Polypropylene "Chain Shuttling" at Enantiomorphous and Enantiopure Catalytic Species: Direct and Quantitative Evidence from Polymer Microstructure

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The synthesis of olefin block copolymers and stereoblock polymers in the presence of Ziegler−Natta (and related) catalysts is a long-standing important industrial target, in view of the peculiar physical properties anticipated for the resulting materials (e.g., thermoplastic elastomers). A possible strategy entails the use of living/controlled catalysts, with sequential (co)monomer feed[1,2] or under conditions of degenerative chain transfer;[3] however, the inherent limitation that only one polymer chain (at most) is produced per transition metal atom makes this approach, otherwise very elegant and well-defined, prohibitively expensive. More convenient in this respect would be "oscillating" catalysis, i.e., a process in which a nonliving fluxional active species undergoes reversible changes of the ancillary ligand framework, resulting in corresponding changes of selectivity;[4] unfortunately, controlling these fast molecular switches turned out to be extremely difficult.[5,6]

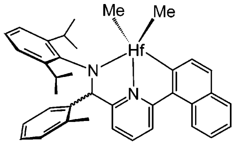
An industrially feasible route to olefin block copolymers based on reversible transalkylation has ultimately been disclosed.[7] It is known that in Ziegler−Natta (and related) olefin polymerizations the active transition metal polymeryls can undergo transalkylation with main group metal alkyls, normally used as cocatalysts and/or scavengers.[8] In most cases, this is a unidirectional chain transfer path, which leads to a decrease of average polymer molecular mass and to an accumulation of "dead" polymer chains bound to the main group metal (eq 1). In ethene polymerization and with certain catalysts, however, it has been found that the transalkylation can be reversible[7,9] and that polyethylene chains can be exchanged between active transition metal species with the mediation of a "dormant" (rather than "dead") main group metal species (eqs 1 and 2 in sequence). When used with two or more distinct catalysts, this process has been given the suggestive denomination of "chain shuttling".[7]

$$L_yM_{(1)}{-}P + R_xM{-}R \rightarrow L_yM_{(1)}{-}R + R_xM{-}P \qquad (1)$$

$$L_yM_{(2)}{-}R + R_xM{-}P \rightarrow L_yM_{(2)}{-}P + R_xM{-}R \qquad (2)$$

$$[M_{(1)} \text{ and } M_{(2)} = \text{transition metal}, \; M = \text{main group metal}, R = \text{alkyl}, \; P = \text{polymeryl, and } L_y = \text{ancillary ligand(s)}]$$

Chart 1



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Catalytic olefin polymerization under chain shuttling conditions has exciting scientific and practical applications. In particular, block copolymers with alternating noncrystallizable ("soft") and crystallizable ("hard") segments have been produced by shuttling growing ethene/1-octene copolymer chains between two distinct catalysts with different chemoselectivities[7] (namely, a (pyridyl-amide)Hf[10] and a bis(phenoxy-imine)Zr[11] catalyst known to be a good and a poor 1-octene incorporator, respectively, and both amenable to fast ZnR_2-mediated polyethylene chain shuttling). The novel block copolymers have remarkable thermoplastic−elastomeric properties,[7] which has already led to the anticipation of large-scale industrial production.[12]

In this Communication we now demonstrate that, under proper conditions, chain shuttling can occur for polypropylene chains as well and that in the presence of a chiral isotactic-selective catalyst used in racemic form it yields stereoblock−isotactic polypropylene.[13,14] We also provide a cross-check of our microstructural assignment and mechanistic conclusions by comparing the results with those achieved with the same catalyst in enantiopure form.

