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Predicted Structure Selectivity Trends: Propylene Polymerization with Substituted *rac*-(1,2-Ethylenebis(η^5-indenyl))zirconium(IV) Catalysts

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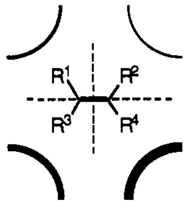
Abstract: The effect of variation of substituents of a zirconium *ansa*-metallocene complex on the polymerization of propylene is studied with molecular mechanics. The hydrogen atoms at the different positions of the indenyl rings are systematically substituted with methyl, ethyl, isopropyl, and *tert*-butyl alkyl groups. We predict that substitution of hydrogen with methyl at the 4,4′-positions will increase the isotacticity of the polypropylene produced but that increasing the size of the alkyl groups in these positions does not provide an increase in isotacticity.

I. Introduction

The isospecific polymerization of substituted olefins by homogeneous Ziegler–Natta catalysts is a topic of considerable interest. Metallocene-based chiral catalysts containing different ligand frameworks have been shown to produce polymers with novel properties,[1-5] including the potential for controlling stereoselectivity by temperature variation[5l] and the possibility of forming block homopolymers.[5b,d]



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The catalysts used currently for the homogeneous isotactic polymerization of propylene are primarily of the general form Cp_2ML_2 in which the Cp ligands are stereoselectively substituted. It is generally acknowledged that the steric environment around the metal contributes to the orientation of the insertion of the monomer into the M–C bond and ultimately the tacticity (enantiomorphic site control).[1,6,7] The isotactic polymerization of propylene (Cossee mechanism) as suggested by Pino and coworkers[7] proceeds by the initial olefin complexation occurring with the olefin methyl group being placed in the least sterically congested quadrant (for **1** this is quadrant 2), followed by the primary (or 1,2) insertion of propylene into the metal–polymer bond, see Figure 1. The next olefin complexation occurs, again placing the methyl group in the least sterically congested quadrant and with complexation by the same prochiral olefin face. Syndiotactic defects occur when the propylene approaches from and complexes with the opposite prochiral face, see Figure 1. The

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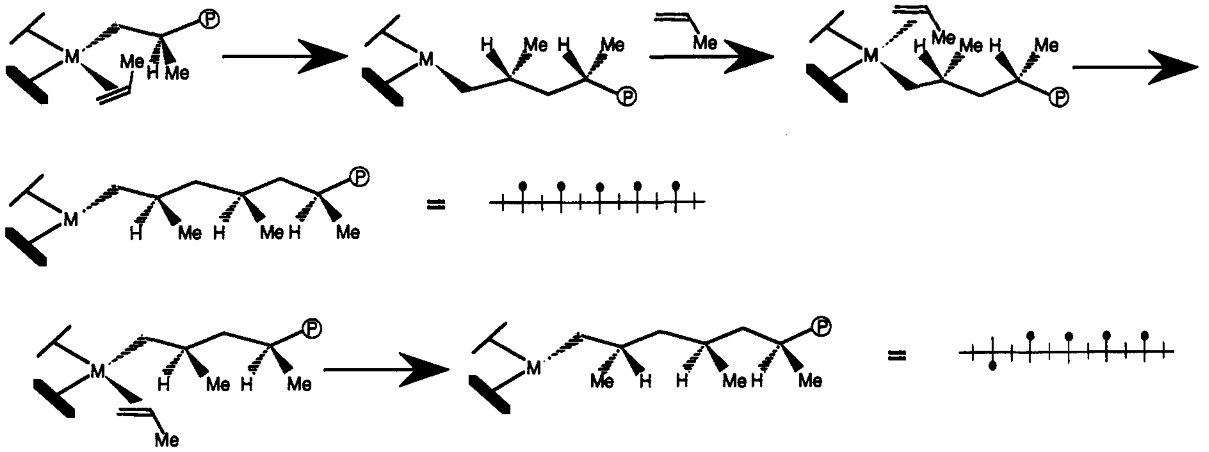

Figure 1. Reaction sequence for isotactic propylene polymerization (top), and generation of a syndiostatic stereodefect in an isotactic polymer chain (bottom).

design of stereochemical control can thus be focused on providing a steric environment that will cause preferential complexation by one olefin face or the other. The concept has guided numerous experimental efforts.

