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NOTE

Stereospecific Cyclopolymerization of α,*ω*-Diolefins by Pyridylamidohafnium Catalyst with the Highest Activity

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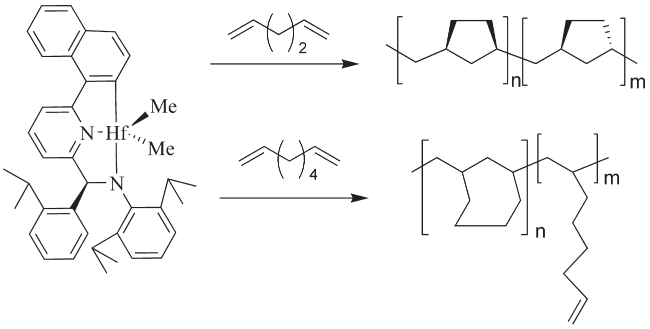
Introduction

The advent of well-defined organometallic catalyst precursors has provided a unique opportunity for producing polyolefins with an exquisite degree of control over stereochemistry and preparation of olefin block copolymers. Among these polyolefins, the cycloolefin polymers (COPs) exhibit remarkable properties, such as good heat and chemical resistance, low dielectric constants, nonhygroscopicity, and high transparency.[1,2] One of the facile and efficient approaches to produce COPs is the cyclopolymerization of α,*ω*-diolefins to produce the polymers with cyclo-groups in repeating units.[2−4,8] The metallocene catalysts were used to catalyze the cyclopolymerization of 1,5-hexadiene (HD) to give poly(methylene-1,3-cyclopentane) (PMCP).[2] The cyclopolymerization of 1,5-HD by fluorinated bis(phenoxyimine)-based titanium catalysts showed the propensity for secondary insertion giving a material composed of 3-vinylteramethylene and MCP.[4] The microphase-separated and well-defined iso-poly(1-hexene)/PMCP block copolymer was synthesized utilizing amidinate-based zirconium catalysts.[3b] However, the polymerization lacks cyclization selectivity, and the obtained polymers contain partial structures having vinyl groups due to an incomplete cyclization of the monomer. It has been a long scientific interest to achieve the stereochemical control over COPs microstructure. Recently, for example, the Fe and Co complexes with bis(imino)pyridine ligands can efficiently catalyze the cyclopolymerization of both substituted and unsubstituted 1,6-heptadienes with high stereoselectivity, which also show high cyclization selectivity.[3e] Meanwhile, the cyclopolymerization of nonconjugated dienes with a tridentate phenoxyamine hafnium complex was documented by Coates. The obtained PMCPs represent the first report of a high *cis*-enriched microstructure with high selectivity for isotactic enchainment ($\alpha = 0.93-0.96$).[3f] However, highly active catalysts with the high cyclization selectivity, which is suitable for the cyclopolymerization of α,*ω*-diolefins especially with high stereoselectivity, are still scarce. Hence, the discovery and development of the efficient selective catalysts for α,*ω*-diolefin cyclopolymerization remain one of the major challenges in the polymerization field. With this in mind, we decided to investigate the cyclopolymerization of α,*ω*-diolefins especially using post-metallocene catalysts.

In this paper, the cyclopolymerization of 1,5-hexadiene (HD) and 1,7-octadiene (OD) by dimethylpyridylamidohafnium catalyst is reported. The catalytic activity is almost 1 order of magnitude higher than that exhibited by the zirconocene-based catalysts under similar conditions, and the cyclization selectivity of the polymerization is close to complete (100%). The isospecificity factor for the PMCP is up to 98.7%. We proposed the mechanism for the process of cyclization of 1,5-HD and verified the mechanism based on the DFT calculations. A good agreement between the modeling and the experimental evidence is observed.

Scheme 1. Structure of the Polymers Prepared by Polymerization of HD or OD Using Catalyst



