Cyclopolymerization of 1,5-Hexadiene by Enantiomerically-Pure Zirconium Salan Complexes. Polymer Optical Activity Reveals α-Olefin Face Preference

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Isospecific polymerization catalysts interact preferentially with one of the two enantiotopic faces of an incoming α-olefin. Therefore, such catalysts that operate by the enantiomorphic-site control mechanism need to be chiral. The correlation between the catalyst's absolute chirality and the interacting *re*- or *si*-face of the α-olefin is probably the most fundamental aspect of isospecificity. Since chirality is diminished upon formation of macromolecular poly(α-olefin) chains, this correlation cannot be addressed by optical rotation measurements of the polymer.[1] In contrast, the chirality may be retained in *cyclopolymerization* of α,ω-diolefins as demonstrated by Coates and Waymouth that had cyclopolymerized 1,5-hexadiene by a BINOL-resolved C_2-symmetric *ansa*-metallocene and obtained optically active poly(methylene-1,3-cyclopentane)—PMCP.[2] To our knowledge, no other catalyst systems have been reported to date that afford optically active PMCP. In this work we describe this polymerization by a series of optically active Salan zirconium complexes. The sign of the optical rotation of the obtained polymers gives clear evidence regarding the olefin face preference, and it indicates that more than a single factor may be involved in controlling it.

The 1-hexene polymerization activities of the zirconium complexes based on chiral Salan ligands closely matched those of the complexes derived from the achiral ligands,[3] i.e., high isospecificity for bulky ligands, and high activity for electron-poor ligands.[4] However, their application in 1,5-hexadiene polymerization led to insoluble polymers, apparently resulting from cross-linking of a few remaining non-cyclized olefin groups. Looking for conditions that will encourage fuller cyclization, we turned to higher temperature polymerization (ca. 55 °C) under dilution (in toluene). The (*R*,*R*)-ligands studied in this work and their diastereoselectively formed Δ-dibenzylzirconium complexes are described in Scheme 1.

The complexes of the bulkiest ligands were expected to exhibit the highest isospecificity in 1,5-hexadiene cyclopolymerization. Complex (*R*,*R*)-Lig^{1}ZrBn$_2$ featuring *tert*-Bu substituents led only to traces of polymeric material, however *rac*-Lig^{2}ZrBn$_2$ did afford a soluble polymer, so we attempted the synthesis of Lig^{2}H$_2$ in an enantiomerically pure form. Condensation of (*R*,*R*)-1,2-diaminocyclohexane with the corresponding salicylaldehyde followed by reduction and methylation, as employed for the other chiral Salan ligands,[4a] failed due to a sluggish reduction. It was therefore synthesized by a Mannich condensation from (*R*,*R*)-1,2-*N*,*N*′-(dimethyl)diaminocyclohexane,[5] formaldehyde, and the substituted phenol (see the Supporting Information). It was obtained as a white crystalline solid having an $[\alpha]_D$ of + 51°, and was reacted with tetrabenzylzirconium to give the corresponding yellow dibenzyl complex (*R*,*R*)-Lig^{2}ZrBn$_2$ as a single diastereomer having an $[\alpha]_D$ of + 205°. Single crystals of (*R*,*R*)-Lig^{2}ZrBn$_2$ were obtained from cold ether and their structure was solved. Two molecules were found in the asymmetric unit, and two molecular views of one of them are described in Figure 1. Notably, both molecules feature the predicted Δ-wrapping of the (*R*,*R*)-ligand around the zirconium. The adamantyl groups are clearly blocking two of the quadrants available for olefin coordination and polymer growth.

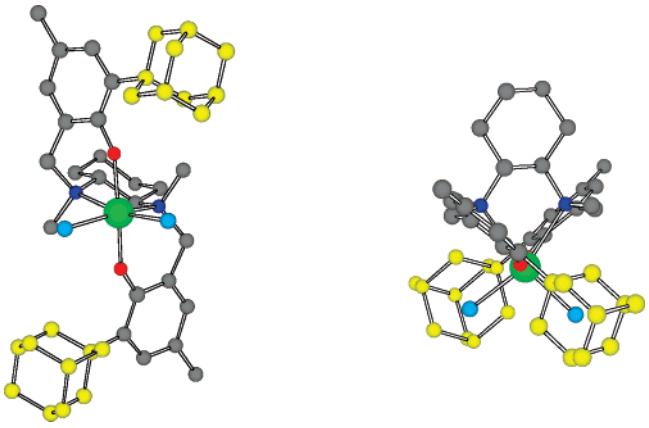

Figure 1. Front (left) and top views of (*R*,*R*)-Δ-(+)-Lig^{2}ZrBn$_2$ (the benzyl phenyl groups were omitted for clarity).

