run 25), (c) 4.0 M (run 26), (d) 2.0 M (run 27). (C) By **4**−MAO catalyst system (at 25 °C, 30 min): (a) HD 8.0 M (run 30), 6.0 M (run 31), 4.0 M (run 32), 2.0 M (run 33).

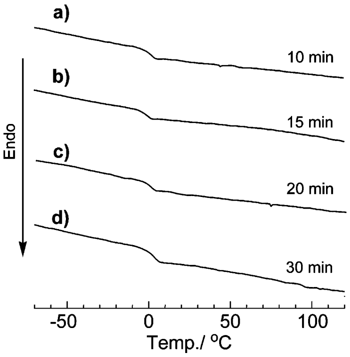


Figure 2. DSC thermograms for poly(HD)s prepared by **1**−MAO catalyst systems (HD 8.0 M at 25 °C). Polymerization time: (a) 10 min (run 5), (b) 15 min (run 2), (c) 20 min (run 6), (d) 30 min (run 8).

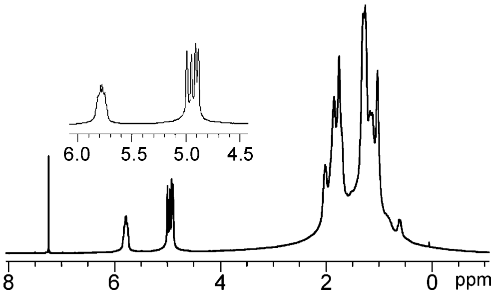


Figure 3. ^1H NMR spectrum (in $CDCl_3$ at 24 °C) for poly(HD) prepared by **1**−MAO catalyst (HD 2.0 M, 25 °C, 20 min, run 14).

(2) The observed catalytic activity in the polymerization by [$Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**2**) was somewhat lower than that by **1**, and the resultant poly(HD)s contained internal olefinic double bond, although **2** also favored the repeated insertion.

(3) Both repeated insertion and cyclization took place in the polymerization by [$Me_2Si(indenyl)_2]ZrCl_2$ (**3**), and degree of the cyclization increased if the polymerization was performed under low HD concentrations. DMA results for the resultant poly(HD)s prepared by **3** under high (bulk) HD concentration suggested that the copresence of both cyclization and cross-linking; the results also suggested that the cross-linking distribution was not uniform.

(4) Favored cyclization was observed in the polymerization by Cp_2ZrCl_2 (**4**), but the partial cross-linking was accompanied under these conditions; the cross-linking distribution was not uniform as suggested by the DMA result.

It is thus clear that the selectivity in the HD polymerization (cyclization, repeated insertion, Scheme 1) was highly dependent upon the nature of catalyst employed.

2. Exploring Factors for Favored Repeated Insertion of 1,5-Hexadiene (HD) in the Polymerization Catalyzed by Nonbridged Half-Titanocenes−MAO Systems. 2.1. HD Polymerization by 1,5−7−MAO Catalysts. On the basis of the

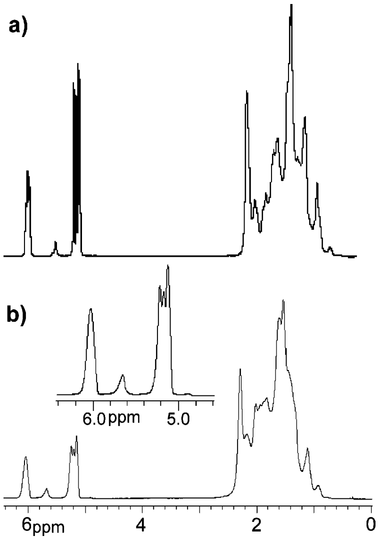
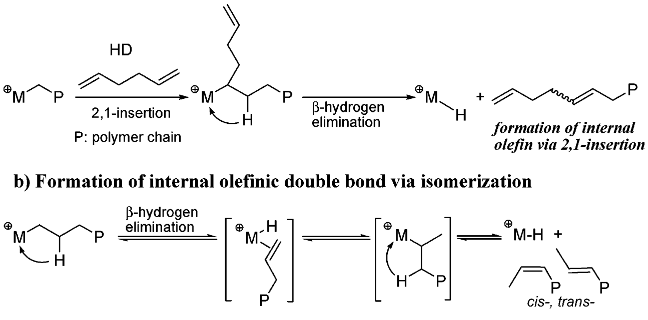


Figure 4. ^{1}H NMR spectra (in $CDCl_3$ at 24 °C) for poly(HD)s prepared by **2**−MAO catalyst (at 25 °C, 20 min): (a) HD 8.0 M (run 16), (b) 2.0 M (run 20).