Results and Discussion

Recently, Arriola and his collogues found that dimethylpyridylamidohafnium is a unique catalyst (Scheme 1) for α-olefin (co)polymerization. The catalyst was successfully used to synthesize olefin multiblock copolymers via chain shuttling polymerization.[5] This type of catalyst exhibits living polymerization character and unexpected isoselectivity for α-olefin polymerization.[6] These unique polymerization behaviors drew our attention to investigate the α,*ω*-diolefin cyclopolymerization. The typical results including polymer yields, catalytic activities, number-average molecular weights (M_n), and polydispersity indices (PDIs) are summarized in Table 1. The dimethylpyridylamidohafnium, activated by $[Ph_3C][B(C_6F_5)_4]$, is highly active in the cyclopolymerization of HD or OD using TIBA as a scavenger. Under the mild conditions ($[B]/[Hf] = 2.0$), the catalytic activity was found to be high up to 10^6 g polymer/(mol$_{Hf}$ h), which was almost 1 order of magnitude higher than that of the zirconocene catalyst reported previously.[2a,e,i] Monomer conversion was high up to 65% in just 10 min. In contrast, it needs several hours to reach the same conversion using metallocene or fluorinated FI catalyst.[2−4,8] As far as the PDIs were concerned, they are all relatively broad. One reason is the chain transfer to the TIBA, and another reason may be that the catalyst is modified by monomer during its activation to generate multiple catalysts with differing molecular weight capabilities proposed by the

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Table 1. Polymerization of 1,5-Hexadiene and 1,7-Octadiene by Pyridylamidohafnium Catalyst[a]

run	monomer (mol/L)	V_{total} (mL)	Al/Hf (mol/mol)	conv (%)	activity[b]	M_n[c] (10^4)	M_w/M_n[c]	[C][d] (%)	cis[e] (%)	T_g[f] (°C)	T_m[f] (°C)
1	HD (0.84)	20	100	65	1.08	6.33	2.44	100	68.7	14	121
2	HD (0.84)	20	400	57	0.94	0.95	3.50	100	69.5	−4	119
3	HD (0.84)	20	600	51	0.84	0.83	2.96	100	67.8	−6	117
4	HD (0.84)	20	1000	59	0.98	0.71	2.50	100	69.4	−11	105
5	OD (0.52)	26	400	50	0.89	2.68	2.44	97.0	100	45	
6	OD (1.35)	20	200	62	0.55	nd[g]	nd[g]	nd[g]	nd[g]		
7	OD (0.68)	40	400	25	0.90	1.33	2.79	84.9	100	51	

[a] Conditions: $[Ph_3C][B(C_6F_5)_4]$ as cocatalyst, Cat. = 5 μmol (runs 1−6), Cat. = 10 μmol (runs 7, 8), [B]/[Hf] = 2.0, time = 10 min (runs 1−4), time = 20 min (run 6), time = 5 min (run 7), 10 °C. [b] Catalytic activity: 10^6 g polymer/(mol_{Hf} h). [c] GPC data in trichlorobenzene vs polystyrene standards. [d] Cyclization ratio of the polymers, determined by ^{1}H NMR spectroscopy. [e] Content of *cis* units in the cyclic units determined by ^{13}C NMR spectroscopy. [f] Glass transition temperature and melting temperature determined by DSC. [g] Insoluble in trichlorobenzene because of formation of cross-linking structure.

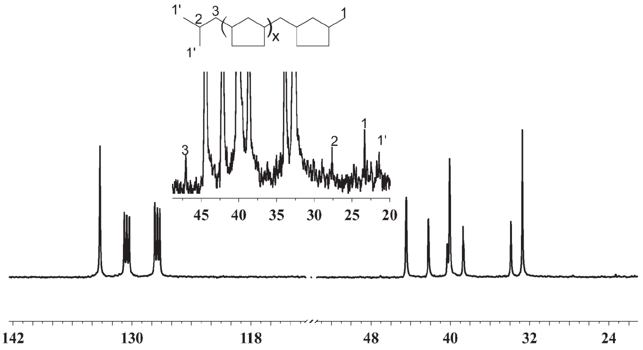


Figure 1. ^{13}C NMR spectrum for low molecular weight sample (run 4).

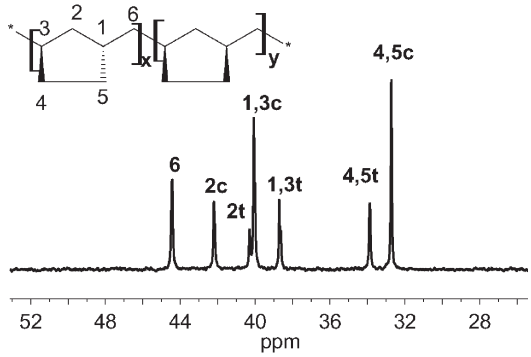


Figure 2. ^{13}C NMR spectrum for PMCP sample (run 3).

