π-Stacking as a Control Element in the (2-PhInd)$_2$Zr Elastomeric Polypropylene Catalyst

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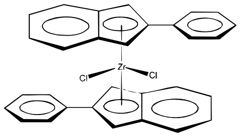
Properties such as the rate of crystallization and degree of crystallinity of polymers formed from vinyl olefins such as propylene can be affected by the tacticity of the material.[1] The tacticity in turn can be controlled by the nature of the active site of the polymerization catalyst.[2] A catalyst active site shape that favors reaction by the same prochiral olefin face will produce isotactic polymer while a catalyst site shape that does not favor one olefin face over the other will produce atactic polymer. With this active site shape knowledge in hand, an interesting intellectual challenge remains: If one can, at will, design a catalyst that will form atactic material or isotacitc material, or even syndiotactic material, can one design a catalyst that will alternate between active site shapes and make well-defined blocks with differing tacticities and hence differing physical properties? Catalysts have recently been discovered which produce polymeric materials with alternating atactic and isotactic blocks. Chien reported the first metallocene catalyst that produced blocks of atactic and isotactic polypropylene.[3] More recently, Coates and Waymouth invented a class of elastomeric polypropylene catalysts that operate through a well-defined, well-constructed interconversion between active site shapes that favor isotactic and atactic polymerization.[4]

The crystal structure of the Coates−Waymouth catalyst precursor, bis(2-phenylindenyl)zirconium dichloride ((2-PhInd)-ZrCl$_2$, **1**) contained two distinct conformers in the unit cell. In one conformer the indenyl ligands were *syn* to one another (a *meso* stereochemistry), while in the other conformer the indenyl ligands were *anti* to one another (a *rac* stereochemistry). Since both conformations appeared in the crystal structure, they must be of similar energy; otherwise, only the thermodynamically favored conformer would be present, barring differential crystal packing. When methylaluminoxane (MAO) was added to the catalyst precursor, polypropylene with atactic and isotactic blocks was formed. Atactic blocks can be ascribed to polymerization when the catalyst is in the *meso* conformation and isotactic blocks to polymerization when the catalyst is in the *rac* conformation. All in all a well-described system.



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An important question that still remains unanswered with the Coates−Waymouth system is the precise source of the barrier between the *meso* and *rac* conformers. This conformational barrier could not be frozen out at low temperatures[4] for the catalyst precursor **1**, but must be of modest but finite size to be competitive with the barrier for olefin insertion since block polymer is formed. Observation of a modest but finite-sized barrier is intriguing because the individual barriers for the conformational degrees of freedom in the catalyst precursor **1** are intrinsically quite small. For example, the barrier to rotation is roughly 1−2 kcal/mol for biphenyls[5] and nearly 0 kcal/mol for cyclopentadienyl rings.[6] The barrier between the *meso* and *rac* conformers must, however, be between 5−12 kcal/mol to be competitive with the insertion barrier.[3]

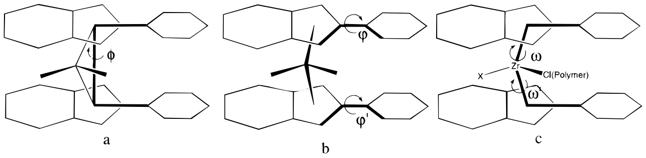

Figure 1. Description of dihedral angles. (a) The Ph−Cp(centroid)−Cp(centroid)−Ph dihedral angle is the conformational coordinate. (b) The indenyl−phenyl dihedral angles determines if π-stacking will occur. (c) The Ph−Cp(centroid)−Zr−Cl(polymer) dihedral angle determines the steric hindrance for the polymer chain.

To understand why the catalyst formed from **1** produces blocks of isotactic and atactic polymer, a UFF[7,8] force field conformational study on the catalyst precursor **1** and a model polymer system, (2-PhInd)Zr(CH$_3$)(C$_7$H$_{15}$), was undertaken.[9] The three important conformational variables of the catalyst precursor are described in Figure 1. The first, ϕ, is associated with interconversion between the *meso* and *rac* conformations (Figure 1a). The second, φ and φ', are associated with "biphenyl" rotation (Figure 1b). The third, ω and ω', describe the orientation of the indenyl rings with respect to the Cl ligands.