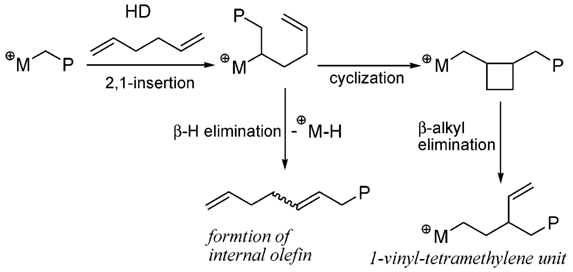
Scheme 2

a) Formation of internal olefinic double bond via 2,1-insertion

b) Formation of internal olefinic double bond via isomerization



Scheme 3



Not observed in the HD polymerization by **1** - MAO catalyst system

above facts, we realized that repeated 1,2-insertion was favored if $Cp^*TiCl_2(OAr)$ (**1**) was employed as the catalyst precursor in the HD polymerization. To obtain more detailed information for designing the efficient catalyst which possesses remarkable selectivity for the repeated HD insertion, we explored the effect of both cyclopentadienyl and anionic ancillary donor ligand in the polymerization using various half-titanocenes. $Cp'TiCl_2(OAr)$ [Cp′ = Cp* (**1**), *tert*-BuC_5H_4 (**5**)] and $Cp'TiCl_2(N{=}C^tBu_2)$ [Cp′ = Cp* (**6**), Cp (**7**)] were chosen because **5** showed better 1-hexene incorporation in the ethylene/1-hexene copolymerization[18b,c] and **7** showed remarkable catalytic activity in the copolymerization[18f] as well as because **6** also showed unique characteristics in ethylene/styrene copolymerization.[18j] The polymerization results under various conditions are summarized in Tables 3 and 4, and ^{13}C CPMAS spectra for the selected samples are shown in Figure 7.[23]

The observed catalytic activities by the *tert*-BuCp analogue **5** were lower than those by the Cp* analogue **1** under the same conditions (runs 3, 35−37, Table 3); the resultant poly(HD)s possessed a weak single glass transition temperature (T_g), and the T_g values increased when the polymerizations were conducted at low HD concentrations as seen in the polymerization by **1**, probably due to the increased extent of cyclization. Note that the observed activity was extremely low if $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)$ (**1′**)[24] was employed as the catalyst precursor (run 34), clearly indicating that the effect of *ortho*-substituent in the phenoxo ligand plays an important key role for exhibiting the remarkable catalytic activity as reported previously in the 1-hexene polymerization.[24]

The observed catalytic activities by the Cp*-ketimide analogue **6** were lower than those by the Cp*-aryloxo analogue **1**, and the resultant poly(HD)s were insoluble in THF in all cases. The T_g values for resultant poly(HD)s increased when the polymerizations were conducted at lower HD concentrations. In contrast, the observed activities by **7** were similar to those by **1** under various conditions; however, the resultant poly(HD) (prepared at low HD concentration, run 54) possessed rather broad molecular weight distributions.

2.2. Microstructure and Thermal Property Analyses for Poly(HD)s Prepared by 1,5−7−MAO Catalysts. Figure 7 shows ^{13}C CPMAS spectra for chosen poly(HD) samples[23] prepared by **1**,**5**−**7**−MAO catalyst systems, and Figures 8−10 show their DMA analyses results. Resonances ascribed to the olefinic double bonds due to the repeated insertion (and remained without incorporation by the other polymer chain) were observed in the ^{13}C CPMAS spectra for poly(HD)s prepared by **1**,**5**,**7**−MAO catalyst systems under high HD conditions, and the percentages of butenyl group remained were close when the polymerizations were performed under the same HD concentration conditions (35−37 mol %, runs 6, 36, 48; HD 8.0 M). Moreover, as shown in Figure 8, the resultant poly(HD)s prepared by the Cp*-aryloxo (**1**) and the *tert*-BuCp-aryloxo analogue (**5**) possessed high tan δ values with narrow peak width by DMA and the $\Delta E'$ ($E'_{-40°C} - E'_{60°C}$) was relatively large, and E' reached a rubbery plateau modulus (constant value). These results clearly suggest that the repeated insertion of HD took place preferably, and the incorporation of cross-linking is uniform. The T_g value (temperature at the maximum tan δ value) by DMA analysis for poly(HD)s prepared between by **1** was somewhat higher than **5**, and the E' value at rubbery plateau by **1** was slightly higher than that by **5**, probably due to the increased extent of cross-linking rather than cyclization by **1**.

