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Block Copolymers of Highly Isotactic Polypropylene via Controlled Ziegler–Natta Polymerization

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Introduction. A polymerization is controlled¹ if chain initiation is rapid relative to propagation, and chain termination and transfer are "negligible" in the time scale of the experiment. When this holds, polymer molecular mass increases linearly with monomer conversion, and M_w/M_n is 1 or slightly higher, similarly to what happens under truly living conditions.

For most catalytic olefin polymerizations, at practical temperatures (>20 °C) a transient-controlled regime is observed for the first few seconds (with metallocene catalysts²) or fractions of a second (with "classical" Ziegler–Natta systems³). With a limited number of catalysts, though, the said regime extends over several minutes or even hours (which has often been described as a "living" character).⁴ Combining this with a high stereoselectivity is a challenging target and can open the way to novel polyolefin architectures and in the first place to block copolymers.

For the 1-alkene of highest market significance, namely propene, block copolymerization has been repeatedly achieved under a *syndiotactic* stereocontrol,⁴ which is of rather limited practical applicability; herein, we describe the first block copolymerization of propene under *highly isotactic* stereocontrol, using a new catalyst obtained by means of rational ligand design.

Kol and co-workers had reported⁵ on the living and highly isotactic polymerization of 1-hexene promoted by the C_2 -symmetric complex **1** of Chart 1 (Bn = benzyl), after activation by B(C₆F₅)₃.

In our hands, $1/B(C_6F_5)_3$ turned out to be inactive toward propene; on the other hand, with 1/methylalumoxane (MAO) and $1/[\text{HMe}_2\text{N}(C_6H_5)][B(C_6F_5)_4]/$ Al(*butyl*)₃ we obtained moderately isotactic polypropylenes of very low average molecular mass in reasonable yields.⁶ ¹³C NMR end group analysis of samples prepared at different propene concentrations revealed a 1,2 insertion regiochemistry and pointed to trans-alkylation by the Al-alkyl and β -H transfer *to the monomer* as the dominating chain transfer pathways.⁶

The former process was easily suppressed by reacting MAO or Al(h butyl)₃ with a sterically hindered phenol.^{7,8} Contrasting the latter and improving the stereoselectivity, instead, required a fine-tuning of the ancillary ligand, as is reported in this communication.

Results and Discussion. Simple quantum mechanics/molecular mechanics (QM/MM) calculations (see Supporting Information) on models of active cations led



Figure 1. QM/MM transition states for propene insertion with the *re* (top, left) and *si* (top, right) enantioface, and for β -H transfer to the monomer (bottom, left), at an active cation with Λ configuration. The growing chain is simulated with an 'butyl (in light green). Bulky R¹ substituents (generically represented with yellow spheres) disfavor the latter two processes due to the repulsive contacts evidenced with circles. The extreme case of β -H transfer to the monomer when R¹ = 1-adamantyl is explicitated (bottom, right).

Chart 1



	\mathbf{R}^{1}	\mathbf{R}^2
1	'Butyl	'Butyl
2	Methyl	Methyl
3	1-Adamantyl	Methyl
4	9-Anthracenyl	Methyl
5	Cumyl	Methyl

us to conclude that the alkyl substituent \mathbb{R}^1 (Chart 1) is crucial not only for the enantioselectivity (which is expected, based on the well-known growing chain orientation mechanism of stereocontrol^{6,9}) but also on the ease of monomer-induced chain transfer. Indeed, a bulkier \mathbb{R}^1 makes chain misorientation (i.e., with the first C–C bond pointing *toward* the nearest-in-space \mathbb{R}^1 , rather than *away* from it) more difficult and at the same time enhances the steric pressure on the spacedemanding six-center transition state of β -H transfer to propene,¹⁰ which is therefore severely destabilized (Figure 1).

