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Journal of Organometallic Chemistry 684 (2003) 206–215

Journal
of Organo
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Chemistrywww.elsevier.com/locate/jorganchem

Structural features of bridged cyclopentadienyl-fluorenyl based metallocene catalyst: origin of syndiospecificity

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Received 7 May 2003; received in revised form 2 July 2003; accepted 2 July 2003

Dedicated to professor Ernst Otto Fischer's on the occasion of his 85th birthday

Abstract

The mechanism of syndiospecific polymerization with ($\eta^5\text{-C}_5\text{H}_4\text{-CMe}_2\text{-}\eta^5\text{-C}_{13}\text{H}_8$) MCl_2 ; $\text{M} = \text{Zr, Hf/MAO}$ catalyst systems is discussed by taking into account the structural characteristics of the metallocene molecules and the chiral particularities of their cationic species within the framework of a chain migratory insertion mechanism. A generally accepted transition state structure that respects the relative importance of different steric interactions of the active participants in the polymerization process, ligand, growing polymer chain and the coordinating monomer is proposed. The model is reexamined on the basis of an isotactic specific ($\eta^5\text{-C}_5\text{H}_3\text{C}_4\text{H}_9\text{-CMe}_2\text{-}\eta^5\text{-C}_{13}\text{H}_8$) ZrCl_2/MAO and a recently discovered syndiotactic specific catalyst system, $\eta^1, \eta^5\text{-tert-butyl}(3,6\text{-bis-tert-butylfluorenyl-dimethylsilyl})\text{amidoMCl}_2/\text{MAO}$; $\text{M} = \text{Zr, Ti}$ and its validity is confirmed.

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Keywords: Olefin polymerization catalysis; Metallocene; Polypropylene; Syndiospecificity; Mechanism

1. Introduction

Syndiotactic polypropylene was first isolated by Natta and co-workers as a minor by-product of isotactic polypropylene produced with a TiCl_3 based catalyst [1]. The nature of the active site and the mechanism of formation of this polymer, which was discovered nearly forty years ago, are still under debate. It is believed that it is formed on the sites with low chlorine coordination via a chain end controlled mechanism. Later Zambelli and coworkers produced syndiotactic polypropylene directly using a vanadium-based catalyst [2]. In this case, more is known about the nature of the active site and the mechanism of the polymerization is elucidated satisfactorily.

It is now certain that the polymer chains are formed at low temperature on homogeneous active sites according to a mechanism that is controlled also by the chirality of the last inserted monomer unit at the end of the polymer chain. No X-ray structure of the catalyst precursor is, however, available due to its very temperature sensitive nature. After the discovery of the first bridged cyclopentadienyl–fluorenyl metallocene based syndiospecific catalyst and the resulting syndiotactic polypropylene [3] one had for the first time the opportunity to make even more accurate statements about the nature of the active site and the mechanism of the polymerization of this fascinating yet very complex systems. By studying the available X-ray structure data of the metallocenes and their stabilized alkylmetallocenium cation (considered as the catalyst precursors) [3b] it has become possible to make reasonable deductions on the nature of the active site and its behavior during the polymerization. On the other hand facile availability of large syndiotactic polymer samples prepared at very

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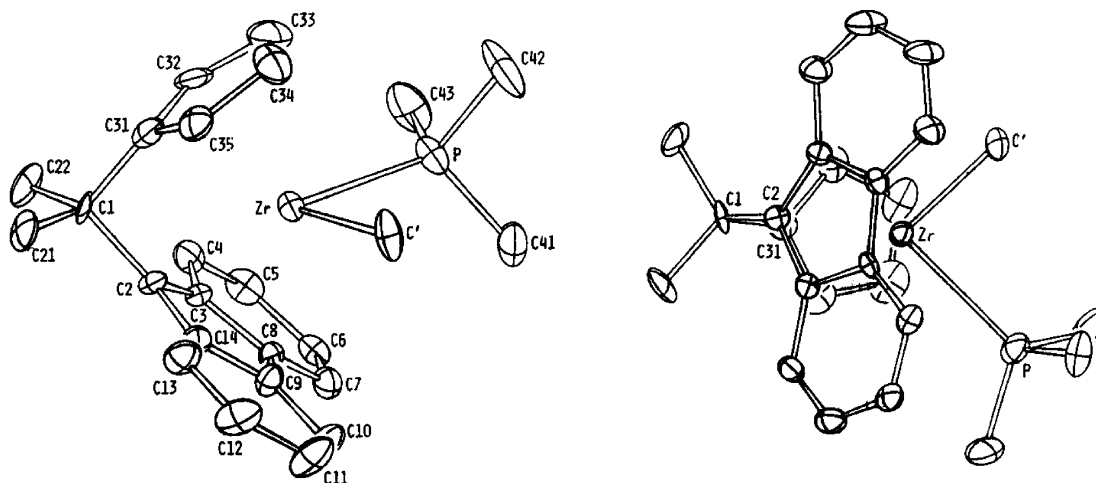


Fig. 2. Two views of the trimethylphosphine stabilized cation in the crystalline state [3b].

