Polymerization of 1,5-Hexadiene by the Nonbridged Half-Titanocene Complex−MAO Catalyst System: Remarkable Difference in the Selectivity of Repeated 1,2-Insertion

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Introduction. Precise, efficient syntheses of functionalized polyolefins by controlled polymerization using transition metal catalysts have attracted considerable attention.[1,2] Two strategies, (1) direct copolymerization with functionalized monomers[2a] and (2) postpolymerization modification,[2b] have been known, and recently, (3) controlled incorporation of a reactive moiety that introduces functionalities through chemical modification[2b] has begun to be considered. This is because the first two approaches would face difficulties due to the catalyst poisoning and interaction of centered metal with functionalized monomers and/or only very limited chemistry like a free radical grafting reaction is available to activate the completely saturated aliphatic molecular structure,[2] although recent rapid progresses[1] offered new possibilities.[1,2]

We have had an interest to explore polymerization of nonconjugated diene (1,5-hexadiene, HD) in order to establish a new route to prepare functionalized polyolefin via a third approach by repeated insertion of HD, although most of previous catalysts such as zirconocene,[3,4] titanocene,[3c] half-zirconocene,[5a] and others[5b] favor cyclopolymerization incorporating the methylene−1,3-cyclopentane unit (Scheme 1, route A). This is because the promising possibilities like incorporation of olefinic double bond (route B) and/or controlled incorporation of cross-linking (route C) that improves heat resistance can be expected if selectivity of the repeated insertion (routes B and C) against cyclization (route A) can be improved by designing the catalyst employed.[6,7] Since we have demonstrated that nonbridged half-titanocenes containing an aryloxo ligand display unique characteristics especially for copolymerization of ethylene with α-olefin, styrene, and norbornene,[8] we thus have decided to explore the possibility.

Results and Discussion. Table 1 summarizes results for polymerization of HD.[9] $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1**) was chosen because **1** efficiently incorporates 1-hexene in ethylene/1-hexene copolymerization,[8b] and $[Me_2Si(indenyl)_2]ZrCl_2$ (**2**) and Cp_2ZrCl_2 (**3**) were also chosen for comparison (Chart 1).[3,10] It turned out that **1** showed notable catalytic activity, affording insoluble gel polymer that possesses a weak glass transition temperature (T_g) by DSC. The activity decreased at lower HD concentrations (runs 2−5), and a $CHCl_3$-soluble polymer that possesses a high M_w value was obtained (run 5). High catalytic activities were also observed by **2** under the same conditions, and both the activities and polymer properties by DSC were affected by the HD concentration. The poly(HD) prepared at low HD concentrations were soluble in THF (run 8) but became insoluble upon increasing the catalyst concentration (run 9) due to the subsequent cross-linking partially. The activities by **3** were low under the same conditions, and resultant polymers possessed typical T_g and T_m ascribed to *trans*-atactic methylene−1,3-cyclopentane (MCP) microstructure.[3e] The resultant polymers were insoluble in $CHCl_3$ and THF due to the cross-linking accompanied partially. These facts by **2**−**3** are relatively similar to those reported previously.[3a,e,f,10]

Scheme 1

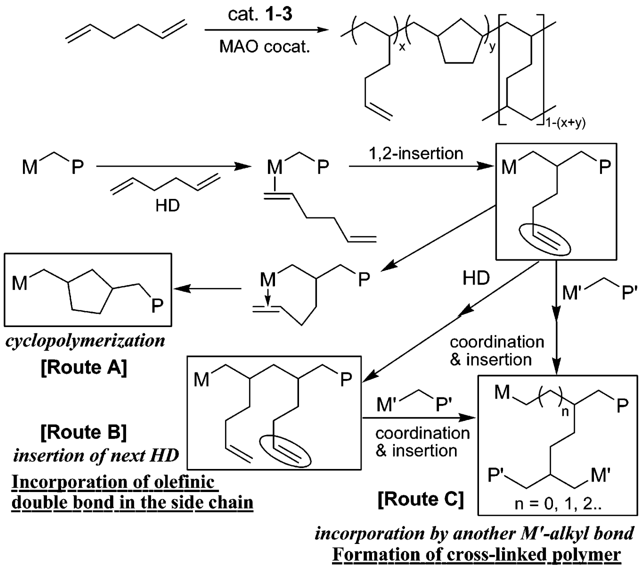
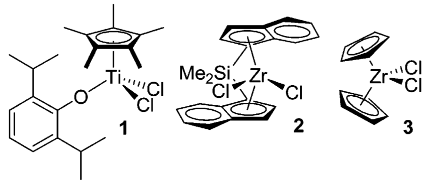