Previous computational models for site control of stereoregularity in Ziegler–Natta catalysis have been limited to rigid model molecular mechanics calculations in which only a limited number of torsional angles are varied.[6] While the results obtained were in agreement with experimental observation in terms of facial preference, the magnitude of the facial preference was incorrect.

As our first step in the characterization of stereospecific Ziegler–Natta polymerization catalysts, we sought to test whether a better activated complex model, combined with substantial conformational searching and geometric flexibility, could reproduce the magnitude as well as the sign of the observed facial selectivity. Castonguay and Rappé have reported[8] an *ab initio* study for a zirconium model catalyst system (the electronic reorganization responsible for the small barrier was essentially the same as found previously[9] for titanium systems), have suggested and provided force field parameters for a realistic activated complex model, and have carried out a molecular mechanics study of several known catalytic systems as well as three predicted catalysts.

As a follow-up to that study we report here the systematic variation in substituents for the isotactic *rac*-(1,2-ethylenebis(η^5-indenyl))zirconium-based catalyst (Figure 2). Based on an examination of the nonbond contacts in the catalytic pocket, the hydrogens at the 3,3′-, 4,4′-, and 5,5′-positions of the indenyl rings were chosen for substitution in an attempt to enhance the isotactic selectivity of the catalytic polymerization of propylene. The 4,4′,5,5′-tetramethyl derivative was studied at the suggestion of a referee, and substitution at the 5,5′,6,6′-, and 4,4′,7,7′-positions was also investigated following the report on these catalysts in the literature.[3] Our results predict that the 4,4′-dimethyl derivative will produce isotactic polypropylene with fewer syndiotactic defects (compared to the unsubstituted parent), while substitution with larger alkyl groups in any position will not enhance the isotacticity further.

II. Calculational Details

The model and method of calculation is described in full in ref 8; only a brief summary is presented here. *Ab initio* calculations on a model system ($Cl_2ZrCH_3^+ + C_2H_4$) were used to determine the geometric position of an activated complex (AC), which was taken as being along the reaction coordinate approximately halfway between the ground and transition states (Figure 3). The degree of isotacticity (ΔIS) is defined by the energy difference between the AC leading to an isotactic insertion and the AC leading to a syndiotactic defect. The growing polymer chain in each AC is approximated by a 2,4,6-trimethylheptyl group.

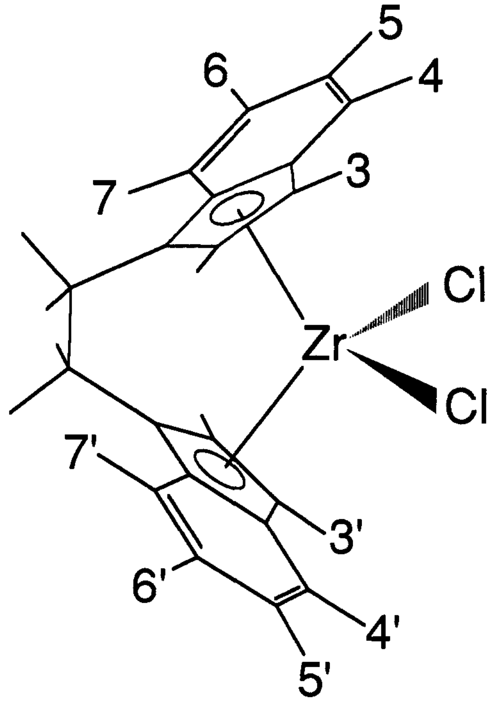

Figure 2. (*S*,*S*)-(1,2-Ethylenebis(η^5-indenyl))$ZrCl_2$.