As a convenient (pre)catalyst for this study we chose the (pyridyl-amide)$HfMe_2$ complex 1 of Chart 1 because (i) it belongs to one of the two catalyst classes used in ref 7 to produce ethene/1-octene block copolymers via chain shuttling, (ii) it is highly isotactic-selective for polypropylene due to enantiomorphic sites control, as shown by the fact that the few stereodefects in the polymer detected by ^{13}C NMR are of $m_x(rr)m_y$ type[10b] (Chart 2a), and (iii) it is chiral due to a configurationally stable stereogenic C in the ancillary ligand, which makes it possible to prepare and use it in enantiopure form. Under chain shuttling conditions, propene polymerization with the racemic catalyst is expected to yield stereoblock−isotactic polypropylene (Chart 2b)[13,14] as a result of the statistical exchange of growing polymer chains between active centers of opposite chirality; this cannot happen with the enantiopure catalyst, which therefore should always end up with the "standard" isotactic polypropylene microstructure (Chart 2a). Discriminating between the two cases of Chart 2 by ^{13}C NMR is straightforward.[13]

The synthesis of *rac*-**1** was carried out by reaction of the Li salt of the pyridylamine ligand (*rac*-L1NH) with $HfCl_4$, followed by methylation with MeMgBr (see Supporting Information). (*R*)-**1** was prepared similarly using the ligand in *R* configuration [(*R*)-L1NH; e.e. ≥98% (HPLC)], as obtained by reaction of *rac*-L1NH with (+)-(1*S*)-camphor-10-sulfonic acid, fractional crystallization of the diastereomeric salt, and subsequent neutralization (Figure 1 and Supporting Information).

Propene batch polymerizations in the presence of either *rac*-**1** or (*R*)-**1** were run at 70 °C in toluene [$\epsilon = 2.4$] or 1,2-difluorobenzene [$\epsilon = 14.3$]. In our studies, good results were achieved using MAO containing $AlMe_3$ as the chain shuttling agent (CSA); the reactions were carried out at constant propene concentration and quenched with methanol at low yield (~1.0 g of polymer/50 mL), so as to avoid mass transfer limitations in viscous solutions/slurries and to keep the concentration of

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Chart 2

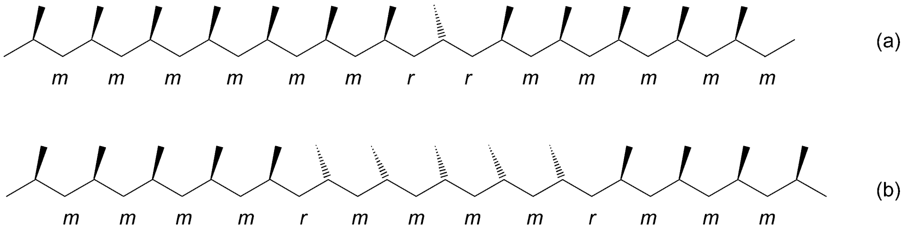


Table 1. Main Results of Propene Polymerization Promoted by 1/MAO/AlMe$_3$ at 70 °C in Toluene (T) or 1,2-Difluorobenzene (DFB) (Solvent Volume, 50 mL; for the Experimental Procedure, see Supporting Information)

entry/sample	catalyst	Hf, μmol	AlMe$_3$, mmol	solvent	[C$_3$H$_6$], M	yield, g	*t*, min	M_w/M_n	M_n,[a] kDa	P_{inv}[a,b]
1	*rac*-**1**	5.0	0.30	T	0.24	0.4	130	3.8[c]	2.8	0.0084
2	*rac*-**1**	5.0	0.30	DFB	0.24	0.7	3.5	1.2	2.0	0.050
3	*rac*-**1**	5.0	0.60	T	0.24	1.0	38	3.8[c]	2.2	0.013
4	*rac*-**1**	5.0	0.60	DFB	0.24	1.0	11	1.1	1.5	0.116
5	*rac*-**1**	5.0	1.20	T	0.24	1.0	56	1.4	1.8	0.023
6	*rac*-**1**	5.0	1.20	DFB	0.24	1.5	20	1.1	1.0	0.18
7	*rac*-**1**	2.5	0.60	DFB	0.24	1.2	17	1.5	2.3	0.038
8	*rac*-**1**	10.0	0.60	DFB	0.24	0.8	6.5	1.1	1.2	0.18
9	*rac*-**1**	5.0	0.60	DFB	0.42	0.9	3.1	1.2	1.5	0.050
10	*rac*-**1**	5.0	0.60	DFB	0.62	1.5	2.0	1.4	2.1	0.028
11	(R)-**1**	5.0	0.60	DFB	0.24	1.1	9.0	1.2	1.7	

[a] Determined by ^{13}C NMR. [b] Probability of inverting the configuration of the propagating center, according to the enantiomorphic-sites model (see text). [c] Bimodal molecular mass distribution.