Chart 1



The ^{13}C CPMAS spectrum[9] for the poly(HD) prepared by **1** under bulk (without solvent) polymerization conditions (Figure 1a,f) showed that repeated 1,2-insertion (incorporation of olefinic double bond in the polymer side chain and subsequent cross-linking) favored cyclization [33 mol % of butenyl group remained based on inserted HD estimated by the ^{13}C DDMAS spectrum].[11] The ^1H NMR spectrum[9] for poly(HD) prepared by the **1**−MAO catalyst at low HD concentration (run 5) showed 25 mol % of the butenyl group remained based on HD inserted, and this value is the same as that estimated from the ^{13}C DDMAS spectrum (25 mol %).[11] Moreover, no resonances due to internal olefins or vinyl group were observed, indicating that isomerization or 2,1-insertion

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Table 1. 1,5-Hexadiene Polymerization by Cp*TiCl$_2$((O-2,6-^{i}Pr$_2$C$_6$H$_3$) (1)−, [Me$_2$Si(indenyl)$_2$]ZrCl$_2$ (2)−, and Cp$_2$ZrCl$_2$ (3)−MAO Catalysts[a]

run no.	cat.	HD concn[b]	time/min	yield/mg	activity × 10^{-3} [c]	TON 10^{-3} [d]	T_g (T_m)/°C[e]	$M_n \times 10^{-4}$ [f]	M_w/M_n[f]
1	**1**	8.0[g]	10	973	58.4	118	0		*h*
2	**1**	8.0[g]	20	1240	37.2	151	2		*h*
3	**1**	6.0	20	890	26.7	108	5		*h*
4	**1**	4.0	20	401	12.0	48.8	11		*h*
5	**1**	2.0	20	167	5.0	20.3	23	28.3	2.3
6	**2**	8.0[g]	10	876	105.1	213	−4[i]		*h*
7	**2**	6.0	10	300	36.0	72.9	0 (99)[i]	8.7	1.8
8	**2**	2.0	10	97	5.8	23.6	35 (101)	5.5	1.9
9	**2**	2.0	20	313	9.4	38.1	6 (102)		*h*
10	**3**	8.0[g]	30	692	2.8	17	−4 (74)		*h*
11	**3**	6.0	30	538	2.2	13.1	−8 (79)		*h*
12	**3**	2.0	30	248	1.0	6.0	−9 (85)		*h*

[a] Conditions: **1**, 0.10 μmol; **2,** 0.05 μmol (run 9, 0.10 μmol); or **3**, 0.50 μmol; 1,5-hexadiene (HD) + *n*-hexane, total 20 mL; MAO, 3.0 mmol; 25 °C. [b] HD concentration charged (mol/L). [c] Activity in kg of polymer/(mol of M h) (M = Ti, Zr). [d] HD consumed (mol)/catalyst (mol). [e] By DSC. [f] GPC data in THF vs polystyrene standards. [g] Under bulk polymerization conditions. [h] Contained insoluble gel polymer. [i] T_m was observed in small amount (T_m = 90−103 °C).

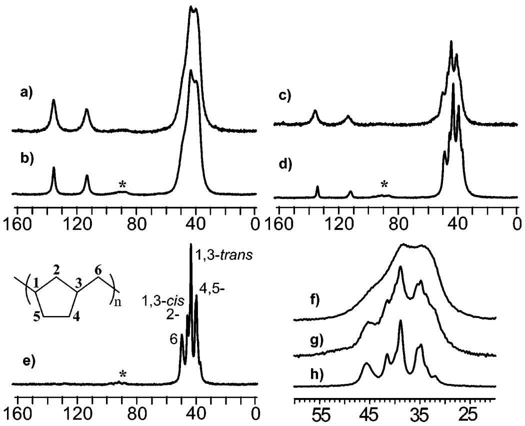

Figure 1. ^{13}C CPMAS spectra for poly(HD)s by **1**−**3**−MAO catalyst systems. Catalyst: (a) **1** (HD 8.0 M, run 2), (b) **1** (HD 2.0 M, run 5), (c) **2** (HD 8.0 M, run 6), (d) **2** (HD 2.0 M, run 9), (e) **3** (HD 8.0 M, run 10), (f−h) expanded charts for (a), (c), and (e), respectively. An asterisk (*) is due to the spinning sideband (resonances ca. 30−50 ppm, rotation 4000 Hz/75 MHz ^{13}C).