Poly(HD) prepared by the Cp*-ketimide analogue (**6**) under high concentration (HD 8.0 M, run 44) possessed lower content of the butenyl group remained (17%, Figure 7c) than that by **1**, and the intensity of the olefins became negligible if the polymerization by **6** was performed at low HD concentrations (Figure 7d, run 47). Although these ^{13}C CPMAS spectra were somewhat analogous to those for poly(HD)s prepared by the **3** (and/or **4**)−MAO catalyst system, the reason for the low percentage was not due to the cyclization but due to the high degree of cross-linking strongly suggested by the DMA results (Figure 9). Since the resultant poly(HD) prepared by **6** under high concentration (run 44) possessed high tan δ values with narrow peak width (by DMA) and the $\Delta E'$ ($E'_{-40°C} - E'_{70°C}$) was large and E' reached a rubbery plateau modulus (constant value), these results thus indicate that repeated insertion of HD took place preferably, and the incorporation of cross-linking is uniform. The results clearly indicate that **6** also favored the

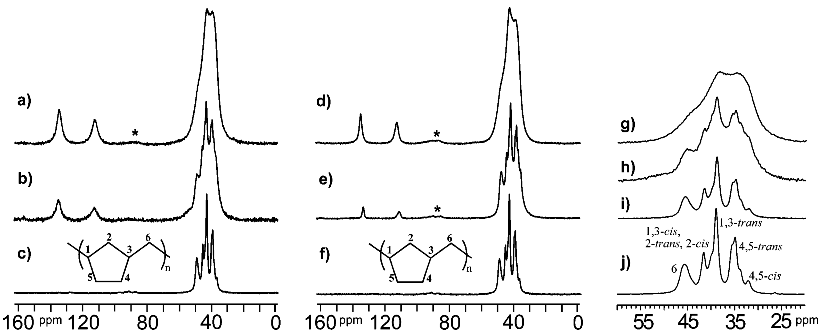


Figure 5. ^{13}C CPMAS spectra for poly(HD)s by **1**,**3**,**4**−MAO catalyst systems. Polymerization conditions: (a) **1** (HD 8.0 M, run 6), (b) **3** (HD 8.0 M, run 23), (c) **4** (HD 8.0 M, run 30), (d) **1** (HD 2.0 M, run 14), (e) **3** (HD 2.0 M, run 29), (f) **4** (HD 2.0 M, run 33), (g−j) expanded charts for (a), (e), (c), and (f), respectively. A mark * (ca. 90 ppm) is due to spinning sideband (resonances ca. 30−50 ppm, rotation 4000 Hz/75 MHz ^{13}C). Degrees of butenyl group that remained based on inserted HD were (a) 37%, (b) 24%, (d) 25%, and (e) 9.1%.

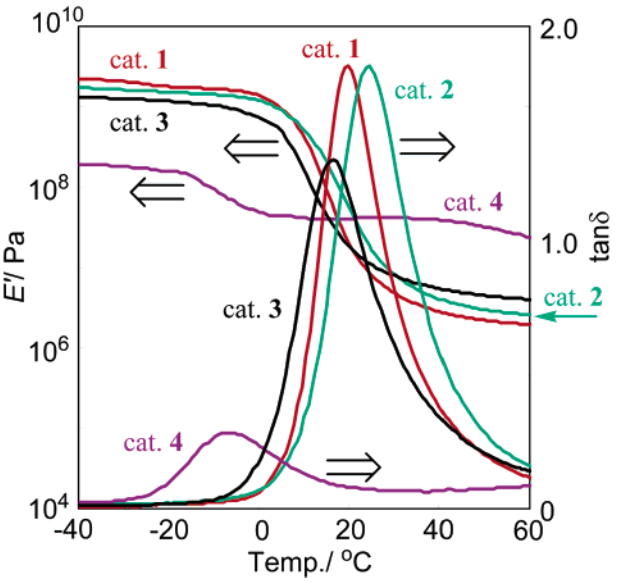


Figure 6. Temperature dependence in storage module (E') and loss factor, tan δ, for poly(HD)s prepared by **1** (run 6), **2** (run 17), **3** (run 23), and **4** (run 30)−MAO catalyst systems (measured by DMA, 1.0 Hz).

