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Origins of Stereoselectivity and Stereoerror Formation in *ansa*-Zirconocene-Catalyzed Isotactic Propene Polymerization. A Deuterium Labeling Study[1]

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Isotactic polypropene can be obtained with chiral *ansa*-zirconocene catalysts: when prepared with the prototypic catalyst $C_2H_4(thind)_2ZrCl_2$/MAO,[2] its stereoregularity is strongly dependent on polymerization temperatures and other polymerization conditions.[2−4] With suitably substituted *ansa*-zirconocene catalysts, very high stereoregularities are obtained, even in the temperature range of 50−80 °C.[5,6] An in-depth understanding of the factors which control the stereoselectivity of these homogeneous catalysts remains a serious challenge.

It has been proposed by Rooney, Brookhart and Green,[7] that insertion of olefins into the metal−alkyl bond of a Ziegler−Natta catalyst might require an agostic interaction of one of the α-H atoms of the metal-bound alkyl chain with the metal center.[8] This can be tested, as proposed by Grubbs and coworkers,[9] by kinetic isotope effects which a D atom in a metal-bound α-CHD group exerts on the stereochemistry of an olefin insertion into the metal−alkyl bond. Stereokinetic isotope effects with values of $k_H/k_D \approx 1.3$ have indeed been observed for hydrocyclizations of (*E*)- and (*Z*)-1,5-hexadiene-*1,6-d*$_2$ and hydrodimerizations of (*E*)- and (*Z*)-1-hexene-*1-d* by scandocene- and zirconocene-based catalysts.[10,11] From a study on polymerizations of (*E*)- and (*Z*)-propene-*1-d* by chiral *ansa*-zirconocene catalysts, we have now obtained direct experimental evidence for the role of α-agostic interactions in the formation of isotactic polypropene and for the origins of occasional stereoerrors in these homogeneous catalyst systems.

Polypropenes obtained with the chiral *ansa*-zirconocene catalysts *rac*-$C_2H_4(thind)_2ZrCl_2$/MAO (**1**),[2] *rac*-$Me_2Si(C_5H_2$-2,4-$Me_2)_2ZrCl_2$/MAO (**2**), or *rac*-$Me_2Si(C_5H_2$-2-Me-4-$^tBu)_2ZrCl_2$/MAO (**3**)[5] are only slightly affected in their isotacticities by the use of either (*E*)- or (*Z*)-propene-*1-d*,[12] the polymers formed from (*Z*)-propene-*1-d* being marginally less isotactic (Table 1). Apparently, the stereochemistry of propene insertion into the Zr−polymer bond is so strongly controlled by the chiral ligand framework that it cannot be influenced significantly by any isotope effects.

Highly significant differences between the propene isotopomers are evident, however, with regard to the mean degrees of polymerization, P_N. Polymers derived from (*E*)-propene-*1-d* have P_N values which are higher than those obtained from (*Z*)-propene-*1-d* by a factor of ca. 1.3 for each of the catalysts employed (Table 1).[13]

For polymers of the type considered here, the mean degree of polymerization is given by the ratio of the rates of polymer growth, ν_P, and chain termination, ν_T, $P_N = \nu_P/\nu_T$.[14] In analyzing how ν_P and ν_T are affected by the (*E*)- or (*Z*)-deuteration of the olefin substrate, we note that insertion by a given enantioface will lead to ZrCHDR units with different configurations of their α-CHD groups. If a given catalyst enantiomer enforces, e.g., *re*-facial olefin insertion, each α-CHD group will be *R*-configurated if derived from (*E*)-deuterated and *S*-configurated if derived from (*Z*)-deuterated propene (Scheme 1).

As chain growth is terminated in these reaction systems mainly by β-H-transfer,[15] it is quite unlikely that ν_T would depend on the configuration of the α-CHD group to any significant degree.[17] The configuration of this group can affect ν_P on the other hand: if insertion of an olefin does indeed require that one of the α-H atoms of this group is in bonding contact with the Zr center, then it is apparent that the steric requirements of the chiral ligand environment will force the H atom of the *R*-configurated α-CHD group derived from (*E*)-propene-*1-d* into this position, while the *S*-configurated α-CHD group derived from (*Z*)-propene-*1-d* must place its D atom in the agostic position. Due to its greater loss in zero-point energy, a transition state with a Zr−H−C(α) bond will lead to a higher rate of insertion than its Zr−D−C(α)-stablized counterpart and hence to a correspondingly higher value of P_N. The P_N values reported in Table 1 indicate that ν_P for the reaction mode with Zr−H−C(α) interaction exceeds that for the Zr−D−C(α) mode by a factor of ca. 1.3. This value of k_H/k_D concurs with values of

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[1] *ansa*-Metallocene Derivatives. 31. For part 30, see: Dorer, B.; Prosenc, M. H.; Rief, U.; Brintzinger, H. H. *Organometallics*, **1994**, *13*, 3868.