A trial structure for each of the ACs was built using the Biograf molecular simulation program, version 2.2.[10a] The Dreiding force field,[10b] augmented with an atom type for zirconium and pseudoatoms for a cyclopentadienyl centroid (Cp) and an olefin centroid (Ci), was used. The structures were minimized with partial charges obtained by the QEq charge equilibration scheme.[10c] Each minimized structure was then subjected to 10 cycles of annealed dynamics from 0 to 600 K with a symmetric energy ramp of 1 deg/fs. The lowest energy conformations obtained from the annealing process were minimized and their charges equilibrated. Of these conformations, the one possessing the lowest energy was used as input for annealed dynamics as above, and the whole process was repeated until no conformations with a lower total energy were found.

All atomic and pseudoatomic positions were varied during the

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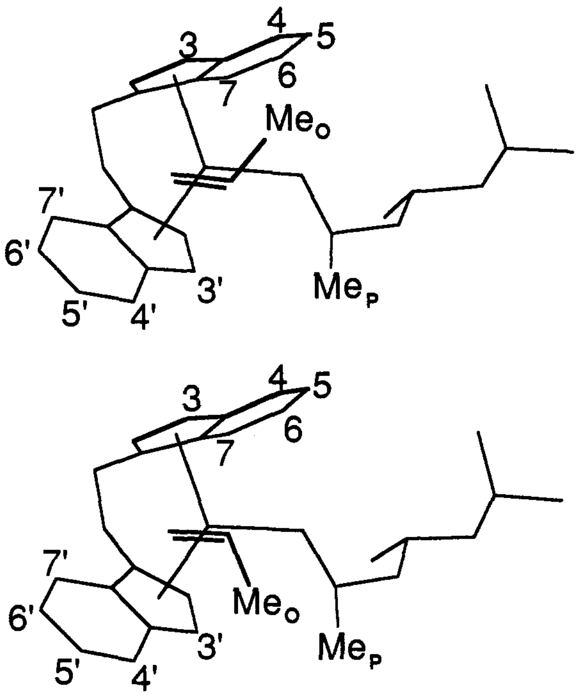

Figure 3. Activated complexes for normal isotactic insertion (top) and for insertion leading to a syndiotactic defect (bottom). All hydrogen atoms have been removed for clarity, and the indenyl positions are marked. Me$_O$ = methyl group of propylene. Me$_P$ = 2-methyl group of the growing polymer chain.

Table I. Calculated ΔIS Results

catalyst	ΔIS (kcal/mol)	catalyst	ΔIS (kcal/mol)
parent	2.4	5,5′-dimethyl	2.9
3,3′-dimethyl	0.6	5,5′-diethyl	2.7
4,4′-dimethyl	4.2	5,5′-diisopropyl	2.5
4,4′-diethyl	2.4	5,5′-di-*tert*-butyl	3.1
4,4′-diisopropyl	4.1	4,4′,7,7′-tetramethyl	2.7
4,4′-di-*tert*-butyl	2.2	5,5′,6,6′-tetramethyl	2.6
		4,4′,5,5′-tetramethyl	3.3

calculations. Only one constraint was used: propylene was constrained to be parallel to the Zr-polymer bond with a torsional constraint of 1000 kcal/mol.[11]

III. Results and Discussion

The lowest energy structure for each dialkyl-substituted AC obtained from the conformational search has the growing polymer chain (i.e., the 2,4,6-tetramethylheptyl group), the bridging ethylene group, and the indenyl rings in similar relative positions. For derivatives with alkyl substitution in the 5- and 5′-positions, the growing polymer chain is in a slightly different position than for the parent complex. For the 4,4′,7,7′-tetramethyl derivative we find a substantial twisting of the ethylene bridge. The ΔIS results are gathered in Table I.

Table II. Calculated $\Delta\Delta G^{\ddagger}$ Values from Experiment

catalyst	% *mmmm*[c]	% (1 event)	$\Delta\Delta G^{\ddagger}$ (kcal/mol)[d]
parent[a]	89.4 (89)	97.8	2.4 (2.4)
parent[b]	83 (89)	96	2.0 (2.4)
3,3′-dimethyl[b]	18 (18)	71	0.6 (0.6)
4,4′,7,7′-tetramethyl[a]	92.2 (93)	98.4	2.6 (2.7)
5,5′,6,6′-tetramethyl[a]	79.4 (92)	95.5	1.9 (2.6)

[a] Reference 3, t = 40 °C. [b] Reference 2, t = 50 °C. [c] Estimated values from ΔIS values (this work) in parentheses. [d] ΔIS valus (this work) in parentheses.