repeated HD insertion rather than cyclization, and the degree of cross-linking by **6** was much higher than that by **1**.[25] Although the favored repeated insertion was suggested in the HD polymerization by **6**, however, the resultant poly(HD) prepared under low HD concentration (run 47) possessed resonance due to the cyclization (ca. 45 ppm) in ^{13}C CPMAS (Figure 7d), and the polymer possessed a low tan δ value with broad bimodal distribution (Figure 10), strongly suggesting that a certain degree of cyclization accompanied and the cross-linking distribution was not uniform. Taking into account the results in the HD polymerization between by the Cp*-aryloxo analogue (**1**) and by the Cp*-ketimide analogue (**6**), it is clear that the anionic ancillary donor ligand strongly affects the selectivity in the HD polymerization as well as the distribution.

Poly(HD) prepared by the Cp-ketimide analogue (**7**) possessed a butenyl group in the side chain, and the percentage was close to those by the Cp*-aryloxo analogue (**1**). This may be due to the fact that **7** incorporated 1-hexene efficiently in the ethylene/1-hexene copolymerization.[18f] However, the DMA result (Figure 9) suggests that the tan δ value was low and the peak width was somewhat broad, suggesting that composition for the resultant poly(HD) by **7** was not uniform and the $\Delta E'$ ($E'_{-40\,°C} - E'_{70\,°C}$) was smaller than those by the Cp*-aryloxo analogue (**1**), Cp*-ketimide analogue (**6**).[26]

Taking into account the above facts that *nonbridged* half-titanocenes (**1**, **5**−**7**) favored the repeated 1,2-insertion in the HD polymerization, it turned out that the degree of subsequent cross-linking by incorporation into the other polymer chain as well as the cross-linking distribution was highly dependent upon the anionic ancillary donor ligand employed (aryloxo vs ketimide). Moreover, the composition in the resultant poly(HD)s prepared by the ketimide analogues (by **6** at low HD concentrations and by **7**) were not uniform. These results suggest that the aryloxo analogues **1** and **5** should be suited for this purpose to obtain poly(HD)s with higher *terminal* olefinic double bonds. We assume at this moment that the observed trend may be explained by the efficiency of 1-hexene incorporation in the ethylene/1-hexene copolymerization [e.g., r_E value, $r_E = k_{EE}/k_{EH}$, in the copolymerization at 40 °C: 32.8 by Cp_2ZrCl_2 (**4**),[27] 6.0 by Cp*$TiCl_2(N{=}C^tBu_2)$ (**6**),[18f] 2.65 by Cp*$TiCl_2$(O-2,6-^{i}Pr$_2C_6H_3$) (**1**)[18c]], in which the next monomer (HD in this case) will be efficiently incorporated rather than the coordination/incorporation of the side chain (or other olefinic double bonds in the side chain or other catalytically active species). We believe that the information presented here should be very important to pave the new methodology for preparation of polyolefins containing reactive terminal olefins at the side chain by using the well-defined complex catalysts.

Experimental Section

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 of reagent grade and were purified by the standard purification procedures. 1,5-Hexadiene (HD, >97%, Aldrich) was stored in the drybox in the presence of molecular sieves after passing through an alumina short column. *n*-Hexane and toluene (Kanto Chemical Co., Inc.) were used as anhydrous grades and stored in a bottle in the drybox under a nitrogen atmosphere in the presence of molecular sieves (mixture of 3A and 4A 1/16 and 13X). Cp*$TiCl_2$(O-2,6-^{i}Pr$_2C_6H_3$) [Cp* = C_5Me_5 (**1**)],[18a] (*tert*-BuC_5H_4)$TiCl_2$(O-2,6-^{i}Pr$_2C_6H_3$) (**5**),[18a] Cp*$TiCl_2$(O-2,6-^{t}Bu$_2C_6H_3$),[24] Cp*$TiCl_2(N{=}C^tBu_2)$ (**6**),[28] Cp$TiCl_2(N{=}C^tBu_2)$ (**7**),[28] and [$Me_2Si(C_5Me_4)(N^tBu)$]$TiCl_2$ (**2**)[29] were prepared according to previous reports. [Me_2Si(indenyl)$_2$]$ZrCl_2$ (**3**, Witco GmbH) and Cp_2ZrCl_2 (**4**, Kanto Chemical Co., Inc.) were used as received without further purification. Toluene and $AlMe_3$ in the commercially available methylaluminoxane [PMAO-S, 9.5 wt % (Al) toluene solution, Tosoh Finechem Co.] were taken to dryness under reduced pressure (at ca. 50 °C for removing toluene, $AlMe_3$, and then heated at >100 °C for 1 h for completion) in the drybox to give the white solids.