Two unique[10] minima and one transition state[11] were indeed found on the potential energy surface for the catalyst precursor. The most striking structural feature of both minima and the associated transition state is that the phenyl groups attached to the indenyl ligands π-stack to other aromatic rings within the complex.[12−14] For the *meso* conformation and the transition state, the phenyl groups are within parallel π-stacking distance of each other. For the *rac* conformation, the phenyl groups are within perpendicular π-stacking distance of the benzo group of the opposite indenyl ligand.[15]

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(8) Consistent with the published UFF force field, electrostatic interactions were not included in the present study. Calculations were carried out with the MCM suite of programs (Skiff, W. M.; Ramachandran, S.; Pietsch, M. A.; McGaughey, G. B.; Rappé, A. K. Unpublished Results). For reference, the barrier for biphenyl rotation in UFF is 4.5 kcal/mol compared to the 1−2 kcal/mol found experimentally. The barrier to rotation for the 2-phenylindenyl ligand in UFF is 0.6 kcal/mol.

(9) For both systems, the conformation coordinate was chosen to be the rotation of the Ph−Cp(centroid)−Cp(centroid)−Ph dihedral angle ϕ (see Figure 1a). ϕ was constrained in 5° increments, while the rest of the geometry was allowed to optimize. The methyl was used to simulate solvent, counterion, or alkane. Since the conformational equilibrium rather than the insertion transition state was studied, it is important to have the fourth coordination site occupied but not necessarily by propylene.

(10) Four minima were actually found, corresponding to two symmetry equivalent *meso* and two symmetry equivalent *rac* conformations.

(11) The transition state was verified as having one negative frequency. In addition, walking along the imaginary mode in both directions produced the respective minima.

(12) Because of their accessable π-cloud, aromatic substituents can participate in stablizing or attractive interactions with other aromatic substituents. These interactions are called π-stacking. Due to the dispersive nature of the interaction, it is largely orientation invariant with both perpendicular, and parallel, orientations observed and nearly isoenergetic with binding energies of roughly 2 kcal/mol.

(13) To distinguish between π-stacking and steric effects, (2-cyclohexyl-Ind)$_2$ZrCl$_2$ was optimized using the UFF force field. Two minima were found. The *meso* ($\phi = 23°$) is 3.1 kcal/mol less stable than the *rac* conformation ($\phi = 119°$). Since the *rac* confromation is prefered over the *meso* conformation, only isotactic polypropylene would be formed by a catalyst generated from this precursor if the catalyst were catalytically active.

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The first minimum, associated with the *meso* conformation $\phi = 23°$, was 0.6 kcal/mol less stable than the second minimum, associated with the *rac* conformation $\phi = 118°$ (see Figure 1a). Although $\parallel$ and $\perp$ π-stacking similarly stabilize a system,[14] the *rac* conformation has two $\perp$ π-stacking interactions while the *meso* conformation has only one $\parallel$ π-stacking interaction. This correlates with the *rac* conformation being more stable than the *meso* conformation. The small energy difference found computationally is consistent with the observation of both conformations in the crystal.[4] In fact, the two minima found computationally for the catalyst precursor resemble the structures found in the crystal.[4,16] Conformational differences between crystal structure and structures found computationally can be ascribed to intermolecular interactions present in the crystal but absent in the isolated molecule computations. In the crystal, the Ph groups interact (i.e., π-stack) intermolecularly as well as intramolecularly. Intermolecular C−C contacts as short as 3.33 Å are observed in the packing diagram. The transition state, $\phi = 47°$, between the minima is 4.4 kcal/mol higher in energy than the *meso* conformation. This barrier is consistent with NMR studies wherein the interconversion between the two conformations could not be frozen out at low temperatures.[4]

Although the distance between the Ph groups and the other aromatic rings determines whether π-stacking can occur, another conformationally significant pair of coordinates are the dihedral angles between the Ind ligands and the pendant Ph groups, φ and φ' (see Figure 1b). The *meso* conformation has $\varphi = 27°$ and $\varphi' = -27°$, allowing the Ph groups to be parallel to one another. For the transition state, the upper Ph has rotated to the opposite orientation with respect to the Ind group ($\varphi = -8°$) while the lower Ph remains near its original orientation ($\varphi' = -43°$). This rotation of φ allows the two Ph groups to remain parallel to one another while ϕ rotates. The *rac* conformation has $\varphi = -19°$ and $\varphi' = -27°$,[17] similar to the transition state. However, the Ph groups are now perpendicular to the benzo groups of the opposite Ind ligand.

The barrier for interconversion between the *meso* and *rac* conformations can be ascribed to the rotation of φ from 27° (*meso*) to −19° (*rac*) *along with* changes in the third set of conformational coordinates ω and ω'. Coordinates ω and ω' describe the position of the chlorine ligands with respect to the benzo and phenyl groups (see Figure 1c). The *meso* conformation has $\omega = 68°$ and $\omega' = -40°$. The Cl ligands are not hindered by the phenyl or indenyl groups since the phenyl groups are off to one side of the Cl ligands and the benzo group of the indenyl ligand is on the other side of the chlorines (see Figure 2). For the transition state, $\omega = 128°$ and $\omega' = -83°$. The upper benzo group is directly above the Cl ligands while the lower benzo group is slightly to one side of the Cl ligands, a more encumbered geometry. For the *rac* conformation, $\omega = -177°$ and $\omega' = -69°$, respectively, the chlorines are placed symmetrically between the two indenyl ligands providing the least steric repulsion (see Figure 2).