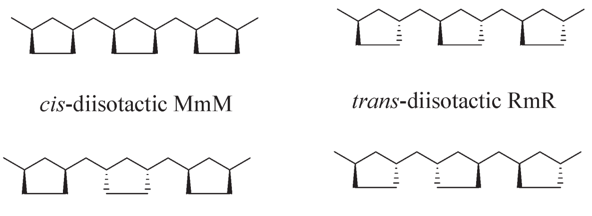
scientists at Dow Chemical.[9] In addition, it was also observed that the T_g values of the obtained polymers decrease with molecular weight (runs 1−4).

The M_n of the resultant polymers (PMCP) is up to 63.3 kg/mol, which is one of the highest value reported.[3,4] The *cis* ratios of 1,3-cyclopenatene units rangs from 67.8 to 69.5%, which have no direct relationship with the reaction conditions. Noticeably, with the increase of the [Al]/[Hf] molar ratio, the M_n of PMCPs gradually decreases from 63.3 to 7.1 kg/mol. At the same time, the PDIs of the result polymers slowly increases (from 2.44 to 3.50), and the catalytic activity decreases slightly, which suggest that the chain transfer reaction was irreversible. Interestingly, the ^{13}C NMR spectrum (Figure 1) reveals that the polymer sample with low molecular weight (run 4) possesses both isobutyl and methyl end-groups, indicating that TIBA also acts as a chain transfer agent. In addition, no end-double bond was observed in the ^{13}C NMR spectra of the polymers (Figure 1 and Figure S1), which shows no β-H chain transfer reaction.

It turned out that the catalyst also showed notable catalytic activity (up to 0.9 kg/(mmol_{Hf} h)) in the polymerization of OD. The insoluble gel polymer was produced when the concentration of OD reaches 1.35 mol/L (run 6) because of the incorporation of the terminal olefinic double bond into another metal−alkyl bond after the 1,2-insertion inducing the cross-linking structure. With the decrease of the concentration of the monomer, the polymers with high cycloselectivity can be easily obtained (run 5 or 7), since the rate of intramolecular cyclization/intermolecular propagation increased under the more dilute conditions. The ^{1}H NMR spectrum of sample 7 (Figure S2) shows the existence of the pendant double bond. The ^{13}C NMR spectrum of sample 7 (Figure S3) exhibits only *cis* cyclo-groups in repeating units because the homofacial insertion/cyclization sequence is facile with the increase of the diene length.[3f,12] The isoselectivity of the cyclo-structure is higher than 99%, which can be calculated according to the reference.

For PMCP, four types of microstructure of maximum order are possible (Chart 1).[2c,f] The microstructure of the PMCPs is

Chart 1. Microstructures of Maximum Order for PMCP



cis-diisotactic MmM

trans-diisotactic RmR

cis-disyndiotactic MrM

trans-disyndiotactic RrR

determined by two factors. The tacticity of the polymer is influenced by the enantioface selectivity of the first insertion step; the *cis*/*trans* selectivity is influenced by the diastereoselectivity of the cyclization step.[3a] In order to describe the tacticity, Waymouth and Coats defined two parameters α and σ. The parameter σ, equaling to the mole fraction of *cis*-rings in the polymer, can be measured by ^{13}C NMR. The parameter α, calculated according to the literature, corresponds to the enantioface selectivity.[3a] The structures of the PMCPs obtained were characterized by ^{1}H and ^{13}C NMR. The typical spectrum is presented in Figure 2 (sample 3). The absence of signals in the region of δ 4.0−6.0 ppm in ^{1}H NMR (Figure S4) indicates the complete cyclization of 1,5-HD. The ratios of *cis*- and *trans*-1,3-cyclopenatene in the polymers are estimated by integration ratio of the $C_{4,5}$ resonances at 32.7 and 33.9 ppm in high-temperature ^{13}C NMR spectra.[3d,10] The *cis* ratios ranged from 67.8% to 69.5%. This result may be ascribed to the more steric encumber showed by the monomer-modified pyridylamidohafnium catalyst, which tends to form twisted boat conformation and favors forming *cis*-rich ring structure.[2a]

According to further investigation of the ^{13}C NMR spectra of the samples, we found that only the MmM and RrR resonances are obvious and the other resonances (MrM and RmR) are negligible as shown in Figure 3, indicating the high enantioface selectivity of the catalyst. The parameter α for sample 3 is up to 98.7%, which is higher than that reported by Coates (up to

96%).[2a,3f] It is worthwhile to mention that the ^{13}C NMR spectra are obviously different from that reported by Coates in the region of 33.5−34.2 ppm. The PMCP synthesized showed only RrR but no trace of RmR. Interestingly, the *cis* ring is isoselective and the *trans* ring is syndioselective, which may derive from the active centers of chirality.[5d] As far as we know, it is a rare example to afford highly *cis*-rich isotactic PMCP with the highest activity using the present catalyst.