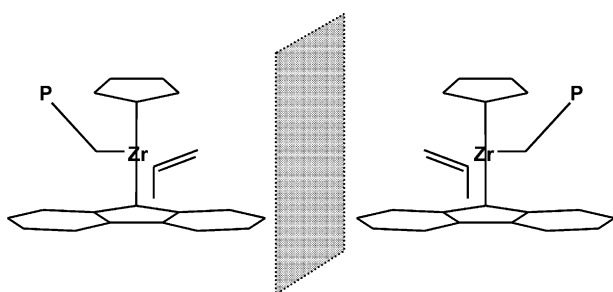


Fig. 3. Mirror image related enantiotopic active species

and their rearrangement is not possible, such an epimerization can take place only when the alkyl group (polymer chain) and the coordinating monomer exchange their positions uninterruptedly (when no excessive steric restrictions are imposed). (7) The meso triad enantiomorphous site stereochemical type errors, mm, are formed whenever the said balanced non-bonded steric interaction is perturbed, and the correct alignment of the substituents of all three main participants (ligand, polymer chain and the monomer) has not been realized. In such a case, a monomer with 'wrong face' will be inserted and a unit with inverted configuration is enchain. The ability to reverse facial selectivity

emanates from inherent static structural factors and is independent of monomer concentration.

To understand how these many factors operate in a concerted manner to create the conditions for syndiospecificity we need to construct a model that explains in a plausible manner the behavior of this complex system.

Fig. 4 depicts the model representing the transition state structure for propylene polymerization. This model is constructed based on relative importance of the non-bonded steric interactions operating on different parts of the catalytic species and its—in the polymerization active participants—aromatic ligand, polymer chain and the coordinating monomer in the following order. The steric interaction between the flat and spatially

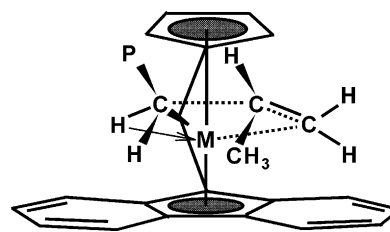
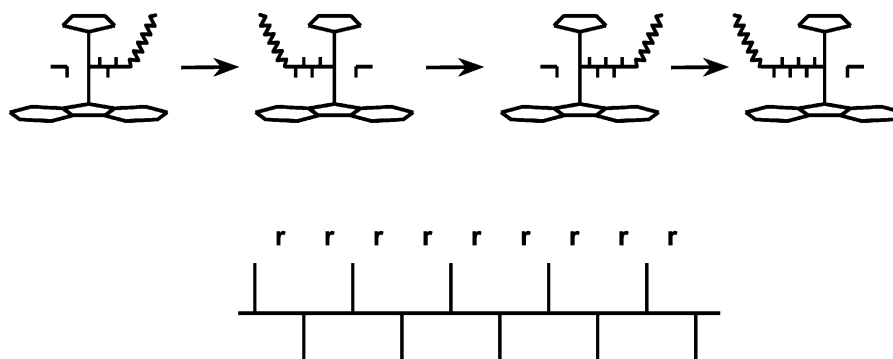


Fig. 4. Syndiospecific transition state structure proposed based on the X-ray structure given in Fig. 2.



Scheme 1. Mechanism of syndiospecific polymerization (top). Fischer projection of a perfect syndiotactic chain (bottom).

extended fluorenyl ligand forces the growing polymer chain to be oriented towards the free space left (or right) to the unsubstituted cyclopentadienyl moiety of the ligand. The incoming monomer—to avoid excessive steric exposure—orients itself in a manner to have its methyl group trans positioned with respect to the growing polymer chain. The system reaches in this way a minimum energy state. In this orientation the coordinated monomer points with its methyl group head down into the empty space in the central region of the fluorenyl ligand. The confirmation for the head down orientation of the monomer was determined after extensive molecular mechanics and force field calculations performed by Corradini and coworkers [4]. The model underwent later additional refinement and took its current form after experiments conducted by several groups [5] supporting an α C–H agostic assistance in the transition state for the propylene polymerization.