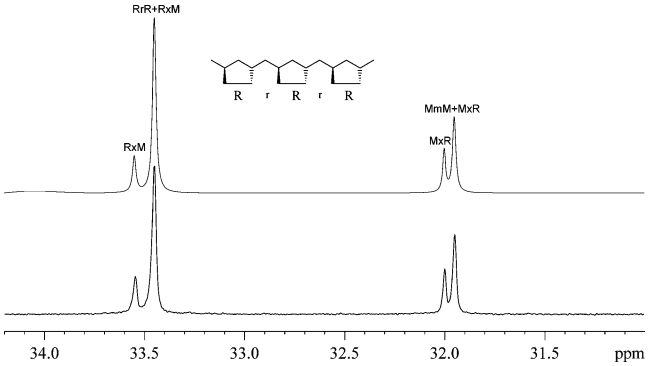

Figure 2. (Bottom) $C_{4,5}$ region of the ^{13}C NMR spectrum of PMCP prepared with Lig^{2}ZrBn$_2$/B(C$_6$F$_5$)$_3$; assignments according to ref 2b. (Top) Simulated spectrum with peak ratios of [RxM]:[RrR + RxM]:[MxR]:[MmM + MxR] of 1.0:4.9:1.0:2.1. (Inset) Trans-isotactic isomer of PMCP.

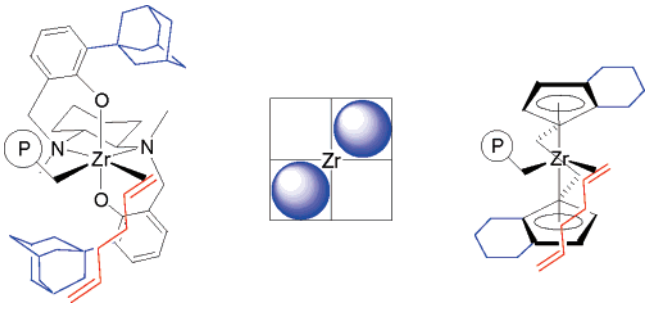

Figure 3. Preferred reinsertion of 1,5-hexadiene in Δ-Salan−Zr (left) and (*S*,*S*)-EBTHI−Zr complexes and a schematic quadrant view.

Out of the four possible ordered microstructures of PMCP only the "*trans*-isotactic" devoid of mirror planes is chiral (Figure 2, inset).[2] "*Tacticity*" refers to the stereochemical relationship between repeat units and is dictated by the

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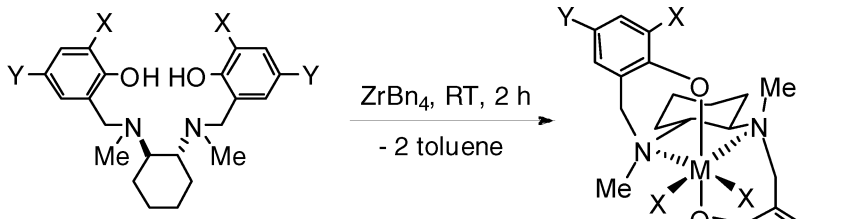
Scheme 1. (*R,R*)-Salan Ligands and Their (Δ)-Dibenzylzirconium Complexes



(*R,R*)-Lig^{1}H$_2$: X,Y = *tert*-Bu
(*R,R*)-Lig^{2}H$_2$: X = 1-Adamantyl, Y = Me
(*R,R*)-Lig^{3}H$_2$: X,Y = Br
(*R,R*)-Lig^{4}H$_2$: X = Me, Y = H

(*R,R*)-(Δ)-Lig$^{1\text{-}4}$ZrBn$_2$

enantiofacial *re*−*si* preference at the insertion step of a new monomer unit. "*Cis*−*trans*" refers to the relative orientation of methylene substituents on a given cyclopentane ring and is dictated by the diastereofacial *re*−*si* preference at the cyclization step. Formation of the *trans*-isotactic stereoisomer requires opposite face preferences in the two events, e.g., *re*-insertion followed by *si*-cyclization.