The existence of $Hf-C_{Arkyl}$ is the distinguishing feature of the dialkyl pyridylamidohafnium catalyst.[9] Scientists at Dow Chemical have found that monomer-modified complex is the true active species based on the computations and experimental evidence. We analyzed the combined filtrates of a large scale polymerization by LC-MS. The result revealed a mixture of compounds including peaks corresponding to 1,5-HD insertion products (m/z 595) (see Figure S5). According to these documents[2a,2g,9] and present experimental evidence, we presumed that the α,ω-diolefin modified complex with a terminal double bond attached to the ligand may be the true active species in this catalyst system and proposed a possible mechanism involving a sequential insertion cyclization sequence as shown in Scheme 2. In order to verify the mechanism proposed and deeply understand the progress of the cyclization reaction, we calculated the conformation on the diastereoselectivity cyclization of 1,5-HD and the energy of the complex with monomer modified ligand or without monomer attached to the ligands. The calculation employed DFT using the Amsterdam Density Functional (ADF) program package.[11]

The DFT information and the typical structures for the DFT calculation are shown in the Supporting Information. According to DFT results, the stability of the monomer modified complex (P_1) is 7.36 kal/mol higher than that of the complex (P_2) without monomer attached to the ligands. This result supports that the monomer modified complex is the true catalyst active species,

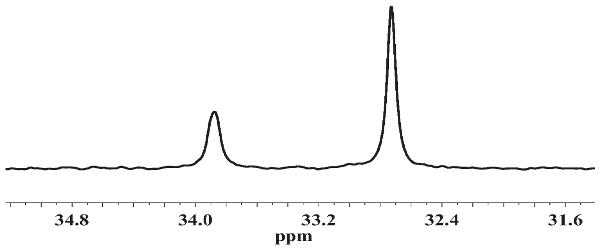


Figure 3. ^{13}C NMR spectra of the $C_{4,5}$ region of the sample PMCP (run 3, 125 °C, o-$C_6D_4Cl_2$).

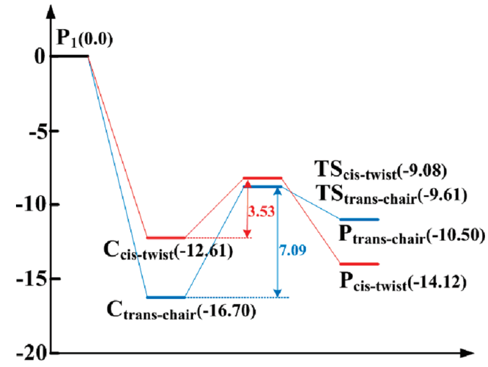
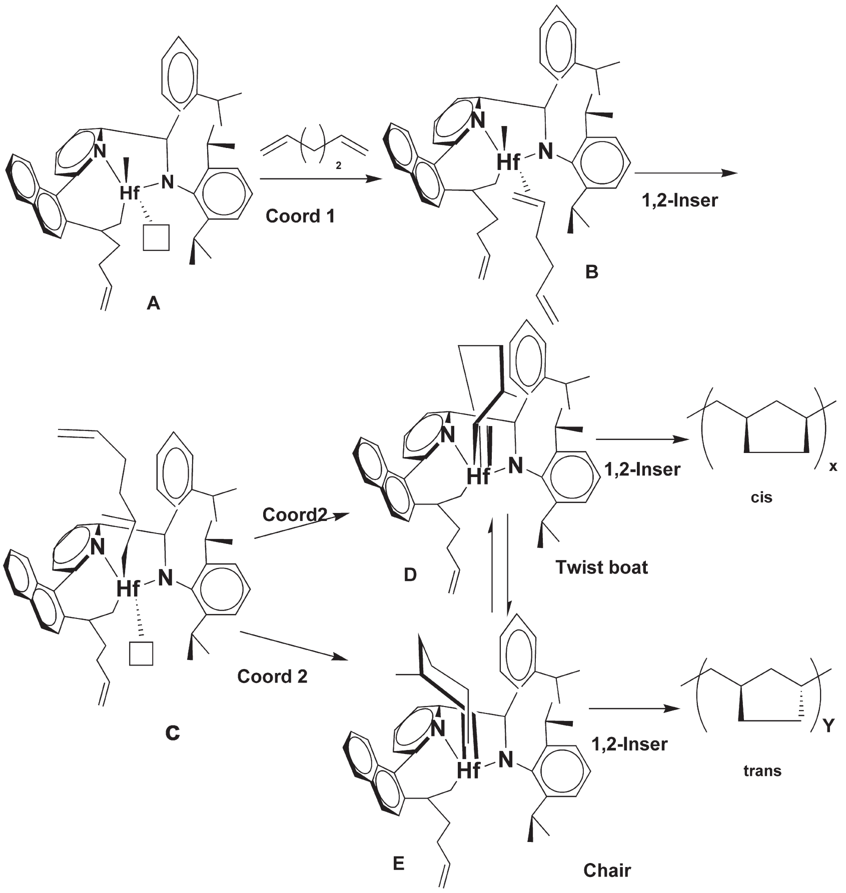