Molecular weights and the molecular weight distributions of the poly(1,5-hexadiene) were measured by means of gel-permeation chromatography (GPC) if the resultant poly(HD)s were soluble in THF. HPLC grade THF was used for GPC and were degassed prior

Table 3. Polymerization of 1,5-Hexadiene by (*tert*-BuC$_5$H$_4$)TiCl$_2$((O-2,6-^{i}Pr$_2$C$_6$H$_3$) (5)−MAO Catalyst[a]

run no.	cat. (μmol)	Al/M[b] × 10^{-3}	HD concn[c]	polymer yield/mg	activity[d] × 10^{-3}	TON[e] × 10^{-3}	T_g (T_m)[f]/°C	M_n[g] × 10^{-4}	M_w/M_n[g]
3	**1** (0.05)	40.0	8.0[h]	390	23.4	95	−2		–[i]
34	**1**[j] (1.00)	2.00	7.9[h]	7	0.02	0.09			
35	**5** (0.10)	20.0	7.9[h]	52	1.6	6.3			–[i]
36	**5** (0.50)	4.0	7.9[h]	335	2.01	8.16	−5		–[i]
37	**5** (1.00)	2.0	7.9[h]	633	1.90	7.71			–[i]
38	**5** (0.50)	2.0	7.9[h]	57	0.34	1.4			–[i]
36	**5** (0.50)	4.0	7.9[h]	335	2.01	8.16	−5		–[i]
39	**5** (0.50)	6.0	7.9[h]	304	1.82	7.4			–[i]
36	**5** (0.50)	4.0	7.9[h]	335	2.01	8.16	−5		–[i]
40	**5** (0.50)	4.0	6.0	168	1.01	4.09	0		–[i]
41	**5** (0.50)	4.0	4.0	128	0.77	3.12	−1		–[i]
42	**5** (0.50)	4.0	2.0	82	0.49	2.0	12	6.61	1.65

[a] Conditions: 1,5-hexadiene (HD) + *n*-hexane total 15 mL, catalyst solution (toluene) 1.0 mL, MAO (prepared by removing toluene and AlMe$_3$ from PMAO-S) 3.0 mmol, at 25 °C, 20 min. [b] Molar ratio of Al/Ti. [c] HD concentration charged (mol/L). [d] Activity in kg of polymer/(mol of Ti h). [e] HD consumed (mmol)/catalyst (mmol). [f] By DSC. [g] GPC data in THF vs polystyrene standards. [h] Under bulk polymerization conditions. [i] Contained insoluble gel polymer. [j] Cp*TiCl$_2$(O-2,6-^{t}Bu$_2$C$_6$H$_3$) was used in place of **1**.

Table 4. Polymerization of 1,5-Hexadiene by Cp′TiCl$_2$(N=C^{t}Bu$_2$) [Cp′ = Cp* (6), Cp (7)]−MAO Catalyst[a]

run no.	cat. (μmol)	HD concn[b]	time/min	polymer yield/mg	activity[c] × 10^{-3}	TON[d] × 10^{-3}	T_g (T_m)[e]/°C	M_n[f] × 10^{-4}	M_w/M_n[f]
43	**6** (0.10)[g]	7.9[h]	20	251	7.53	30.6			–[i]
44	**6** (0.10)	7.9[h]	20	255	7.65	31	5		–[i]
45	**6** (0.10)	6.0	20	174	5.22	21.2	8		–[i]
46	**6** (0.10)	4.0	20	141	4.23	17.2	12		–[i]
47	**6** (0.10)	2.0	20	81	2.4	9.9	20		–[i]
48	**7** (0.10)[g]	7.9[h]	10	699	41.9	85.1	7		–[i]
49	**7** (0.05)	7.9[h]	10	309	37.1	75.2			–[i]
50	**7** (0.05)[g]	7.9[h]	10	334	40.1	81.3			–[i]
51	**7** (0.05)	7.9[h]	10	132	15.8	32.1			–[i]
52	**7** (0.10)[g]	6.0	20	295	8.85	35.9	10		–[i]
53	**7** (0.10)[g]	4.0	20	159	4.77	19.4	25		–[i]
54	**7** (0.10)[g]	2.0	20	56	1.68	6.8	44	22.1	3.27