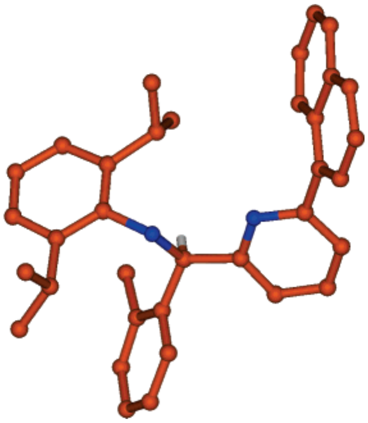


Figure 1. Details of the single-crystal X-ray diffraction structure of [(*R*)-L1NH$_2$][(+)-(1*S*)-camphor-10-sulfonate], showing the absolute configuration of the [(*R*)-L1NH$_2$]$^+$ cation (N atoms in blue; H atom on chiral C added for clarity). For the complete crystal structure, see the Supporting Information.

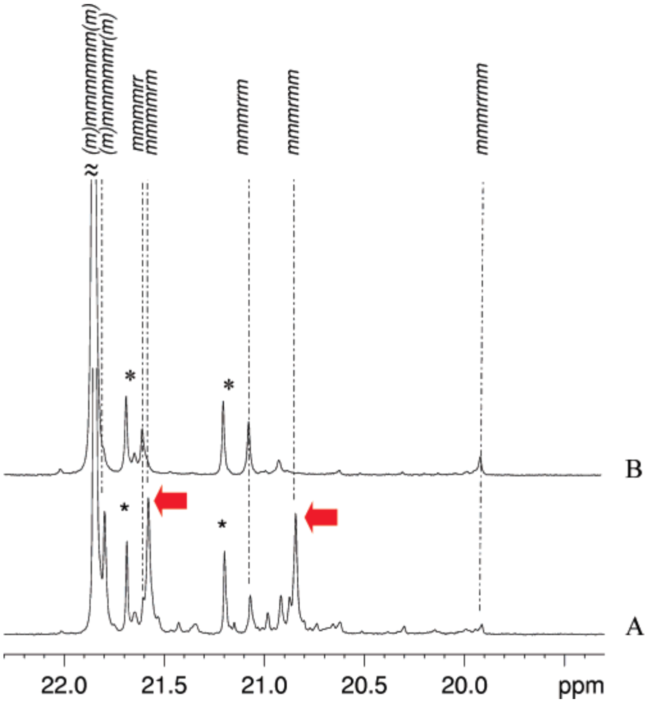


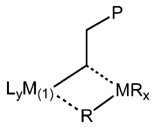
Figure 2. Methyl region of the 100 MHz ^{13}C NMR spectra (in tetrachloroethane-1,2-d_2 solution at 120 °C) of the polypropylene samples of which at entry 4 (A) and entry 11 (B) of Table 1, revealing a stereoblock−isotactic and a site-controlled isotactic microstructure, respectively. In the former case, peaks arising from $m_x(r)m_y$ junctures between stereoblocks of opposite relative configuration are evidenced with arrows. Peaks marked with asterisks (∗) are due to isobutyl chain ends.

AlR$_3$ (which also acts as an impurity scavenger) at a reasonably constant value. No appreciable advantages were observed by using ZnEt$_2$ in the place of AlMe$_3$.

The main results are summarized in Table 1. A convenient parameter to be monitored throughout the set of experiments is polymer polydispersity (i.e., the M_w/M_n ratio), which for a single-center catalyst is close to 2.0 when chain shuttling does not occur, whereas it approaches 1.0 when chain shuttling is fast.[7,9] On the basis of these results, the rather surprising conclusion is that AlMe$_3$ can be an effective CSA for the system under study, *provided that one operates in a polar solvent like 1,2-difluorobenzene*.

