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Improving the Behavior of Bis(phenoxyamine) Group 4 Metal Catalysts for Controlled Alkene Polymerization

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A rarity until the past decade, alkene polymerizations with controlled kinetics (i.e., with fast chain initiation and negligible chain transfer/termination in the time scale of a practical experiment) are possible nowadays with a variety of molecular transition metal catalysts and usable to synthesize well-defined block copolymers via sequential comonomer additions.[1] Only few of these catalysts, however, are also *highly* stereoselective in the polymerization of propene; this limits the access to copolymers containing high-melting crystalline polypropylene blocks.[2,3] Certain bis(phenoxyimine)Ti(IV) catalysts[1,4] yield *syndiotactic* polypropylene (sPP) with [*rrrr*] > 0.95, and block copolymers of sPP with polyethylene (PE) or ethylene/propylene rubber (EPR) have been prepared and thoroughly characterized.[1,5] Chiral (α-diimine)Ni(II) catalysts can produce *isotactic* polypropylene (iPP) with a melting point (T_m) up to 149 °C, but only at very low (< −60 °C) temperature and with exceedingly low TOF.[6] Potentially more relevant for application are some bis(phenoxyamine)Zr(IV) catalysts bearing bulky *ortho*-substituents on the phenoxy rings (e.g., **Zr-1** in Chart 1, L = benzyl), which produce iPP with [*mmmm*] > 0.95 at room temperature (RT).[1,7,8] With the latter catalysts, however, the time scale of chain growth in ethene polymerizations is too fast for a clean attainment of sequential feeding conditions; in fact, a controlled regime of a few minutes at most at RT[7−10] proved to be enough for the synthesis of iPP-*block*-PE and iPP-*block*-EPR[8,9] but hampered the preparation of multiblock materials such as iPP-*block*-EPR-*block*-iPP, highly desirable for use as thermoplastic elastomers or phase compatibilizers.[1]

We have demonstrated[7−10] that the function of the R^1 substituents in the ligand framework of Chart 1 is to ensure that in the chiral active pocket of the $[(ONNO)Zr-P]^+$ active cations the following two conditions are fulfilled: (i) the growing polymer chain (P) undergoes a strong chiral orientation favoring the 1,2 insertion of propene with the enantioface which directs the methyl group *anti* to the first chain C−C bond (like in Chart 2A);[11] (ii) not enough space is left for the large six-membered transition state of β-H transfer to propene (Chart 2B), otherwise the dominant chain transfer pathway for this catalyst class in the absence of Al−trialkyls.[7−10]

Tuning the steric demand of R^1 proved to be a delicate endeavor. We found that the catalyst deriving from precursor **Zr-1** of Chart 1 (R^1 = 1-adamantyl) at RT or slightly above yields an almost monodisperse iPP with [*mmmm*] > 0.98 and a melting temperature T_m > 150 °C.[7,8] The homologue with R^1 = α,α-dimethylbenzyl (from precursor **Zr-2**) is slightly less stereoselective.[7,8] As soon as R^1 gets somewhat smaller (e.g., *tert*-butyl), the stereoselectivity and the controlled behavior fade out.[7−10] With bulkier R^1s (e.g., R^1 = triphenylmethyl), on the other hand, the active pocket is too tight, and both the stereoselectivity and the regioselectivity are lost (a partly counterintuitive result that has been explained in detail elsewhere[7]).

The reason why the catalysts optimized for polypropylene do not perform well with ethene can be understood on inspection of Chart 2B. Indeed, it is easy to realize that for R^1 to effectively destabilize the transition state of β-H transfer to the monomer (either propene or ethene) the growing chain must be β-branched, because the main repulsive contact in the active pocket is between R^1 and a chain β-alkyl substituent when present; this obviously is not the case when the last-inserted monomeric unit is an ethylene one. Therefore, acting on R^1 alone cannot provide a simple solution to this problem.

It is worthy to recall at this stage that for many classes of group 4 metallocene[12] and nonmetallocene[13,14] alkene polymerization catalysts Hf-based active species yield polymers with much higher average molecular weights than the Zr-based homologues (a factual observation whose theoretical interpretation is still uncertain[15]). Therefore, we decided to investigate the performance of the Hf homologues of **Zr-1** and **Zr-2**, hoping that a higher chain propagation to transfer ratio would be associated with a longer duration of the controlled regime.