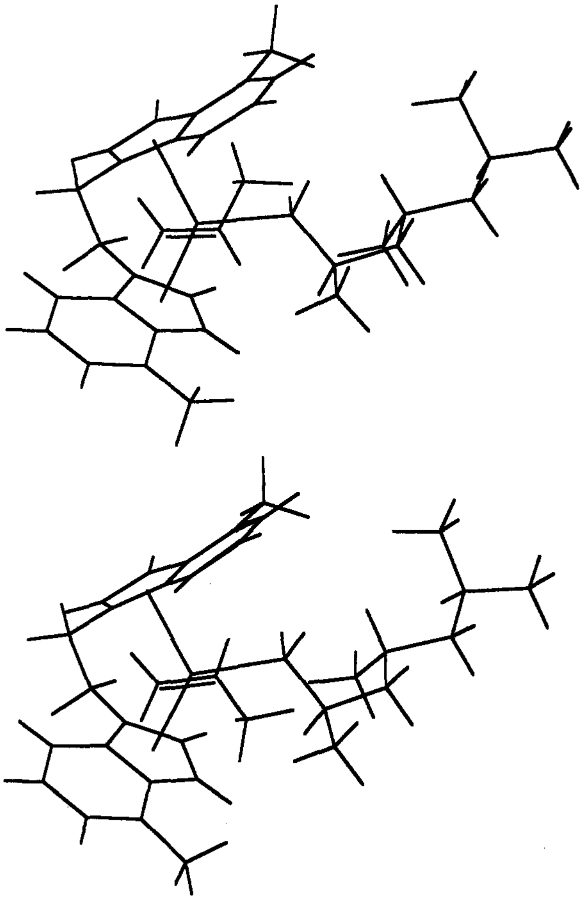

Figure 4. 4,4′-Dimethyl derivative activated complexes leading to normal isotactic insertion (top), and insertion leading to a syndiotactic defect (bottom).

The calculated energy difference between the activated complexes can be related to the experimentally (NMR pentad) determined isotacticity in the following way. The difference in activation energies ($\Delta\Delta G^{\ddagger}$) for two competing processes is related to their rate constants k_1 and k_2 by (1). Here the two approaches

$$\Delta\Delta G^{\ddagger} = -RT \ln (k_1/k_2) \qquad (1)$$

of propylene leading to either an isotactic or syndiotactic insertion are the two competing processes. The % *mmmm* for a pentad as determined by NMR is related to one isotactic insertion by (2). If $T\Delta\Delta S^{\ddagger}$ is small compared to $\Delta\Delta H^{\ddagger}$ for these systems,

$$1 \text{ event} = (\% \, mmmm/100)^{0.2} \qquad (2)$$

then ΔIS can be compared directly with $\Delta\Delta G^{\ddagger}$. The results for the experimentally known catalysts are gathered in Table II, with our calculated ΔIS values in parentheses.

The unsubstituted parent catalyst, C_2H_4-bis(indenyl)$ZrCl_2$, is experimentally observed to yield isotactic polypropylene.[2,3] Here, with the 2,4,6-tetramethylheptyl group as a model for the growing polymer chain, we predict that the catalyst will produce isotactic polypropylene, with a ΔIS greater than 2 kcal/mol.

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[11] Recently it was proposed that the transition state for the insertion step in the polymerization of olefins by Ziegler–Natta catalysts involves a puckered rather than a planar four-membered ring (including the metal, the two olefin carbon atoms, and the terminus carbon of the polymer chain).[9a] Without a torsional constraint, we also find conformations in which the torsional angle defined by the carbon–carbon double bond and the zirconium–carbon (growing polymer) bond (ϕ) is not 0°. However, we believe that a planar transition state is more physically realistic, and we have constrained this torsional angle to 0°. The energetic consequences of puckering are calculated to be small and do not account for the stereodifferentiation. For example, ϕ for the 4-position methyl-substituted isotactic and syndiotactic ACs are −16° and +17°, respectively. The energy required to bring ϕ to 0° is 1 kcal/mol for each AC, so there is no differential effect determined by our calculations.