The methyl region of the ^{13}C NMR spectrum of a typical polypropylene sample made with *rac*-**1**/MAO/AlMe$_3$ in 1,2-difluorobenzene (entry 4 of Table 1) is shown in Figure 2A; the intense sharp peaks due to $m_x(r)m_y$ stereosequences are immediately diagnostic for the stereoblock−isotactic microstructure of Chart 2b. Additional peaks are due to the isobutyl chain ends inherent to transalkylation with AlMe$_3$ and to the occasional $m_x(rr)m_y$ stereodefects.[13] Unambiguous evidence that this microstructure is indeed the result of chain shuttling between enantiomorphous catalytic species was achieved by duplicating the polymerization experiment with the enantiopure catalyst (*R*)-**1** in the place of *rac*-**1** (entry 11 of Table 1); in the ^{13}C NMR spectrum of the polymer thus obtained (Figure 2B) all $m_x(r)m_y$ resonances are absent, and the simple pattern is that typical of a low-molecular-mass site-controlled isotactic polypropylene (Chart 2a).

Chart 3



To the best of our knowledge, this is the first ^{13}C NMR evidence of chain shuttling for polyolefins in general. For polypropylene in particular, in previously claimed cases[15−17] the microstructural analysis of the polymer was inconclusive, and fractionation results revealed that the samples were largely physical blends, with at most a minor fraction of stereoblock chains.

A quantitative statistical analysis of polymer configuration can be carried out with a simple enantiomorphic-sites stochastic model in Coleman−Fox version.[13] The model, which was explained in detail and used for the microstructural analysis of stereoblock−isotactic polypropylenes prepared with so-called "oscillating" metallocene catalysts,[6,14] has two adjustable parameters, namely the probability σ ($\sim$0.99 in the present case[10b]) to insert propene with the favored enantioface at a catalytic species with a given configuration and the probability P_{inv} that the said configuration is inverted. Of course, in case the latter event is traceable to chain shuttling between enantiomorphous active species of a racemic catalyst, the shuttling probability is $2P_{\mathrm{inv}}$. The effect of relevant reaction parameters on P_{inv}, as measured by ^{13}C NMR on the corresponding polypropylene samples (for details, see Supporting Information), is shown in the last column of Table 1; it can be seen that—in agreement with common sense—P_{inv} increases with decreasing propene concentration (see entries 4, 9, 10) and with increasing catalyst (entries 7, 4, 8) and CSA (entries 2, 4, 6) concentration. Under a fast chain shuttling regime, the stochastic probabilities of chain shuttling ($2P_{\mathrm{inv}}$) and of monomer insertion ($1-2P_{\mathrm{inv}}$) are comparable (see, e.g., entries 6 and 8); in the limit of $2P_{\mathrm{inv}} = 0.5$, an atactic polypropylene will be obtained out of a highly stereoselective catalyst.

The nature and concentration of the CSA are of primary importance. In this study using $AlMe_3$, Table 1 shows a trend of decreasing catalyst productivity with increasing Al concentration. From on-line measurements of propene uptake, we could conclude that this is due to an increasingly long induction *and* to a lower activity at steady state; the induction period is particularly long for polymerizations in toluene (up to 1 h under the conditions used). Our interpretation is that the concentrations of Al-alkyls and mononuclear (pyridyl-amide)Hf-polypropenyl active cations are inversely proportional and that methyl-bridged hetero-bimetallic species are more difficult to split than homologous ones having larger alkyl residues (Chart 3), as has been found before with metallocenes.[17−19]

The results reported in this Communication, along with those of ref 7, demonstrate the wide scope of chain shuttling in catalytic olefin polymerization but also a fairly narrow operation window. In particular, for a given catalyst/CSA combination, the precondition that the alkyl-bridged, hetero-bimetallic intermediates assumed to be involved[7,9] (Chart 3) are labile seems to be exquisitely dependent (inter alia) on the chemical identity of the monomer (and therefore of the growing polymeryl), of the catalyst activator, and—last but not least—of the reaction solvent.

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Supporting Information Available: Synthesis of precatalysts *rac*-1 and (*R*)-1; X-ray structure determination of [(*R*)-L1NH$_2$][(+)-(1*S*)-camphor-10-sulfonate].(+)-(1*S*)-camphor-10-sulfonic acid; experimental details on propene polymerizations and on ^{13}C NMR and GPC polypropylene characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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