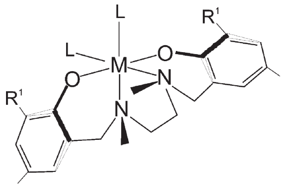
The novel bis(phenoxyamine)Hf−dibenzyl complexes **Hf-1** and **Hf-2** of Chart 1 were prepared similarly to the Zr ones.[7,8,16] The NMR spectra in solution are indicative of the C_2-symmetric *trans*-{O,O},*cis*-{*N*,*N*} configuration observed for the latter.[7,8,17] Full details on this part can be found in the Supporting Information. The complexes were activated with methylalumoxane (MAO) in combination with 2,6-di-*tert*-butylphenol (TBP) to scavenge "free" trimethylaluminum and thus inhibit chain transfer via trans-alkylation[7−9,18] and tested comparatively with **Zr-1** and **Zr-2** in ethene and propene polymerization at 25 °C in toluene solution. The results are summarized in Table 1, along with those of polymer characterization by means of ^{13}C NMR and high-temperature GPC. Specific rates of chain propagation (k_p) and cumulative frequencies of chain transfer (f_t) were calculated from the values of M_n as a function of polymerization time (t_p) based on the well-known Natta's equation[19] (where P_n is the number-average degree of polymerization, and M_1 is the molar mass of the monomer):

$$1/P_n = M_1/M_n = f_t/(k_p[C_nH_{2n}]) + 1/(k_p[C_nH_{2n}]t_p)$$

Looking at the table, the following facts can be noted:

(i) For a given ligand framework, with both monomers the chain propagation rate at Hf was significantly lower than at Zr. This is not an obvious finding: despite the long-standing reputation of Hf-based catalysts, and of hafnocenes in particular, to be much less active than their Zr homologues,[12] recent results have demonstrated that with a proper activation homologous Hf

Chart 1



	M	R^1
Zr-1	Zr	1-Adamantyl
Zr-2	Zr	α,α-Dimethylbenzyl
Zr-3	Zr	Cyclohexyl
Hf-1	Hf	1-Adamantyl
Hf-2	Hf	α,α-Dimethylbenzyl
Hf-3	Hf	Cyclohexyl

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Chart 2

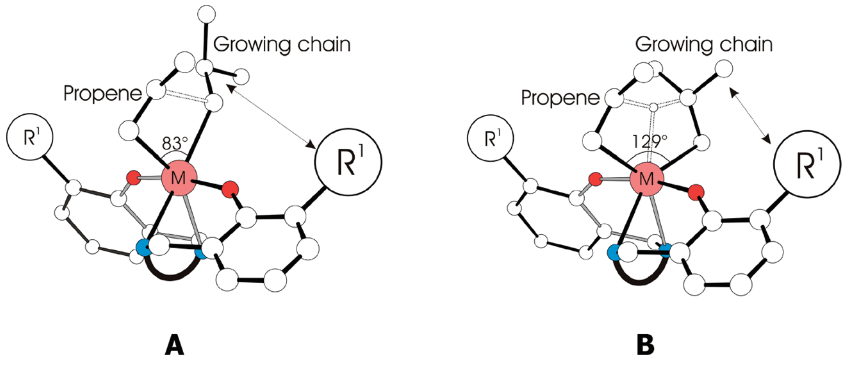

Table 1. Results of Ethene and Propene Homopolymerization at 25 °C with the Investigated Bis(phenoxyamine)Zr and Hf Catalysts (Cocatalyst, MAO/TBP; $[C_2H_4]$ = 0.22 M, $[C_3H_6]$ = 1.36 M in Toluene)

precatalyst	monomer	t_p, min	M_n, kDa	M_w/M_n	k_p, M^{-1} h^{-1} [a]	f_t, h^{-1} [b]	[*mmmm*][c]	σ[d]	$x_{2,1}$[e]
Hf-1	ethene	30	3.7	1.1	$(1.6 \pm 0.3) \times 10^3$	0.5 ± 0.2			
		60	6.7	1.2					
		120	8.6	1.2					
	propene	210	2.5	1.1	15 ± 4	0.08 ± 0.04	0.995	0.999	0.10
		390	3.2	1.1					
		1200	7.2	1.3					
Zr-1	ethene	1.5	9.8	1.2	$(9 \pm 1) \times 10^4$	11 ± 2			
		3	16	1.3					
		5	18	1.4					
		10	27	1.7					
		20	41	2.3					
	propene	115	14	1.3	$(2.3 \pm 0.4) \times 10^2$	0.41 ± 0.08	0.985	0.997	0.4
		240	21	1.5					
		360	22	1.6					
Hf-2	ethene	40	12	1.2	$(3.6 \pm 0.6) \times 10^3$	0.18 ± 0.07			
		60	23	1.2					
		120	27	1.2					
		180	49	1.3					
		240	51	1.4					
	propene	180	6.2	1.3	44 ± 1	0.071 ± 0.007	0.970	0.994	0.20
		270	8.8	1.3					
		360	10.5	1.4					
		540	13.9	1.5					
Zr-2	ethene	1.5	27	1.5	$(4.6 \pm 0.5) \times 10^5$	48 ± 5			
		3	33	1.8					
		6	39	2.0					
		15	47	2.0					
	propene	4	14	1.3	$(3.7 \pm 0.1) \times 10^3$	1.0	0.904	0.980	1.0
		8	28	1.3					
		15	55	1.5					
		30	105	1.6					