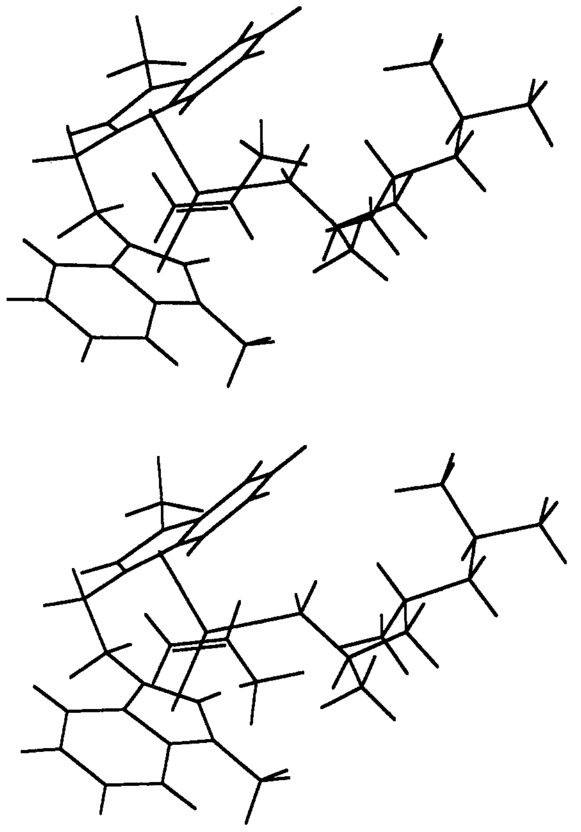


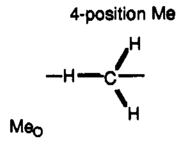
Figure 5. 3,3′-Dimethyl derivative activated complexes leading to normal isotactic insertion (top), and insertion leading to a syndiotactic defect (bottom).

We calculate the two activated complexes of the 3,3′-dimethyl derivative to be separated by less than 1 kcal/mol, so we predict that this catalyst will produce polypropylene with a large number of syndiotactic defects. This is in agreement with experiment, where this catalyst was found to produce polypropylene with a *mmmm* of 18%.[2] The 5,5′-dialkyl derivatives (alkyl = methyl, ethyl, isopropyl, or *tert*-butyl all display the same increase (less than 1 kcal/mol) in ΔIS over the unsubstituted catalyst.

The results for the 4,4′-dialkyl derivatives are more interesting. The 4,4′-dimethyl derivative has a ΔIS of more than 4 kcal/mol. One would predict that by increasing the size of the alkyl substituents in the 4,4′-positions, ΔIS would also increase. This is not what we calculate. For the 4,4′-diethyl and 4,4′-di-*tert*-butyl derivatives, ΔIS is approximately 2 kcal/mol, the same as for the unsubstituted parent, while ΔIS for the 4,4′-isopropyl derivative is about 4 kcal/mol.

These results can be rationalized by a comparison of the nonbonded interactions in the substituted and unsubstituted ACs leading to isotactic or syndiotactic insertion. For the unsubstituted case, the three-way interaction (double stereodifferentiation[5c]) of the methyl group of the coordinated propylene ($\mathrm{Me_O}$) with the indenyl group and the first methyl side group of the growing polymer chain ($\mathrm{Me_P}$) for the syndiotactic AC is enough to favor the isotactic AC by 2 kcal/mol.

Since the growing polymer chain, the bridging ethylene group, and the indenyl rings are in the same relative positions for all of the 4,4′-dialkyl ACs, the only difference between the derivatives is the interaction of the alkyl groups with the indenyl rings and the propylene. In the 4,4′-dimethyl derivative (Figure 4), a methyl at the 4′-position increases the unfavorable steric interactions for the syndiotactic AC. The methyl substituent at the 4-position does not interact with $\mathrm{Me_P}$ in the isotactic AC. For the 4,4′-diethyl-substituted isotactic AC, the lowest energy conformation of the 4-position ethyl group has a hydrogen pointed directly at $\mathrm{Me_O}$, because the ethyl methyl group prefers to be perpendicular to the aromatic ring.[12,13] This creates a new repulsive interaction for the ethyl-substituted isotactic AC which is not present for the methyl-substituted isotactic AC, causing ΔIS to decrease relative to the 4,4′-dimethyl derivative (compare **2** with **3**).