(then affording the vinyltetramethylene unit[6]) did not take place.[12] 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 butenyl group decreased gradually for longer reaction hours.[13]

No olefinic resonances were seen in ^{13}C CPMAS spectra for polymers prepared by **3**, and typical MCP microstructure was observed (Figure 1e,h).[3a] The content of the butenyl group for polymer by **2** under bulk conditions was 24 mol % (run 6),[11] and the content decreased at lower HD concentrations (9.1 mol %,[11] run 9). These are similar to the fact that cyclization took place (96.8%) predominantly under lower HD conditions.[3f,10]

Dynamic mechanical analyses (DMA) were explored to observe differences in both the microstructure and the thermal properties for resultant polymers (Figure 2).[9] The polymer prepared by **3** showed similar property to that reported previously,[3e] indicating that cyclopolymerization took place predominantly. On the other hand, polymer by **1** possessed a high tan δ value (at ca. 5 °C) with narrow peak width and the observed E' value at 60 °C was the lowest among these samples. Moreover, the $\Delta E'$ ($E'_{-40°C} - E'_{60°C}$) was relatively large, and E' reached a rubbery plateau modulus (constant value). These results indicate that repeated 1,2-insertion of HD took place preferably and also suggest that incorporation of cross-linking is uniform. Polymer by **2** 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 indicates that the cross-linking distribution was not uniform compared to that by **1**. Taking into account these results, it is clear that the degree of cyclopolymerization increased in the order **3** ≫ **2** > **1**, and the cross-linking distribution was influenced by the nature of catalyst.

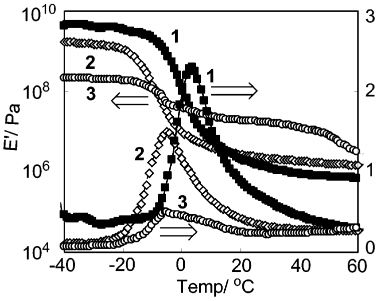

Figure 2. Temperature dependence in storage module (E') and loss factor, tan δ, for poly(1,5-hexadiene)s prepared by **1** (run 2)−, **2** (run 6)−, **3** (run 10)−MAO catalyst systems (measured by DMA, 10 Hz).

We have shown that **1** favored repeated 1,2-insertion rather than cyclization, affording a polymer with an olefinic double bond in the side chain. Since an efficient introduction of various functionalities by chemical modification should be possible in both direct and precise manner from the olefinic double bond, therefore, the applications for synthesis of functionalized and/or graft polyolefins using this unique technique should be the next attractive target on this project.

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Supporting Information Available: General procedures, additional HD polymerization results, DSC charts for poly(HD)s, ^{1}H NMR spectrum for poly(HD) prepared by **1**−MAO catalyst (run 5), and ^{13}C DDMAS spectra for poly(HD)s. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) For experimental details, see the Supporting Information.

(10) HD polymerization by **2** (HD 0.842 mol/L in toluene, 40 °C),[3f] activity = 8400 kg of polymer/(mol of Zr h), cyclization selectivity = 96.8%, $T_g = 24.6$ °C.

(11) Both ^{13}C CPMAS and DDMAS spectra were measured, and contents of the butenyl group based on inserted HD were estimated quantitatively by the ^{13}C DDMAS spectra.[9] This is because use of DDMAS should be favored than CPMAS to estimate the contents quantitatively.

(12) Syntheses and some reactions of $Cp^*TiR[O(CH_2)_nCH{=}CH_2](O\text{-}2,6\text{-}{}^iPr_2{-}C_6H_3)$ [$R = Me, CF_3SO$; $n = 2, 4$]: Nomura, K.; Hatanaka, Y. *Inorg. Chem. Commun.* **2003**, *6*, 517. The facts that no β-H elimination took place and olefin did not coordinate to Ti may be related to the present observation.

(13) The content of butenyl group was 13 mol % after 40 min under the same conditions of run 5. Detailed results are shown in the Supporting Information.

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