In Table 1, we summarize the main results of our calculations, for the cases of \mathbb{R}^1 = methyl, 'butyl, 1-adamantyl, 9-anthracenyl, and cumyl. In particular, for each model system we report the difference in internal energy between the transition states of 1,2 propene insertion with opposite enantiofaces ($\Delta E^{\#}_{\text{enantio}}$) and that ($\Delta E^{\#}_{\text{T/P}}$) between the transition states of chain transfer to the monomer and of chain propagation via 1,2 insertion with the favored enantioface. The values of $\Delta E^{\#}_{\text{T/P}}$ are scaled to the case with $\mathbb{R}^1 = \mathbb{R}^2 = \mathbb{H}$, used as a reference ($\Delta E^{\#}_{\text{T/P}} = 0$) and computed at full-QM level; this means that such values can be used to predict

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Table 1. Calculated Values of $\Delta E^{\text{#}}_{\text{enantio}}$ and $\Delta E^{\text{#}}_{\text{T/P}}$ (for Definitions, See Text) for Propene Polymerization at Model Active Cations Derived from 1 to 5 of Chart 1^a

precursor	\mathbb{R}^1	\mathbb{R}^2	$\Delta E^{\!\!\#}_{\rm enantio}$	$\Delta E^{\!\!\!\#}{}_{\mathrm{T/P}}$
reference	Н	Н	0	0
2	methyl	methyl	0	0.2
1	⁴ butyl	^t butyl	1.7	1.8
3	1-adamantyl	methyl	4.1	3.5
4	9-anthracenyl	methyl	1.0	-1.5
5	cumyl	methyl	3.7	2.2

^aAll energy values in kcal/mol.

relative trends but not absolute average polymerization degrees. In all cases, R^1 , R^2 = alkyl (Chart 1) were modeled at the MM level, and the growing polypropylene chain was simulated with an ^{*i*}butyl.

From the table, it is immediate to note that for "spherical" $R^{1}s \ \Delta E^{\#}_{enantio}$ and $\Delta E^{\#}_{T/P}$ follow parallel trends. Indeed, both parameters increase regularly with increasing van der Waals radius, the highest values corresponding to $R^{1} = 1$ -adamantyl. At the other extreme, system **4**, with the big but flat $R^{1} = 9$ -anthracenyl, was predicted to afford a nonstereoregular polymer of lower average molecular mass than that with $R^{1} =$ methyl. With its bulky albeit conformationally flexible $R^{1} =$ cumyl (α, α -dimethylbenzyl), system **5** instead would lie in between **1** and **3**.

Complexes **3–5** of Chart 1 were prepared on purpose (see Experimental Section in the Supporting Information). They were then tested in propene polymerization at 25 °C, comparatively with the known^{5–7} complexes 1 and 2. The results, summarized in Table 2, are in nice agreement with the QM/MM-predicted trends, with one partial exception (vide infra).

The catalytic performance of **3**, in particular, is truly remarkable. It produces an isotactic polypropylene (iPP) which, at the ¹³C NMR characterization (see Supporting Information and Figure 2a), reveals only very low amounts of rr stereodefects (0.3 mol %) and of isolated 2,1 regiodefects in *erythro* configuration (0.4 mol %).⁹ The melting temperature of 151 °C and enthalpy of 110 J g⁻¹ are among the highest ever reported for "singlesite" iPP.9 Moreover, 13C NMR end group analysis of samples obtained at reaction times up to 3 h indicated a linear increase of $M_{
m n}$ (9.5 imes 10 3 Da at 1 h, 2.0 imes 10 4 Da at 2 h, 2.8×10^4 Da at 3 h), with the initial benzyl ends and the saturated ends deriving from reaction quenching with acidified methanol in 1:1 mole ratio within the experimental error (see again Figure 2a); consistently, M_w/M_n values ≤ 1.3 were measured by GPC (Supporting Information). Traces of terminal vinylidenes became detectable in the ¹H NMR spectra for reaction times in excess of 3 h.

Compared with the original catalyst **1**, the above corresponds to an increase in enantioselectivity from 96% to 99.7%, in average chain growth time (at 25 $^{\circ}$ C and under the conditions described) from less than 0.5

Table 2. Selected Results of Propene Polymerization (at 25 °C, $[C_3H_6] = 1.36$ M) Promoted by 1–5 (for Experimental
Details, see Supporting Information)

precursor	$R_{ m p}{}^a$	$k_{ m p},~{ m M}^{-1}~{ m s}^{-1}$	$f_{\mathrm{t,m}},^b \mathrm{s}^{-1}$	$t_{\rm cg}$, ^c min	$M_{\rm n}$, ^d kDa	$[mmmm]^e$	$T_{\mathrm{m}}, {}^{f} \circ \mathrm{C}$
2 g	0.9	n.d.	n.d.	n.d.	4	0.02	am ⁱ
1 <i>g</i> , <i>h</i>	1.6	0.045	$6 imes 10^{-4}$	28 ± 5	4	0.80	123
3 g	4.1	0.053	$3 imes 10^{-5}$	550 ± 150	110 ± 40	0.985	151
4 g	32	n.d.	n.d.	n.d.	0.8	0.02	am ⁱ
5 ^g	70	0.85	$3 imes 10^{-4}$	55 ± 20	180 ± 60	0.89	136