The working hypothesis, active site model and the transition state structure discussed in the preceding paragraphs account perfectly for justifying the syndiotactic specificity of the catalysts and formation of the syndiotactic polypropylene chain. However, for a model and a mechanism to be acceptable it is not sufficient to correctly describe the polymerization behavior and polymer's microstructure in general. It must also justify the details of the formation of microstructural stereo errors and monomer misplacements in the backbone of the polymer chain. From two types of stereo errors—the meso triads (mm) and meso dyads (m)—encountered in the back bone microstructure of the syndiotactic polymers prepared with metallocene catalysts the former—we have discussed it above briefly—is related to the enantiofacial misinsertion and is monomer concentration independent. This type of stereo error has been detected and explained long ago in connection with isotactic polymers prepared with the classical ZN systems. The origin of the formation of the monomer concentration dependent stereo errors the so-called meso dyad (m) type errors was more complex and more difficult to discern. Their investigation, however, turn out to be more exiting and conclusive for the understanding of the functioning of the syndiospecific catalysts. Their formation can be explained according to site epimerization scheme shown in Fig. 5.

The *R* and *S* configured active sites are equi-energetic and can interconvert during the polymerization parti-

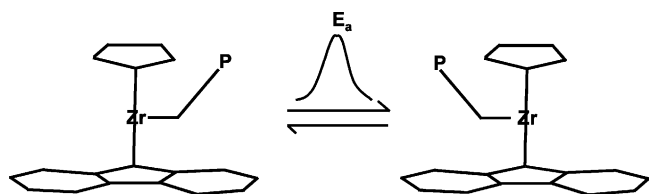


Fig. 5. Endothermic active site epimerization.

cularly in the absence of a coordinating monomer or solvent molecules. If the rate of this interconversion is faster than the actual rate of the monomer insertion then occasionally the sites epimerize before any insertion occurs and two (in case of Hf catalyst more) consecutive insertions will take place at the same enantiomorphic coordination position enchaining two monomer units with the same prochiral face. This causes the formation of meso dyads within the polymer backbone (isotactic blocks for Hf). Even though the interconverting species are equi-energetic, the epimerization requires an activation energy since the chain, while swinging back or forth, will be exposed to different parts of the ligand and has to overcome the resulting non-bonded steric repulsion. That is why at lower polymerization temperature the concentration of the meso dyad is relatively low and only with increasing temperature their number increases rapidly. The concept of site epimerization is in fact very close to the mechanism of chain back skip proposed already by Cossee and Arlman in 1964 [6] for the non-symmetric sites in TiCl_3 catalyst systems. The only difference between the two mechanisms is related to the forces that drive the 'back migration' or the site epimerization in each system. The, in the rigid ionic lattice imbedded active TiCl_3R sites have no real contribution to the chain back migration and only the relative ionicity/non-ionicity and the immediate polarity of the environment of the chain is the driving force for its back migration (back skip) [6]. Whereas in the case of metallocene based catalysts, the flexible structure of the aromatic ligand, the haptotropic nature of its bonding and the counter ion effect probably are major contributing factors to the epimerization processes (vide infra). We have discussed static (contact ion pairing) and steric (ligand/polymer chain substituent) interactions as the possible causes for the epimerization [7] elsewhere here we shall focus only on its impact. Despite its uncertain origin, the occurrence of the site epimerization process can be easily demonstrated and/or explored by disrupting coordination sites' equivalency and by intentionally increasing the epimerization rate and consequently enlarging the isotactic sequence length from isoblocks up to the extreme of obtaining 'pure' isotactic polymers [8,9]. This can be done by implanting selectively a substituent at one of the distal positions of the cyclopentadienyl moiety. Several modifications have been made, yet the substituent, tertiary butyl group, has been most expeditious in this respect [9]. In this case the process of epimerization can be manipulated to the extent that the tactic behavior of the catalysts is completely reversed and an originally syndiospecific catalyst produces instead 'purely' isotactic polymer chains. The increasing isospecificity [10a,b] of these C_1 symmetric metallocene molecule based catalyst with increasing polymerization temperature—in drastic contrast to the behavior of the bridged isotacticspecific

bridged bisindenyl metallocene catalyst systems—can be seen as a clear evidence for the operating epimerization processes. Additionally, the complete absence of rrm pentad sequences (an indication of low probability of the chain dwelling at the more crowded coordination position) in the microstructures of isotactic polypropylene produced with the same catalysts [10b,c] provides further clue suggesting the functioning of the epimerization process. The epimerization rate of course increases its rate with increasing polymerization temperature and provokes the formation of ever longer isotactic sequences. The mechanism of the formation of these polymers can be explained by complete malfunctioning of the chain migration replaced by rapid and continuous epimerization of the site due to steric repulsion between the chain and the substituent during the insertion process (Fig. 6) assisted by phenomena such as haptotropy and ring slippage (vide infra). From the point of view of the incoming monomer, the chain appears ‘stationary’ by attacking always from the same position [9].