[a] Conditions: 1,5-hexadiene (HD) + *n*-hexane total 15 mL, catalyst solution (toluene) 1.0 mL, MAO white solid (prepared by removing toluene and AlMe$_3$ from PMAO-S) 2.0 mmol (runs 43, 48, 50, 52−54 3.0 mmol), at 25 °C. [b] HD concentration charged (mol/L). [c] Activity in kg of polymer/(mol of Ti h). [d] HD consumed (mmol)/catalyst (mmol). [e] By DSC. [f] GPC data in THF vs polystyrene standards. [g] MAO 3.0 mmol. [h] Under bulk polymerization conditions. [i] Contained insoluble gel polymer.

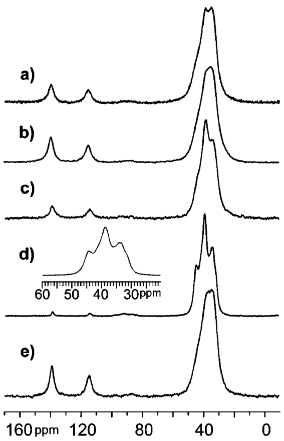


Figure 7. ^{13}C CPMAS spectra for poly(HD)s by **1**,**5**−**7**−MAO catalyst systems. Polymerization conditions: (a) **1** (HD 8.0 M, run 6), (b) **5** (HD 7.9 M, run 36), (c) **6** (HD 7.9 M, run 44), (d) **6** (HD 2.0 M, run 47), (e) **7** (HD 7.9 M, run 48). Degrees of butenyl group that remained based on inserted HD were (a) 37%, (b) 37%, (c) 17%, (d) trace, and (e) 35%.

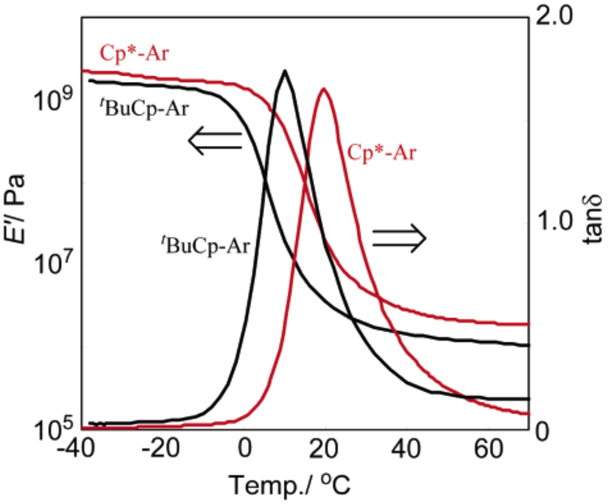


Figure 8. Temperature dependence in storage module (*E*′) and loss factor, tan δ, for poly(HD)s prepared by **1** (Cp*-Ar, run 6), and **5** (^{t}BuCp-Ar, run 36)−MAO catalyst systems (measured by DMA, 1.0 Hz).

to use. GPC were performed at 60 °C on a Shimadzu SCL-10A using a RID-10A detector (Shimazu Co. Ltd.) in THF (containing 0.03 wt % 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 mL/min). GPC columns (ShimPAC GPC-806, -804, and -802, 30 cm × 8.0 mm diameter) were calibrated vs polystyrene standard samples.

^{1}H NMR spectra for resultant poly(HD)s prepared by **1**,**2**−MAO catalyst systems were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, ^{1}H), and CDCl$_3$ was stored over molecular sieves under a nitrogen atmosphere. All chemical shifts are given in ppm and are referenced to Me$_4$Si, and all spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. Both ^{13}C CPMAS and ^{13}C DDMAS spectra were recorded on a Bruker ASX300 (75.0 MHz) using 7 mm diameter (or 4 mm diameter) tube with the rotation speed of 4000 Hz. Teflon tape and/or inner cap were used for fixing sample in the tube. The contents of the butenyl group (olefinic double bond) remaining based on inserted HD were calculated on the basis of the peak integration ratio of both olefinic and aliphatic carbons.