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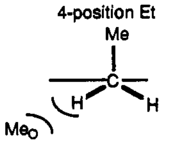

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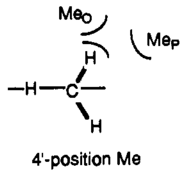
For the 4,4′-dimethyl and 4,4′-diethyl syndiotactic ACs, the three-way interaction of the 4′-position methyl (or ethyl) group with $\mathrm{Me_O}$ and $\mathrm{Me_P}$ can be schematically represented as in **4** and **5**. In the lowest energy conformations of each AC, determined in large part by alkyl-indenyl interactions, a hydrogen atom points into the space between $\mathrm{Me_O}$ and $\mathrm{Me_P}$, so no significant new repulsive interactions are introduced in going from methyl to ethyl. The reduction in isotacticity of the ethyl-substituted catalyst relative to the methyl catalyst is due to the differential introduction of repulsive steric interactions in the isotactic AC, **3**.



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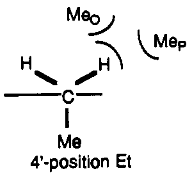

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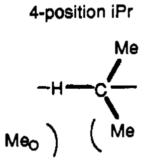
The predicted energetics for the isopropyl-substituted catalyst are explained by similar arguments. For the isotactic AC, **6**, the isopropyl groups are staggered relative to the indenyl rings. The isopropyl methyl and $\mathrm{Me_O}$ are close enough for a repulsive interaction to exist. For the syndiotactic AC, **7**, the 4′-isopropyl group rotates (~10°) to avoid the steric interaction with $\mathrm{Me_O}$ in spite of the unfavorable Me–indenyl interaction. However,



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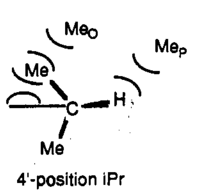

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(12) Seeman, J. I.; Secor, H. V.; Breen, P. J.; Grassian, V. H.; Bernstein, E. R. *J. Am. Chem. Soc.* **1989**, *11*, 3140.

(13) This analysis is dependent upon torsional barriers being of sufficient size for discrete conformations to have meaning. To test this, rotational barriers were calculated for rotation of a single substituent, methyl groups for toluene and the methyl 4,4′-substituted *ansa*-metallocene system and ethyl groups for ethyl benzene and the ethyl 4,4′-substituted *ansa*-metallocene system. For the methyl 4,4′-substituted system, the rotational barrier for an individual methyl group is 2.3 kcal/mol larger than that calculated for toluene (which is calculated to be 0.9 kcal/mol larger than experiment). For the ethyl 4,4′-substituted system, the rotational barrier for an individual ethyl group is >9 kcal/mol larger than that calculated for ethylbenzene (which is calculated to be 0.3 kcal/mol)—the ethyl substituent has a preferred orientation that is not dictated by the torsional parameters present in the Dreiding force field but is due to nonbonded interactions present in the *ansa*-metallocene system.[10b]