To emphasize further the vital role of the presence of the steric balance and the free central space and to avoid giving any superstitious impression that the syndiospecificity is somehow linked to the presence of the fluorenyl groups, we shall discuss briefly the syndiospe-

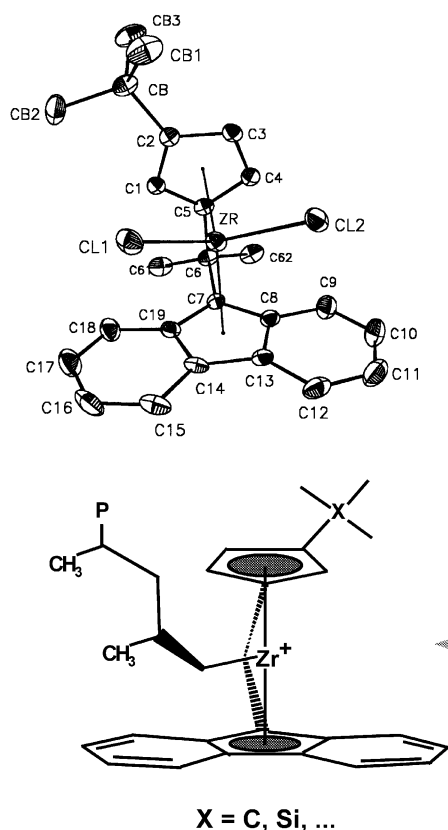


Fig. 6. Two perspective views of the molecular structure of **3** (top). Non-bonded steric repulsion between polymer chain and β -substituent provoking the site epimerization (bottom).

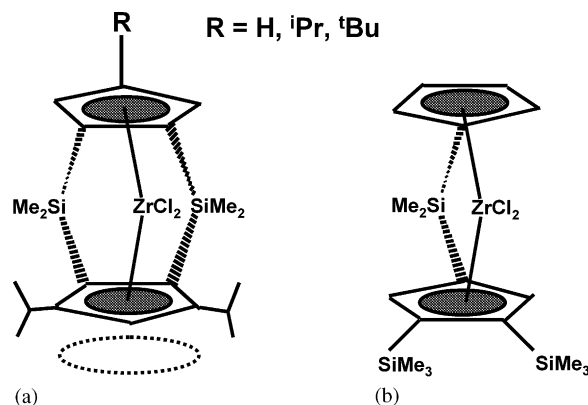
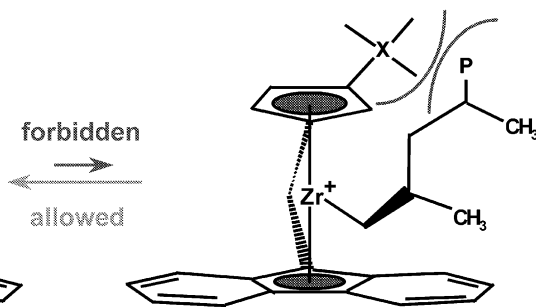
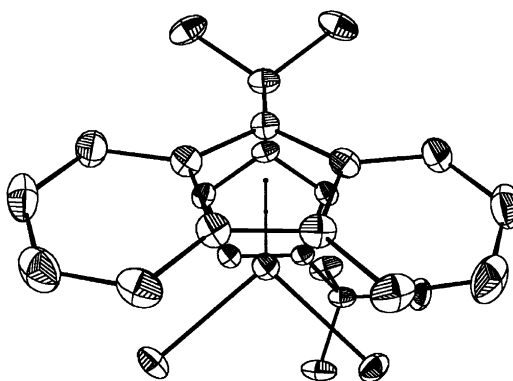


Fig. 7. Bercaw's non-fluorenyl syndiospecific (a) and non-syndiospecific (b) structures.

cific system reported by Bercaw and coworkers [11]. The double-bridged zirconocene molecules shown in Fig. 7a fulfill all structural and symmetry prerequisites for the syndiospecificity. They resemble very much in their structures the molecules of Fig. 1 in having one unsubstituted cyclopentadienyl linked to a symmetrically substituted cyclopentadienyl (replacing fluorenyl) via a structural bridge. The structures given in Fig. 7a are in fact syndiotactic specific and produce highly syndiotactic polypropylene yet they do not contain any



fluorenyl group. What is essential, however, that the substituted cyclopentadienyl group, which is replacing the fluorenyl in the original structure, maintains the free space in the central position to accommodate the methyl group of the coordinating monomer. The importance of the free space in central region of the larger cyclopentadienyl group for monomer's head-down coordination is reiterated by the molecule depicted in Fig. 7b. Because of the presence of the substituents blocking the central position this metallocene does not fulfil the imposed requirements nor behave in its activated form in a syndiospecific manner.