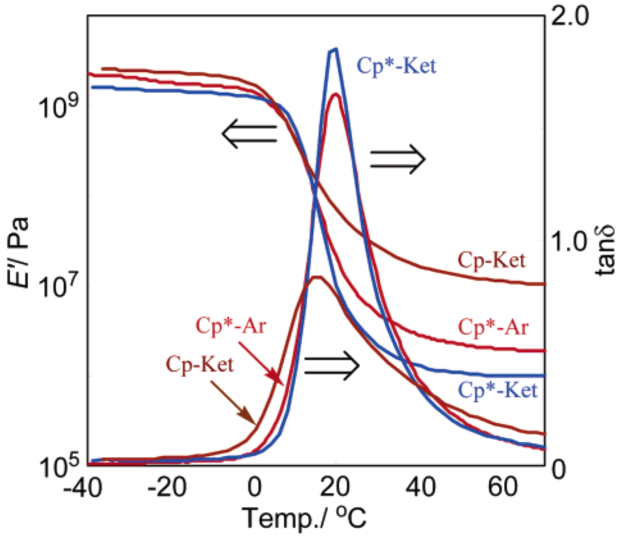


Figure 9. Temperature dependence in storage module (E') and loss factor, tan δ, for poly(HD)s prepared by **1** (Cp*-Ar, run 6), **6** (Cp*-Ket, run 44), and **7** (Cp-Ket, run 48)−MAO catalyst systems (measured by DMA, 1.0 Hz).

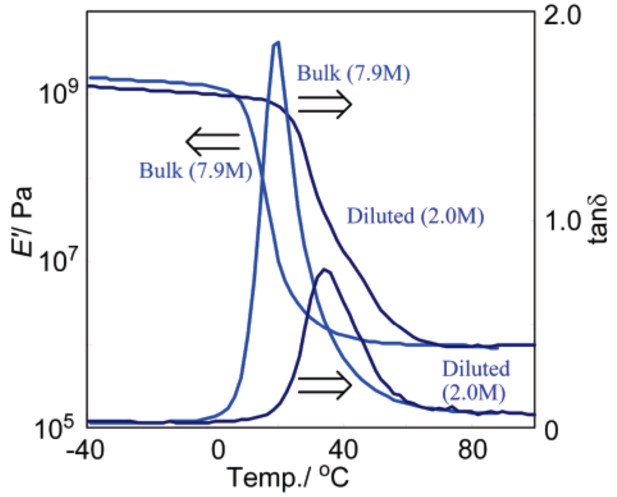


Figure 10. Temperature dependence in storage module (E') and loss factor, tan δ, for poly(HD)s prepared by **6**−MAO catalyst systems. Polymerization conditions: HD 7.9 M (run 44) or 2.0 (run 47) at 25 °C, 20 min, measured by DMA, 1.0 Hz.

Dynamic viscoelastic properties of resultant poly(HD)s were measured by a dynamic mechanical analyzer (Rheogel-E4000FZ, UBM Co., Ltd.). The frequency was adjusted to 1.0 Hz, and the heating rate was 3 °C/min from −50 to 100 °C in air. The sample specimens were prepared by compression-molding the powder sample at 120 °C into thin film. Storage modulus (E') and loss tangent (tan δ) were plotted against temperature. Differential scanning calorimetric (DSC) data for the polymer were recorded by means of DSC6100 (Seiko Instruments Co.) under a nitrogen atmosphere [preheating: from room temperature to 150 °C (20 °C/min), cooling to −100 °C under N_2; measurement: from −100 to 200 °C (10 °C/min) under N_2].

1,5-Hexadiene Polymerization. A typical procedure was performed as follows: a prescribed amount of MAO (3.0 mmol) and 1,5-hexadiene, 20 mL (or 15 mL), were added to a round-bottom flask (25 mL) in the drybox. Polymerization was started by the addition of a toluene solution (1.0 mL) containing a prescribed amount of complex (0.05, 0.10, or 0.50 μmol). The reaction mixture was stirred for a prescribed time at 25 °C, and the polymerization was terminated by addition of EtOH. Resultant white precipitate was washed several times with ethanol and was then dired in vacuo when the polymer samples prepared were insoluble in chloroform. If the polymer samples were soluble in chloroform, the reaction product was extracted with $CHCl_3$, which was washed with HCl aqueous solution and then rinsed with water. The chloroform extract was dried over Na_2SO_4, and the remaining chloroform and 1,5-hexadiene were then removed in vacuo.