[a] Specific rate of chain propagation. [b] Cumulative frequency of chain transfer. [c] ^{13}C NMR fraction of isotactic pentad. [d] Site enantioselectivity, calculated from [*mmmm*] ($=\sigma^5$). [e] ^{13}C NMR fraction of 2,1 regiodefects.

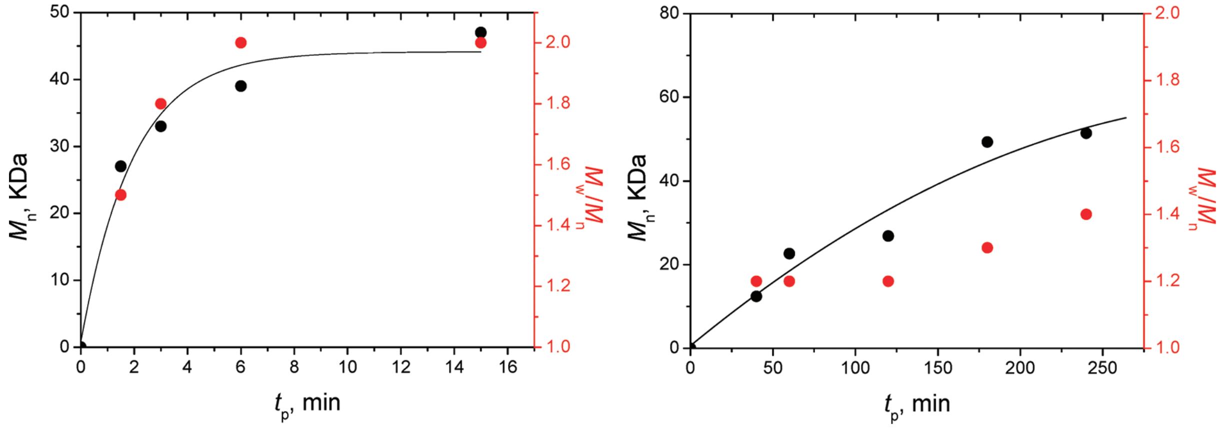

Figure 1. M_n and M_w/M_n values as a function of polymerization time for PE samples prepared at 25 °C with **Zr-2**/MAO/TBP (left) and **Hf-2**/MAO/TBP (right). For polymerization conditions see Table 1 and Supporting Information.

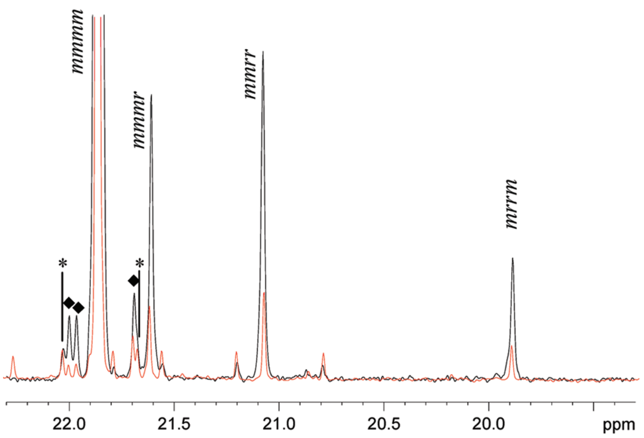

Figure 2. Overlay of the methyl region of the 100 MHz ^{13}C NMR spectra of two representative iPP samples prepared at 25 °C with **Zr-2**/MAO/TBP (black trace; t_p = 4 min) and **Hf-2**/MAO/TBP (red trace; t_p = 270 min). Peaks arising from stereoirregular and regioirregular units are attributed explicitly (the latter with the ◆ symbol).[12,21] The degree of stereo- and regioregularity of the samples can be estimated on inspection by comparison of the said peaks with the $^{13}C-^{13}C$ satellites (starred) of the *mmmm* pentad peak; quantitative data are provided in Table 1.