Finally, an interesting syndiospecific case will be presented to check the validity of the working hypotheses, active site model and the transition state structure. The main ingredients of these new syndiospecific catalyst systems are the amido complexes η^1, η^5 -*tert*-butyl(2,7-bis-*tert*-butylfluorenyl-dimethylsilyl)amidoMCl₂ and η^1, η^5 -*tert*-butyl(3,6-bis-*tert*-butylfluorenyl-dimethylsilyl)amidoMCl₂ (M = Ti, Zr). Fig. 8 represent the single crystal X-ray structure of the η^1, η^5 -*tert*-butyl(3,6-bis-*tert*-butylfluorenyl-dimethylsilyl)amidodichlorozirconium. After activation with MAO both Zr and Ti complexes polymerize propylene to syndiotactic polypropylene very efficiently, however, only Ti related catalysts produce high molecular weight polymers [12], the stereo selectivity is almost complete, the few stereo defects being mostly of mm-type and arising from occasional reverse monomer enantio face selection; as a result, the polymers have remarkably high melting points ($T_m > 160$ °C). The syndiotacticity of the polymer produced at lower polymerization temperatures instead of different polymerization temperatures measured as the concentration of racemic pentads rrrr is higher than that reported recently by us for η^1, η^5 -*tert*-butyl(2,7-bis-*tert*-butylfluorenyl-dimethylsilyl)amidodichlorozirconium [12,13].

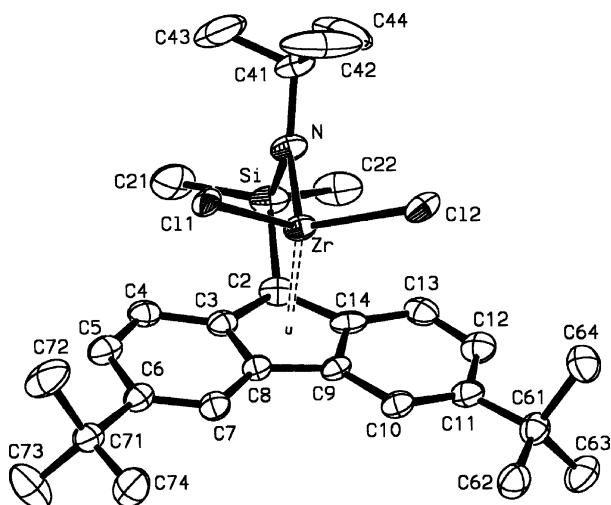


Fig. 8. Structure of the complex η^1, η^5 -*tert*-butyl(3,6-bis-*tert*-butylfluorenyl-dimethylsilyl)amido-dichlorotitanium [12].

These structures are the only examples of titanium based syndiospecific catalysts and are also in many other aspects different from the original syndiotactic specific systems discussed above. They are half sandwich molecules, contain an amido type N–Ti (or Zr–N) bond and are 12 electron system (14 electron system at the most if one considers the participation of the lone pair electrons on the nitrogen to N–Ti bond) leaving 10 (maximum 12) electrons for the cationic active site. Nevertheless, a glance at the structure shown in Fig. 8 reveals that they have all structural and symmetry characteristics required in order to be syndiotactic specific. These latest additions to the syndiospecific catalyst systems demonstrate that no matter what the make up of the metallocene precursor is, once its structure fulfils the prerequisites discussed; based on the model given above, it will act in a syndiotactic specific manner after its activation at least with respect to propylene monomers.

The above proposed model combined with the chain migratory insertion mechanism is fit to explain the formation of syndiotactic polymers with metallocenes of Fig. 1. According to the Scheme 1 the regularly alternating enantiofacial preference for monomer that leads to syndiotactic polymer arises from olefin insertion taking place at regularly alternating sides of the wedge of the pseudo tetrahedral structure of the active site. Despite its simplicity and convenience the model has a major handicap. It has been conceived of images coming from X-ray analysis performed on molecules contained in solid state structure. These rigid and static images reflect only a snap-shot or ‘moment-aufnahme’ of the constantly vibrating, bending and ‘breathing’ molecules in all directions and disregard the effect of counter-ion. They should be considered only as frozen images of dynamic molecules that reflect only one aspect, the general shape and outline of the molecules. They do not reflect the whole ‘reality’ of individual molecules freely floating in a solvent medium without the restrains of the crystal packing effects. Both IR and NMR data and the chemistry of these compounds are indicative of constant bonding related movements of different parts of the molecules and their fluxionality [14] (Fig. 9). They are often neglected intentionally for the sake of simplicity and the fact that to prove their existence and impact is very difficult. However, one should be aware that at least two dynamic phenomena are actively involved in one way or the other in different steps of the polymerization and influence its mechanism in one or the other direction. For example, the phenomenon of hapticity change or variation of bond order between the transition metal and the aromatic ligands should be seriously considered as being involved in certain metallocene catalysts as we have demonstrated [14]. The haptotropy and ring slippage can influence the electronic properties of the active site and the steric environment surrounding