Polymerization of 1,5-hexadiene by (*R,R*)-Lig^{2}ZrBn$_2$/B(C$_6$F$_5$)$_3$ yielded a soluble polymer having $[\alpha]_D$ of −24°.[6] The $C_{4,5}$ region of the ^{13}C NMR spectrum of a polymer sample in $CDCl_3$ is shown in Figure 2 (bottom). The peaks at ca. 33.5 ppm correspond to *trans*-tetrads and the peaks at 32.0 ppm correspond to *cis*-tetrads.[2] A simulated spectrum with peak ratios of 1.0:4.9:1.0:2.1 for the four peaks ([RxM]:[RrR + RxM]:[MxR]:[MmM + MxR]) is shown in Figure 2 (top). This ratio corresponds to a mild *trans*-preference of $1 - \sigma = 0.66$, and a very high isospecificity factor of $\alpha \geq 0.99$. In comparison, a somewhat higher *trans*-preference ($1 - \sigma = 0.72$) and a lower isotacticity factor ($\alpha = 0.91$) were reported for polymerization with (EBTHI)ZrBINOL. As the polymerization with the Salan complex was performed at higher temperature (55 vs 23 °C for the *ansa*-zirconocene), its relative isospecificity induction is even more pronounced.

The $[\alpha]_D$ of the PMCP's derived from the Salan and from the *ansa*-metallocene catalysts are comparable, indicating that the different degrees of tacticity and *trans*-preference counterbalance. Assuming that similar sources of stereocontrol operate in both catalysts,[7] the sign of the polymer's optical rotation supports an olefin face-selectivity equivalence between the Δ-Salan−Zr complex (derived from the *R,R*-ligand) and the (*S,S*)-EBTHI−Zr complex, namely an insertion event via a *re*-face of 1,5-hexadiene for these two enantiomers. The two equivalent catalysts are represented side by side in Figure 3, together with a quadrant view. In both cases, a *re*-inserting olefin avoids severe steric interactions with the ligand's hindered quadrants. The parent nonchiral Salan ligands featuring an ethylene bridge between the two *N*-donors wrap in the same *fac*−*fac* mode around group 4 transition metals to yield C_2-symmetric racemic complexes.[3] We propose that the isospecific polymerization of α-olefins by the racemic complexes of the bulky nonchiral Salan ligands is due to the same directing preference observed herein.

Assuming a common enantiomorphic site control mechanism for all linear α-olefins implies that the monomer approaches the metal so that its alkyl substituent points away from the bulky *o*-phenolate substituent (mediated by the growing polymeryl chain).[8] On the basis of the proven relationship between ligand steric bulk and isotacticity induction, we presumed that the Salan−Zr complexes of the less bulky ligands would yield PMCP's of reduced or negligible optical rotations. Both (*R,R*)-Lig^{3}ZrBn$_2$ and (*R,R*)-Lig^{4}ZrBn$_2$ gave soluble polymers whose ^{13}C NMR supported a *trans*-preference, but considerably less pronounced isotacticity (see the Supporting Information). Both polymers were found to be optically active to some extent but, unexpectedly, the signs of their $[\alpha]_D$'s were positive, i.e., opposite to that observed for (*R,R*)-Lig^{2}ZrBn$_2$. Consistently, (*S,S*)-Lig^{4}ZrBn$_2$ yielded PMCP having a negative $[\alpha]_D$. While the source of the opposite sign of optical rotation of the PMCP is not clear at this stage, it may indicate that for a Salan complex of a given chirality, reduction of the size of the directing phenolate substituents leads to reversal of α-olefin enantiofacial preference.

In conclusion, we have demonstrated a stereochemical directing equivalence between a bulky (*R,R*)-(Δ)-Salan−Zr complex and the (*S,S*)-EBTHI−Zr complex. While such equivalence may be explained in terms of quadrant similarity between these two systems, a more complex stereochemical control seems to operate in the case of the less bulky ligands. In contrast to the *ansa*-metallocenes, a broad variety of enantiomerically pure Salan−Zr complexes may be prepared directly from the chiral ligands. We are currently extending the range of these chiral complexes in an effort to achieve tighter control over olefin approach and polymer structure.

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Supporting Information Available: Text giving details of the syntheses and characterization of the complexes, and polymerization procedures and polymer characterization, a table of polymerization data, and figures showing NMR spectra and DSC thermograms. This information is available free of charge via the Internet at http://pubs.acs.org. CCDC 662991 contains the crystallographic data for (*R,R*)-Lig^{2}ZrBn$_2$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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(6) (*S*,*S*)-Lig^{2}ZrBn$_2$/B(C_6F_5)$_3$ yielded a polymer having the opposite $[\alpha]_D$ of + 24°. See the Supporting Information.

(7) Enantiomorphic-site control mechanism in isospecific polymerization by complexes of nonchiral Salan ligands was previously demonstrated. See refs 3b for 1-hexene and 8b for propene.

(8) For a theoretical calculation of propylene insertion into a Salan−Zr complex, see: (a) Corradini, P.; Guerra, G.; Cavallo, L. *Acc. Chem. Res.* **2004**, *37*, 231. (b) Busico, V.; Cipullo, R.; Pellecchia, R.; Ronca, S.; Roviello, G.; Talarico, G. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15321.

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