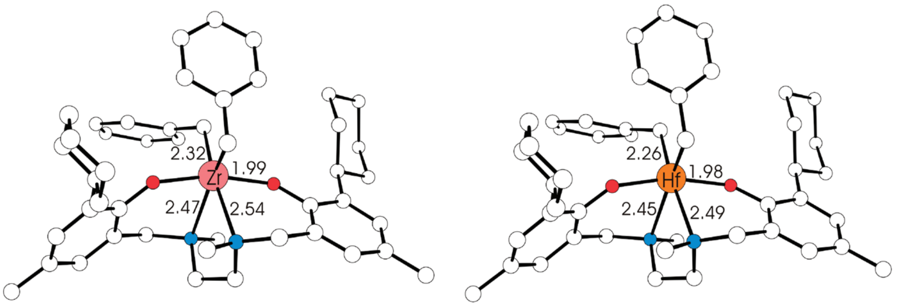

Figure 3. Detail of the solid state structures of **Zr-3**[7] and **Hf-3**. Selected bond lengths are in angstroms.

and Zr catalytic species (including metallocene ones) can have very similar activities.[14,20]

(ii) Chain transfer via residual β-H transfer was also significantly slower at Hf. Therefore, the molecular weight capability of each homologous catalyst couple, that is, the value of the $k_p[C_nH_n]/f_t$ ratio under the same experimental conditions, was rather similar, at odds with our expectation based on the literature.[12−14] The average lifetime of a polymer chain ($1/f_t$), on the other hand, was extended by 2 orders of magnitude upon changing from Zr to Hf. In ethene polymerization, in particular, the duration of the controlled kinetic regime was stretched from minutes with Zr to hours with Hf. This can be readily appreciated from Figure 1, where the M_n and M_w/M_n values of PE samples produced with **Hf-2** and **Zr-2** under identical conditions are plotted as a function of polymerization time.

(iii) Quite unexpectedly, in propene polymerization the Hf catalysts are much more regio- and stereoselective than the Zr ones (as revealed by the ^{13}C NMR microstructural analysis of the polymers). The active species of **Hf-1**, in particular, is one of the most selective ever reported,[1,12,13] with a regioselectivity in favor of 1,2-propene insertion and an enantioselectivity of the said insertion both as high as 99.9% (to be compared with corresponding values of 99.6% and 99.7% for that of **Zr-1**[7,8]). The catalyst derived from **Hf-2** turned out to be almost as good (99.8% regioselectivity, 99.4% enantioselectivity), with an even more striking improvement relative to **Zr-2** (99.0% regioselectivity, 98.0% enantioselectivity;[7,8] Figure 2).

We trace the higher selectivity of the Hf catalysts, and tentatively the lower activity as well, to a slightly tighter active pocket. In fact, the solid state structure of two homologous dibenzyl complexes with R^1 = cyclohexyl (**Zr-3**[7] and **Hf-3** of Chart 1) revealed M−X bond lengths shorter by up to 6 pm for **Hf-3** (Figure 3 and Supporting Information). It appears that this subtle modulation, likely associated with a higher stereorigidity of the ligand framework around the active metal due to the stronger coordination bonds, is enough to modify the polymerization behavior in a highly desirable direction.

Looking at activity, selectivity, molecular weight capability, and controlled kinetic properties altogether (Table 1), the best compromise for application in block copolymerizations is provided by **Hf-2**. Indeed, we successfully employed a **Hf-2**/MAO/TBP catalyst system to prepare iPP-*block*-EPR-*block*-iPP architectures. As an example, a sample obtained at 25 °C by sequential polymerization of propene (p_{C3} = 2.0 bar, t_p = 3 h), propene and ethene in mixture (p_{C3} = 1.2 bar, p_{C2} = 1.0 bar, t_p = 1 h), and propene again (p_{C3} = 2.0 bar, t_p = 3 h) exhibited the following properties: M_w/M_n = 1.2, M_n = 22 kDa, M_n(iPP block) = 8 kDa (each), M_n(EPR block) = 6 kDa, 70 mol % ethene in the EPR block, T_m = 143 °C, Δh_m = 67 J g^{-1} (see Supporting Information for the polymerization protocol and the GPC, NMR, and DSC characterizations).

In the near future we will report at length on the physical properties of these materials as well as on their remarkably good performance as phase compatibilizers in iPP/EPR physical blends.[22]

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Supporting Information Available: Text giving detailed experimental procedures for the preparation and characterization of the Zr and Hf precatalysts, the ethene and propene homopolymerization and block copolymerization experiments, and the NMR, GPC, and DSC polymer characterizations; details on the elucidation of the solid state structure of **Hf-3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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