Figure 4. Potential energy surface for the cyclization reaction of 1,5-hexadiene.

Scheme 2. A Possible Mechanism for the Cyclopolymerization of HD



similar to the case of α-olefin polymerization.[9a] The sketch map of P_1 and P_2 is shown in Figure S6.

The cyclization step was investigated through modeling the nonbonded interactions. The potential energy surface for the cyclization reaction of 1,5-HD is shown in Figure 4. The π-coordination of the second double bond to the metal forms a twist-boat conformation (D) and a chair conformation (E) (see Figure S7 in Supporting Information). The twist boat cyclization π-complex $C_{cis\text{-twist}}$ and the chair cyclization π-complex $C_{trans\text{-chair}}$ are formed in an exothermic reaction ($\Delta H = -12.61$ and $\Delta H = -16.70$ kcal/mol, respectively). From the superficial perspective, the $C_{trans\text{-chair}}$ is the favorite conformation. However, the $C_{cis\text{-twist}}$ is the favorite conformation from the whole cyclization process and the experimental evidence. As can be seen from Figure 4, the activation barrier for the twist boat model insertion transition state $TS_{cis\text{-twist}}$ is 3.53 kcal/mol, which is lower than that of $TS_{trans\text{-chair}}$ (7.09 kcal/mol). The product of the *cis* form cyclization $P_{cis\text{-twist}}$ is more stable than the $P_{trans\text{-chair}}$. The energies of the $P_{cis\text{-twist}}$ and $P_{trans\text{-chair}}$ are −14.12 and −10.50 kcal/mol, respectively. The $P_{cis\text{-twist}}$ is 1.51 kcal/mol more stable than the π-complex $C_{cis\text{-twist}}$. Hence, the cyclization reaction of *cis*-form is exothermic. However, in contrast, the stability of $P_{trans\text{-chair}}$ is 6.20 kcal/mol lower than that of the π-complex $C_{trans\text{-chair}}$, which means that the cyclization reaction of *trans*-form is endothermic. The above analyses based on the DFT calculation support that this catalyst favors the *cis*-twist conformation. As a result, the model becomes *cis*-specific, which is in good agreement with the selectivity observed from the experimental evidence.

In summary, we herein reported a non-metallocene hafnium catalyst used in polymerization of α,ω-diolefins. It shows high cyclization selectivity, high monomer conversion (up to 65% in just 10 min), and the highest activity (up to 10^6 g of polymer/($\mathrm{mol_{Hf}}$ h)), which is almost 1 order of magnitude larger than that exhibited by the zirconocene-based catalyst under the similar conditions. The M_n value of the PMCP obtained is up to 63.3 kg/mol, which is one of the highest values reported. The highly *cis*-rich isotactic PMCPs were obtained with the highest activity. This catalyst system not only exhibits excellent control over the *cis*/*trans* selectivity (*cis* up to 69.5% for HD and 100% for OD) but also shows the high isotactic selectivity (α up to 98.7% and >99% for OD). In the meanwhile, the cyclization step was investigated through modeling the nonbonded interactions based on DFT, which is in good agreement with the selectivity observed from the experimental evidence.

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Supporting Information Available: DFT information, the typical structures for the DFT calculation, ^{1}H NMR, ^{13}C NMR, and experimental procedure. This material is available free of charge via the Internet at http://pubs.acs.org.

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