^{*a*} Productivity, in kg (polymer)/[mol (Zr) × $[C_3H_6] \times h]$. ^{*b*} Frequency of chain transfer to the monomer. ^{*c*} Average chain growth time. ^{*d*} Upper limit of M_n , calculated as $M_1k_p[C_3H_6]/f_{r,m}$, and reached approximately at $t_p > 3t_{cg}$. ^{*e*} ¹³C NMR fraction of isotactic pentads in fully regioregular sequences. ^{*f*} Maximum of the melting endotherm in second DSC heating scan for polypropylene samples at the upper limit of M_n . ^{*g*} Cocatalyst, [HMe₂N(C₆H₅)][B(C₆F₅)₄]/Al(^{*i*}Butyl)₃/2,6-di-^{*b*}butylphenol. ^{*h*} Data from ref 7. ^{*i*} Amorphous. n.d. = not determined (M_n and stereoregularity too low for accurate measurements).



Figure 2. 100 MHz ¹³C NMR spectra (in tetrachloroethane-1,2- d_2 at 120 °C) of (a) an iPP sample prepared with **3**/[HMe₂N-(C₆H₅)][B(C₆F₅)₄]/Al(^butyl)₃/2,6-di-^butylphenol at 25 °C and a reaction time of 1 h and (b) and of the sample of iPP-*block*-PE (see Experimental Section). The chemical shift scale is in ppm downfield of TMS. In (a), resonances labeled with a, b, c, d are due to benzyl ends, ^butyl ends, 2,1 regiodefects, and *rr* stereodefects, respectively;^{7,9} peaks not explicitly assigned in (b) arise from the regio- and stereodefects in the iPP block (refer to (a)).

to 9 h and in the limiting value of $M_{\rm n}$ from 4 to 110 kDa. This opens the door to the synthesis of block copolymers of highly isotactic polypropylene.

In Figure 2b, we show the fully assigned quantitative ¹³C NMR spectrum of a sample of iPP-*block*-PE (PE = polyethylene), prepared as described in the Experimental Section, with block lengths at the upper limit for end group and juncture detectability. From peak integration, by averaging over the said sets of resonances (in 1:1:1 integral ratio within the experimental error), we calculated a number-average polymerization degree of 2.4×10^2 for the iPP block and of 2.9×10^2 for the PE block; consistently, the GPC characterization gave a M_n value of 22 kDa and a M_w/M_n ratio of 1.3. The sample showed two DSC melting peaks, at 126 °C ($\Delta h_m = 65 \text{ J g}^{-1}$) and 152 °C ($\Delta h_m = 62 \text{ J g}^{-1}$), for the PE and iPP block, respectively (for GPC and DSC traces, see Supporting Information).

Let us now give a look at the performance of the other two new catalysts. In agreement with the QM/MM prediction, **4** turned out to afford an oligomeric, oily polypropylene, with just a slight enrichment in *syndiotactic* diads ([r] = 0.6, measured by ¹³C NMR) due to a weak stereocontrol exerted by the growing chain,⁹ similarly to **2**.⁶

The only system that performed partly at odds with the forecast of our relatively simple theoretical approach is **5**. Indeed, if the experimental enantioselectivity in propene insertion is intermediate between those of **1** and **3**, as anticipated, the molecular weight capability turned out to be *higher* than that of **3**, due to a *faster* chain transfer combined with a *much faster* chain propagation. The obvious conclusion is that the conformationally flexible cumyl fragment would require a more sophisticated computational analysis taking into account the contributions of *all* accessible transition state structures; this however was out of the scope of the paper.

In conclusion, by elaborating on a known ancillary ligand framework, we have developed the first catalyst for the highly isotactic controlled polymerization of propene and used it successfully in block copolymerization. Further developments, including a more detailed investigation of the structure and performance of the new catalysts, and the synthesis and characterization of a variety of novel iPP-*block*-polyolefin materials with different compositions and block lengths, will be reported in due course.

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Supporting Information Available: Experimental section, computational details, and GPC and DSC traces of iPP*block*-PE. This material is available free of charge via the Internet at http://pubs.acs.org.

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