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(19) HD polymerization by **3** (HD 0.842 mol/L in toluene, 40 °C, Table 1, run 8 in ref 12f), activity = 8400 kg of polymer/(mol of Zr h), cyclization selectivity = 96.8%, $T_g = 24.6$ °C.

(20) The DSC thermograms for the resultant poly(HD)s for this description were shown in the Supporting Information in our previous communication.[17]

(21) Based on the ^{1}H NMR spectra, molar ratios for terminal/internal olefin were (a) 36/1 (HD 8.0 M, run 16) and (b) 8.2/1 (HD 2.0 M, run 20), respectively, and the integration ratios for aliphatic/olefinic protons were (a) 5.56/1 and (b) 8.70/1, resepectively. It is thus assumed that (a) ca. 51.3 and (b) ca. 35.6% of olefins remained based on the HD insertion, clearly indicating that the repeated HD insertion should be favored over the cyclization. However, as described in the text, we could not estimate the extent of β-hydrogen elimination after 2,1-insertion and/or isomerization because the M_n values vs polystyrene standards by GPC were higher than those estimated values if internal olefins were formed only by the β-hydrogen elimination. The reason for the low catalytic activity by **2** may be due to stabilization by coordination of internal olefin after the isomerization.

(22) Both ^{1}H NMR and ^{13}C CPMAS spectra indicate that the polymerization by **1** took place in preferable 1,2-insertion or 2,1-insertion. No resonances ascribed to internal olefins as well as with 1-vinyltetramethylene unit (formed via 2,1-insertion and subsequent β-alkyl elimination) were seen, and resonances ascribed to internal olefins (formed via β-hydrogen elimination after 2,1-insertion) were not seen as the polymer chain end in the resultant poly(1-hexene)s, poly(1-octene)s prepared by **1**−MAO catalyst. These results along with the results by ordinary metallocenes and linked half-titanocenes strongly suggest that the HD insertion by **1**−MAO catalyst proceeded in favored 1,2-insertion and not in favored 2,1-insertion. Moreover, the resonance ascribed to methylidene ($CH_2{=}CHR$) as the polymer chain end was observed in poly(ethylene-*co*-2M1P)s (2M1P: 2-methyl-1-pentene) prepared by **1** under high 2M1P concentration conditions (for the copolymer with high 2M1P content), and this clearly suggests that 2M1P insertion in the copolymerization takes place in 1,2-insertion mode, and the chain transfer in the copolymerization is due to the β-hydrogen elimination after 2,1-insertion (misinsertion): Nomura, K.; Itagaki, K., unpublished results. The result also suggests that the present HD polymerization by **1** took place in the preferred 1,2-insertion.

(23) Both ^{13}C CPMAS and DDMAS spectra were measured, and contents of butenyl group based on inserted HD were estimated quantitatively by the ^{13}C DDMAS spectra.[17] This is because use of DDMAS should be favored over CPMAS to estimate the contents quantitatively.

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(25) It can be assumed that there are two types of possible cross-linking in the present HD polymerization such as (i) intermolecular cross-linking (incorporation of the olefinic double bonds into the other polymer chain) and (ii) intramolecular cross-linking (incorporation of the olefinic double bonds into the same polymer chain, making large rings). The observed difference in the E' value at the rubbery plateau for resultant poly(HD)s prepared between by the Cp*-aryloxo analogue (**1**) and by the Cp*-ketimide analogue (**6**) would be assumed to be due to the nature of the cross-linking because the E' value at the rubbery plateau should be low if some extent of case ii accompanied, because these are not the actual network structure in the resultant polymers.

(26) As described in the text, the resultant poly(HD) prepared by **7** possessed a low tan δ value with the broad peak width, suggesting that the distribution of cross-linking was not uniform, and the observed fact was somewhat analogous to the fact that the molecular weight distribution in the poly(HD) prepared at low HD concentration was somewhat broad ($M_w/M_n = 3.27$, run 54). Moreover, since the E' value at the rubbery plateau was somewhat higher than those for poly(HD)s prepared by **1** and **6** and also since the content of olefinic double bonds in the polymer was close to that by **1** under the same conditions (7a and e), these results should suggest that some extent of cyclization took place in addition to cross-linking. These results should also indicate that the selectivity was affected by both cyclopentadienyl and anionic ancillary donor ligand employed.

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