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[12] Reaction conditions: 0.271 μmol of the respective *ansa*-zirconocene dichloride in 2 mL of toluene and 0.6 mL of a 10% solution of methylaluminoxane in toluene (0.88 mmol $Al(CH_3)O$; Al:Zr 3250:1) were diluted to 20 mL with toluene ($[Zr] = 1.35 \times 10^{-5}$) and incubated for 30 min at the temperature indicated; (*E*)- or (*Z*)-propene-*1-d* was then added and kept at a constant pressure of 1 bar. After 30−50 min, the reaction was quenched with CH_3OH/HCl and the polymer isolated by filtration and drying at room temperature for 1 day.

[13] Propene-d_0 yields polymers with P_N values lower than those obtained with (*E*)-propene-*1-d* by a factor of ca. 0.93.

[14] Flory P. J. *Principles of Polymer Chemistry;* Cornell University Press: Ithaca, NY, 1986; p 317.

[15] Only 2-propenyl and *n*-propyl end groups, arising from β-H transfer,[16] are observed in the ^{13}C NMR spectra of polypropene made with catalysts **1** and **2**. With catalyst **3**, isopropyl end groups (from alkyl exchange with the methyl aluminum activator) have similar intensities as n-propyl and 2-propenyl ends.

[16] Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. Tsutsui, T.; Mizuno, A.; Kashiwa, N. *Polymer* **1989**, *30*, 428.

[17] The presence of a D atom at the α-C atom is likely to affect ν_T by a secondary kinetic isotope effect, since β-H transfer must cause electron density changes at both the α- and β-C atoms. While this secondary isotope effect undoubtedly contributes to the differences in P_N between undeuterated and propene-*1-d* polymers,[13] its magnitude is unlikely to be different for (*E*)- and (*Z*)-propene-*1-d*.

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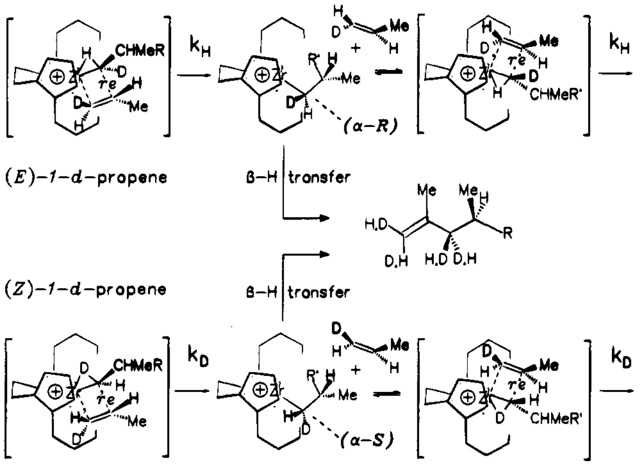
Table 1. Isotacticity ([*mmmm*], %) and Mean Degree of Polymerization (P_N) for Poly(*Z*)- and -(*E*)-Propene-*1-d* Obtained with Chiral *ansa*-Zirconocene Catalysts

	catalyst[a] (T_P[b])					
	1 (30 °C)		**2** (50 °C)		**3** (50 °C)	
	Z	E	Z	E	Z	E
[*mmmm*]	72	75	78	79	>98[20]	>98[20]
P_N[c]	96	134	46	59	94	124
$P_N(E)/P_N(Z)$	1.32		1.29		1.32	

[a] **1**, *rac*-$C_2H_4(\text{thind})_2ZrCl_2$/MAO; **2**, *rac*-$Me_2Si(C_5H_2\text{-}2,4\text{-}Me_2)_2ZrCl_2$/MAO; **3**, *rac*-$Me_2Si(C_5H_2\text{-}2\text{-}Me\text{-}4\text{-}{}^tBu)_2ZrCl_2$/MAO. [b] Polymerization temperature; other conditions as given in ref 12. [c] Determined as the ratio of the total integral of all CH_3 groups (22.6−19.0 ppm) divided by that of the terminal *n*-propyl CH_3 group at 14.1 ppm.