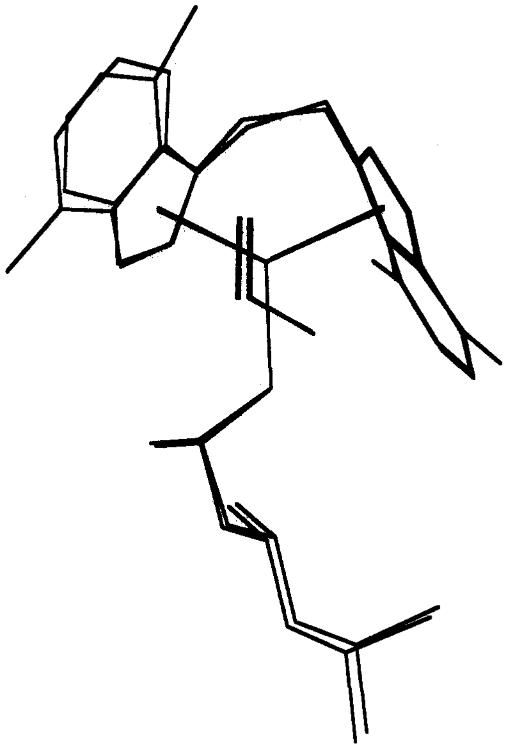

Figure 6. Superimposed activated complexes leading to a normal isotactic insertion for the parent catalyst and the 4,4′,7,7′-tetramethyl derivative. All hydrogen atoms have been removed for clarity.

the Me_O – H – Me_P repulsive interaction is reduced relative to the methyl-substituted catalyst. These competing factors result in no net change in the isotacticity for the isopropyl-substituted catalyst relative to the methyl-substituted one.

For *tert*-butyl substitution at the 4-position, the methyl groups of the 4-position *tert*-butyl group in the isotactic AC are in the same relative positions as the methyl hydrogens in the 4,4′-dimethyl derivative. The methyl in the plane of the indenyl and the one below the plane both interact strongly with Me_O in a repulsive manner. For the syndiotactic AC, the 4′-position *tert*-butyl group adopts a conformation in which one methyl group points between Me_O and Me_P. In going from the methyl- to the *tert*-butyl-substituted catalyst, the increase in the magnitude of the repulsive interactions is greater for the isotactic AC than for the syndiotactic AC, and the net effect is that the isotacticity for this catalyst is reduced to the level of the unsubstituted and ethyl-substituted catalysts.

The results for substitution at the 3,3′- and 5,5′-positions are not as difficult to understand. The 3-methyl group is very close to Me_O in the isotactic AC for the 3,3′-dimethyl derivative (Figure 5). This unfavorable interaction is large enough to raise the energy of the isotactic AC, causing the energy difference between the two ACs to be less than 1 kcal/mol.

Substitution at the 5,5′-positions yields catalysts in which the steric interactons are reduced significantly. The alkyl groups are simply too far away from the coordinated olefin to have much of an effect. Therefore less than a 1 kcal/mol increase in the isotacticity is observed between the unsubstituted catalyst and each of the substituted ones, independent of the alkyl group. This slight increase in ΔIS is probably due to the interaction of the alkyl groups with the growing polymer chain.

As is the case of the 3,3′-dimethyl derivatives, our results for the 5,5′,6,6′- and 4,4′,7,7′-tetramethyl derivatives can be compared directly with experiment, where it was found that both of these yield isotactic polypropylene. The polymer produced by the 4,4′,7,7′-tetramethyl derivative was slightly more stereoregular and the polymer produced by the 5,5′,6,6′-tetramethyl derivative slightly less stereoregular than the unsubstituted parent catalyst.