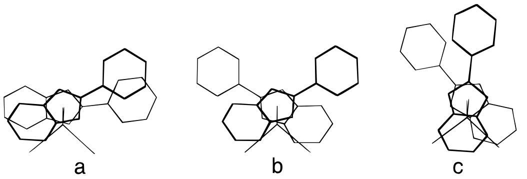

Figure 2. The top view of the (a) *meso* and (b) *rac* rotameric forms and the (c) transition state of **1**.

Once the catalyst precursor was characterized and the force field shown to produce results consistent with experiment, force field calculations were performed on a model polymerization active site to understand the conformational characteristics of the polymerization process. Details of this study are provided as Supporting Information.

For the model polymerization system, the same basic *rac* and *meso* conformational minima were found. The conformations are structurally similar to their catalyst precursor counterparts differing by less than 3° in ϕ. Again, the phenyl groups of the *meso* conformations are within $\parallel$ π-stacking distance and the phenyls of the *rac* conformations are within $\perp$ π-stacking distance to the indenyl groups of the opposite ligand. Consistent with the catalyst precursor, the *meso* are less stable than the *rac* conformations, but the surface is more complex.

In summary, the present computational model contains four main features. (1) The *rac* and *meso* conformations of the metallocene system observed by Coates and Waymouth are nearly isoenergetic (within 0.6 kcal/mol of each other). (2) The barrier between the *rac* and *meso* conformations is comparable to observed insertion barriers. (3) The shape of the *rac* conformation is consistent with the established stereochemical model of metallocene polymerizations.[2] (4) Both the *rac* and *meso* conformations display π-stacking interactions.

Because of these features, the catalyst is able to produce blocks of atactic and isotactic polypropylene. π-Stacking clearly influences the conformations that the catalyst adopts during the polymerization process. By adding substituents to the phenyl groups or changing the solvent, one can alter the π-stacking effects to favor one conformation or the other. For example, electronegative substituents increase the magnitude of π-stacking interactions. Since the *rac* conformation has two such interactions and the *meso* one, the isotactic blocks should be longer for a catalyst with halogen substituted phenyls. This has been observed by Hauptman and Waymouth.[18] Aromatic solvents decrease the importance of intramolecular π-stacking interactions. This would likely induce the production of atactic polymer.[14] By favoring one conformation over the other, one can begin to control the properties that the polymer possesses.

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Supporting Information Available: Additional information about the catalyst model study (12 pages). See any current masthead page for ordering and Internet access instructions.

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(15) The special nature of this $\pi-\pi$ interaction can be seen from UFF studies of the parent bis(indenyl) and 2-*tert*-butyl complexes. The barrier for converting between the nearly isoenergetic *meso* and *rac* conformations (computed energy difference of 0.3 kcal/mol) was found to be only 1.2 kcal/mol (with respect to the more stable *rac* conformation) for the parent complex. For the 2-*tert*-butyl complex, the *meso* and *rac* conformations only differ by 0.2 kcal/mol *but* the steric congestion due to the *tert*-butyl group in both *rac* and *meso* conformations will prevent either from being viable catalysts (Supporting Information gives molecular structure pictures).

(16) Computed and X-ray (in parentheses) distances were found to be quite similar: The average Zr−C(Cp) distance is 2.538 (2.506) and 2.542 (2.512) Å for the *meso* conformation and 2.548 (2.502) and 2.546 (2.502) Å for the *rac* conformation. The Zr−Cl distances in the *meso* comformation are 2.42 (2.47) and 2.43 (2.49) Å. The Zr−Cl distances in the *rac* conformation are 2.42 (2.49) and 2.43 (2.49) Å. The distances between the indenyl ligands and the phenyl groups are 1.47 (1.48) and 1.49 (1.49) Å for the *meso* conformation and 1.48 (1.48) and 1.47 (1.48) Å for the *rac* conformation. The dihedral angles φ and φ' are 27° (3°) and −27° (12°) for the *meso* and −19° (−11°) and −27° (−4°) for the *rac* conformations.

(17) The *rac* conformation is C_2 symmetric. To be consistant with the *meso* conformation, φ and φ' correspond to the front and back dihedral angle, respectively. The corresponding dihedral angles for the bottom back and top front are −27° and −19°, respectively.

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