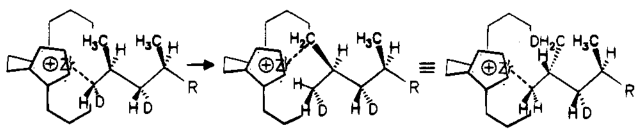
Scheme 1. Growth of Isotactic Polypropene from (*E*)-Propene-*1-d* via Zr −H-Stabilized Transition State (Top) and from (*Z*)-Propene-*1-d* via Zr −D-Stabilized Transition State (Bottom) and Chain Termination by *β*-H Transfer (R ′ = CHDCH(CH_3)R)



$k_H/k_D \approx$ 1.3 previously found for olefin insertions in hydrocyclization and hydrodimerization catalysis.[10,11] We can thus safely conclude that α-agostic interactions of the same type are indeed operative also in isotactic propene polymerization reactions with chiral *ansa*-zirconocene catalysts.

The stereochemical consequences of this α-agostic interaction are evident from Scheme 1. Of the two hydrogen atoms of an α-CH_2 group, only one can bind to the Zr center in accord with the steric requirements of the chiral ligand environment, while attachment of the other α-H atom would lead to prohibitive steric repulsions between the polymer chain and *β*-substituents at the C_5 ring ligands. The enantiofacial orientation of an inserting olefin is controlled, as established by ^{13}C NMR studies by Zambelli's group[18] and by molecular mechanics calculation by Corradini, Guerra, and co-workers,[19] by the requirement to place the olefin substituent trans to the C(α)−C(*β*) segment of the growing alkyl chain. The orientation of this segment is dictated by the steric accessibility of the two alternative Zr−H(α) interactions; placement of the *β*-C atom of the growing alkyl chain into the more open of its two possible positions at a rigid three-membered $\underline{\mathrm{Zr{-}H(\alpha){-}C(\alpha)}}$ ring thus appears to be the primary cause for the stereoselectivity of chiral *ansa*-zirconocene catalysts.

Scheme 2. Stereoerror Formation by Isomerization of the Last-Inserted Unit



The inaccessibility of one of the alternative Zr−H(α) interactions, implied by our model, raises the question of how such a catalyst might allow occasional stereoerrors to occur. A clue in this regard is provided by the D atom coupled ^{13}C NMR signals of the polymers obtained from (*E*)- or (*Z*)-propene-*1-d* with catalysts **1** and **2**.[20] In addition to triplet signals expected for the CHD groups of the polymer backbone,[21] we find, to our surprise, another triplet signal with $J(^{13}C,^2D)$ = 18.9 Hz for the *mrrm*-framed methyl groups of isolated stereoerrors at 19.4 ppm, the normal *mrrm* CH_3 signal at 19.7 ppm being reduced to about 20% of its expected size. This observation documents that most of the methyl groups associated with a stereoerror carry a deuterium atom and must hence originate from the α-CHD group and not from the CH_3 substituent of the olefin.

The main portion of stereoerrors in isotactic polypropene produced by *ansa*-zirconocene catalysts such as **1** or **2** thus appears to arise from an isomerization of the type represented in Scheme 2. Busico and Cipullo[3] and Resconi et al.[4] have recently proposed that an isomerization of the last-inserted Zr−$CH_2CH(CH_3)$−polymer unit might account for an increase in stereoerror incidence at decreased olefin concentrations. Our data provide direct experimental evidence that the stereoerrors produced in these catalyst systems arise predominantly from chain-end isomerization rather than from errors in the enantiofacial orientation of the inserting olefin.[22] The detailed mechanisms of the isomerization represented in Scheme 2[23] and the ways in which it is suppressed in more highly stereoselective *ansa*-zirconocene catalysts[5,6] remain to be elucidated.

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Supplementary Material Available: ^{13}C NMR spectra (CH_3 group region) of polypropenes obtained with catalysts **1**−**3** from (*E*)- and (*Z*)-propene-*1-d* and from undeuterated propene, measured on a JEOL JMN GX 400 spectrometer operated at 96.4 MHz, with peak assignments and legend (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(20) In the polymers obtained with catalyst **3**, the stereoerror pentad signals are not detectable by ^{13}C NMR.

(21) Triplets with $J(^{13}C,^2D) \approx$ 19 Hz are observed in the backbone methylene region (45.0−46.5 ppm) and in the positions expected for the CHD groups of *n*-propyl and iso-propyl chain ends.[14]

(22) The size of the undeuterated part of the *mrrm* signal corresponds roughly to that fraction of stereoerrors which persist even at high olefin concentrations;[3,4] it might thus be a measure for genuine errors in enantiofacial olefin orientation.

(23) In accord with Scheme 2, the *mmrr* pentad signal is split into two equally large signals with $\Delta\delta \approx$ 0.04 ppm in poly-(*E*)-propene-*1-d* (and broadened in poly-(*Z*)-propene-*1-d*): one of the *mmrr* CH_3 groups next to each *mrrm* CH_2D group is flanked by two γ-CHD groups, the other one by a γ-CHD and a γ-CH_2 group.