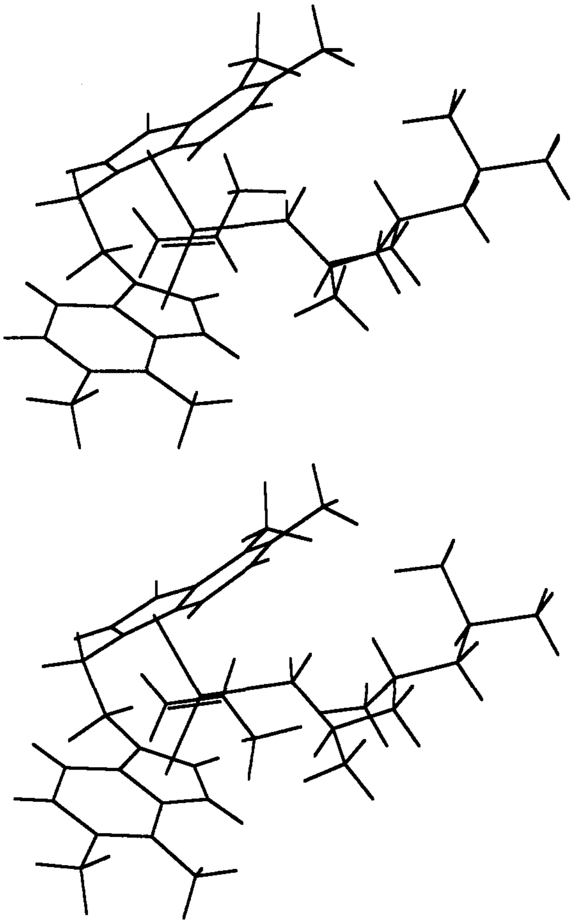

Figure 7. 4,4′,5,5′-Tetramethyl derivative activated complexes leading to normal isotactic insertion (top), and insertion leading to a syndiotactic defect (bottom).

Our results predict both of these catalysts to produce polypropylene with a higher degree of stereoregularity than that produced by the parent. These findings do not necessarily contradict our results. Alkyl–alkyl interactions should be the dominant factor in determining ΔIS in these catalysts. As was previously pointed out,[8] the present force field produces heats of sublimation for hydrocarbons in error by up to 0.4 kcal/mol. Taking this error estimate into account, our results would lead us to predict that substitution with methyl in the 5,5′-, 5,5′,6,6′-, and 4,4′,7,7′-positions should lead to catalysts all possessing ΔIS values in the same ballpark as the parent catalyst. An interesting observation from our calculations on the 4,4′,7,7′-tetramethyl catalyst is that the methyl groups in the 7- and 7′-position interact with the ethylene backbone, causing the molecule to twist significantly (Figure 6) to relieve this strain.

At the suggestion of a referee, the 4,4′,5,5′-tetramethyl derivative was also studied to determine if the effect of methyl substitution is additive (Figure 7). Our results do not predict this to be the case. We find ΔIS to be only 3.3 kcal/mol. The adjacent methyl groups interact with each other so they are no longer free rotors, and, as is the case for the 5,5′-dialkyl derivatives, the growing polymer chain is in a slightly different position for this catalyst compared to the 4,4′-dialkyl derivatives.

In addition to the rigid model work of Corradini, Guerra, and co-workers[6] discussed above, quite recently Kawamura-Kuribayashi, Koga, and Morokuma[14] used a combined *ab initio* molecular orbital–molecular mechanics approach to study the stereoselectivity of a set of silicon-bridged zirconium *ansa*-metallocenes. The geometry of the actual transition state for

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(14) Kawamura-Kuribayashi, H.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1992**, *114*, 8687.

ethylene insertion into a Zr-methyl bond of the $(SiH_2Cp_2)ZrCH_3^+$ complex was obtained using an *ab initio* restricted Hartree–Fock wave function. This structure was used as a base for molecular mechanics calculations on larger complexes where hydrogens on the Cp ligands, the ethylene, and the methyl group (polymer) were substituted. When the methyl polymer model was replaced by a 2-methylbutyl group, a stereoselectivity of 5.5 kcal/mol was obtained for the achiral parent Cp complex (as this complex is achiral experimentally, this complex would have no observed stereoselectivity)—this calculated stereoselectivity must be due to the lack of adequate conformational flexibility in the model used. Substitution of the Cp rings in the 3,4′-position does induce chirality into the complex and the calculated selectivity increases to 7.2 kcal/mol. Experimentally,[15] this complex yields polypropylene with a % *mmmm* pentad of 92.5 (corresponding to a $\Delta\Delta G^\ddagger$ of approximately 2.5 kcal/mol at 30 °C).

IV. Conclusions

In summary, this study demonstrates the challenge in *a priori* predicting the degree to which a given catalyst modification will produce isotactic or syndiotactic polypropylene. Anticipated trends in the predicted degree of isotacticity were not found for this family of catalysts. We predict that substitution of hydrogen with methyl at the 4,4′-positions will increase the isotacticity of the polypropylene produced. Substitution with larger alkyl groups will not increase the isotacticity further. In fact, ethyl and *tert*-butyl substitution at the 4-position is predicted to increase the number of syndiotactic defects relative to the methyl-substituted catalyst.

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