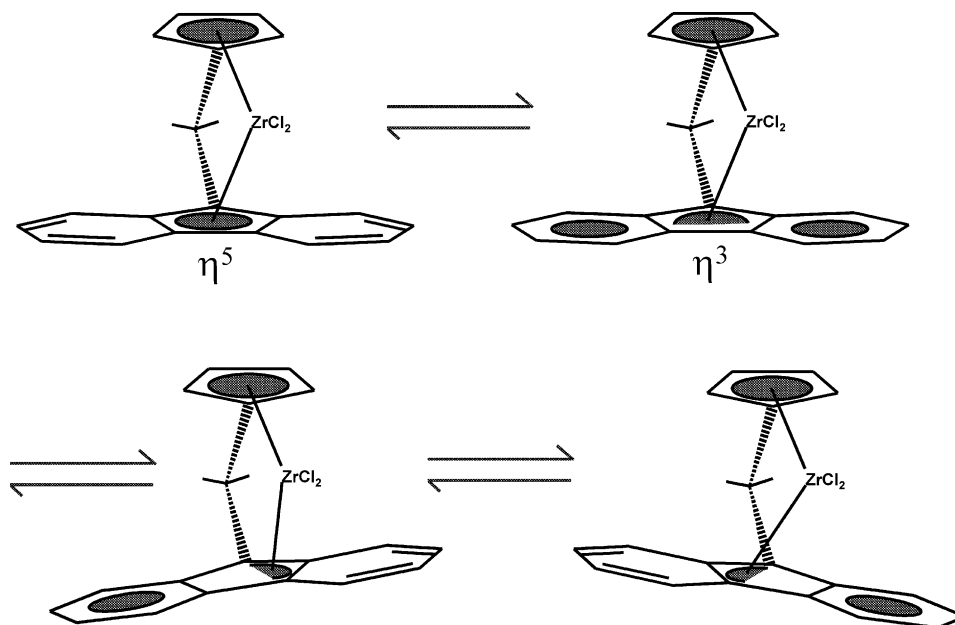


Fig. 9. Fluorenyl bond haptotropy and ring slippage.

it temporarily or permanently and have an impact on the molecular weight and tacticity of their polymers. The second phenomenon is related to geometry change of the catalysts during the coordination and insertion steps. The pseudo tetrahedral geometry, which is assumed for the tetra-coordinated transition metal in the transition state, cannot be further extended to the geometry it assumes in the step just after the insertion. At this stage the tetra-coordinated structure collapses due to the disappearance of a ligand leaving a tri-coordinated species behind in which the repulsive forces acting upon the bonding electron pairs are different and require a new geometry. The most logical structure that can be suggested for this step would be a trigonal pyramid (Fig. 10, right). After the next monomer coordination, again the structure will adopt a tetrahedral geometry (Fig. 10, left). This change in geometry, operating on all metallocenium catalyst systems, is

probably of more importance for the syndiospecific cases, where dynamic processes such as chain migration and site epimerization (*vide supra*) are vital for their existence. Finally, another, ligand / transition metal related, dynamic behavior that can be envisaged to be acting on the transition structure is the lateral semi-rotational displacement of the whole ligand system around the transition metal (or vice versa) reported by Petersen [15] is also noteworthy in this context. This movement that can be described as a kind of wind shield wiper type oscillation of the metalacyclobutane moiety within the 'fixed' ligand system might have a facilitating effect on the site epimerization and/or chain migration mechanisms (Fig. 11).

Before concluding this report and for the sake of completion a final subject with respect to the regio specificity of syndiospecific catalyst systems should be treated. A different type of microstructural defects—the

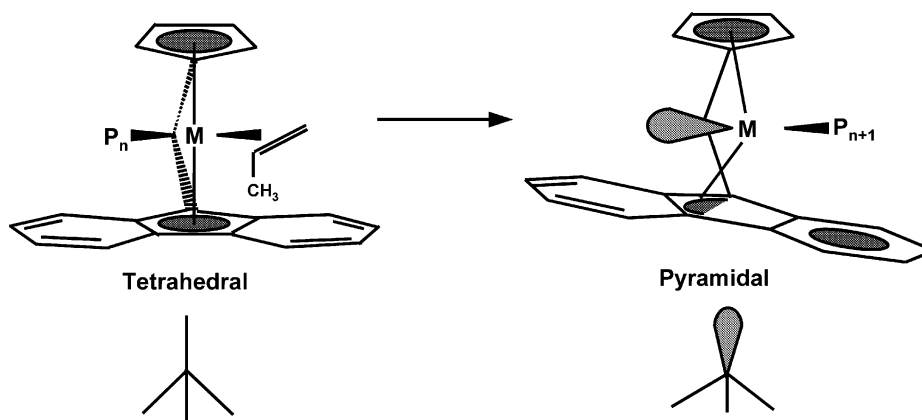


Fig. 10. Systematic structural change and geometry variation during coordination and insertion steps.

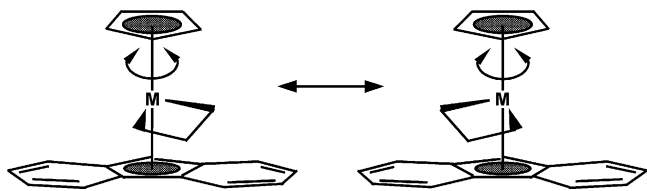


Fig. 11. Lateral displacement of ligand system around the centroids–Zr bond axis (the bridge is omitted for the sake of clarity).

so-called regio defects—arises from a mechanism known as the secondary insertion (structures **3** and **4** in Fig. 12), causes the enchainment of two consecutive monomer units in a head to head or tail to tail fashion. These types of microstructural defects have substantial consequences on physical properties of the polymer and are of prime importance for the elucidation of the mechanism of the polymerization. Contrary to the very regio irregular nature of vanadium based syndiospecific catalysts [2], all syndiospecific, metallocene based catalyst systems reported here (and elsewhere [16]) are very regio specific. Practically no regio defects have been detected so far with any of the syndiotactic polymers prepared with metallocene based catalysts [17]. Yet it is well known that most isospecific metallocene based catalysts, even some with very high stereospecificities, show poor regioselectivity. So far, except for the publications from Corradini and coworkers, not many reports have been published covering this subject. These authors treat the subject in a series of papers [18] based on molecular mechanics calculations in a very comprehensive and elegant way. We should bring the essence of these papers first and add some qualitative comments at the end. According to these authors, the substantial difference between isospecific and syndiospecific model complexes is that the low energy pathway for the secondary and primary insertions correspond to oppo-

site chiralities of the coordinated monomer for the isospecific complexes and the same chiralities for the syndiotactic complexes (the situation for the syndiospecific case is shown in Fig. 12). This difference accounts for the lower regioselectivity of the isospecific catalyst complexes, if the energy barrier for the rotation of the coordinated propylene from coordination suitable for the primary insertion versus coordination suitable for the secondary insertion (and vice versa) are lower than the activation energy for the secondary insertion of the monomer. For the syndiospecific model, since its enantioselectivity is in favor of the same monomer enantio face for both primary and secondary insertion, when the coordination of the monomer with the wrong monomer face for primary insertion occur (structure 2), the most probable event is the dissociation of the monomer (or a stereoirregular insertion). Hence, for the syndiospecific case, the amount of regioirregularities in the polymer chain would be determined by the difference between the activation energies for the secondary and primary insertion. This model which is essentially constructed by the consideration of the non-bonded steric interaction between the ligand and the monomer substituents, holds very well when the regioselective C_2 symmetric isospecific catalysts are compared with those of the C_s symmetric syndiospecific catalyst systems. However, this line of evidence does not probably work if one considers the regioselectivity of the C_1 symmetric isospecific catalysts. These catalysts, that have a cyclopentadienyl–fluorenyl ligand structure and thus exhibit similar ligand/monomer substituents non-bonded steric interactions as in the case of C_s symmetric syndiospecific catalyst systems, are generally of low regio specificity and their polymers have a substantial number of regio errors (up to 0.5%).

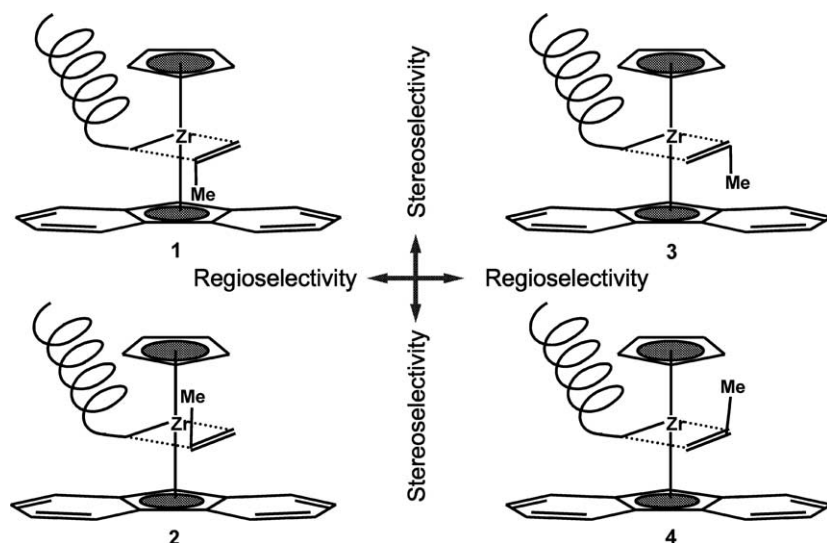


Fig. 12. Four different coordination modes of propylene including those leading to regio- and stereo-errors.

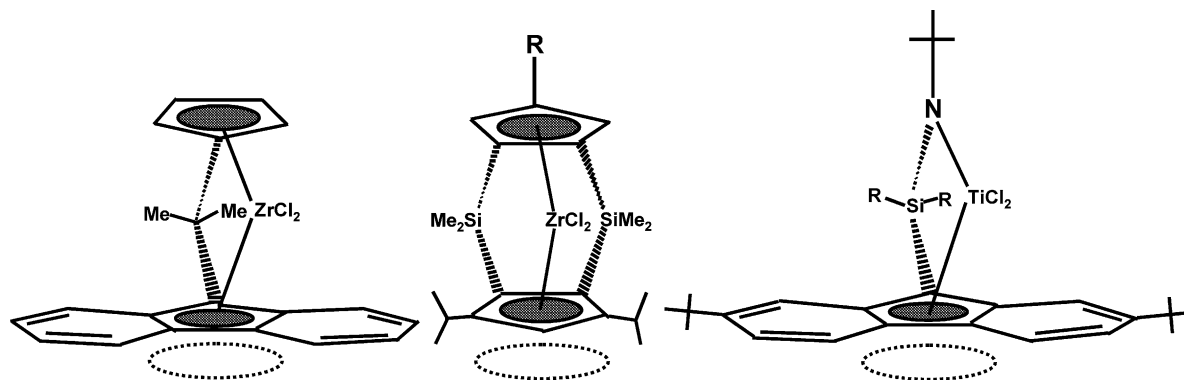


Fig. 13. Three different syndiotactic specific molecules with similar symmetry characteristics.

3. Conclusion

It is shown that the static model that has been proposed for the active site and the transition state structure explains elegantly the syndiospecific character of the catalysts and the origin of the microstructural particularities of the syndiotactic chains. Being conceived of images taken from the solid state X-ray structure analysis, the model is too static to provide any explanation for dynamic phenomena such as chain migration and site epimerization omnipresent during all stereospecific polymerizations performed with metallocene based catalysts. It is therefore, proposed that a more dynamic model should take into consideration the haptotropic nature of the transition metal/aromatic rings and ring slippage phenomena as well as transition state structural collapse leading to a permanent tetrahedral/pyramidal geometry change. The origin and/or the driving force for the chain migration and site epimerization may well be lying here. The validity of the models and the working hypothesis for syndiospecific polymerization of the propylene is tested on two other syndiospecific catalyst systems, the double bridged, differently substituted biscyclopentadienyl zirconium dichloride reported by Bercaw and the new titanium based half sandwich complexes, η^1, η^5 -*tert*-butyl(2,7-bis-*tert*-butylfluorenyl-dimethylsilyl)amidodichlorotitanium and η^1, η^5 -*tert*-butyl(3,6-bis-*tert*-butylfluorenyl-dimethylsilyl)amidodichlorotitanium. Both systems demonstrate clearly and confirm the validity of the proposed ideas no matter the make up of the catalysts. Once the structural requirements, imposed by the model proposed here, is fulfilled, the catalysts behave syndiospecific, independent of the nature of the transition metal and the presence of varying number of the aromatic rings in the π ligand. Fig. 13 compares the structure of three systems discussed highlighting the main factors for the syndiospecificity. Of course, the degree of syndiospecificity of the catalyst and stereoregularity of the resulting polymer depends on the stereorrigidity of the bridging ligand and the size, type

and position of the substituent(s). Finally the regioselectivity of the syndiospecific system, the way it was reported by Guerra and coworker is reviewed [18]. They explain—based on molecular mechanics calculation—the regiospecific behavior of the three main types of catalyst systems, aspecific unbridged biscyclopentadienyl zirconium dichloride, a dimethylsilyl(cyclopentadienyl–fluorenyl) zirconium dichloride and the bridged bisindenyl zirconium dichloride based on ligand monomer interaction in a comprehensive and elegant way. However, the question of non-regio selective behavior of most C_1 symmetric cyclopentadienyl–fluorenyl based catalyst will remain still unanswered. These isospecific catalysts display the same secondary coordinated monomer/ligand steric relations as their syndiospecific counterparts. Yet they produce a relatively large percentage of regioerror related chain defects.

References

- [1] G. Natta, I. Pasquon, P. Corradini, M. Peraldo, M. Pegoraro, A. Zambelli, *Atti Accad. Nazl. Lincei Rend. Classe Sci. Fis. Mater. Nat.* 28 (1960) 539.
- [2] (a) G. Natta, I. Pasquon, A. Zambelli, *J. Am. Chem. Soc.* 84 (1962) 1488; (b) A. Zambelli, G. Natta, I. Pasquon, *J. Polym. Sci.* 4 (1964) 411.
- [3] (a) A. Razavi, J.L. Atwood, *J. Organomet. Chem.* 459 (1993) 117; (b) A. Razavi, U. Thewalt, *J. Organomet. Chem.* 445 (1993) 111; (c) A. Razavi, J.J. Ferrara, *Organomet. Chem.* 435 (1992) 299; (d) J.A. Ewen, L.R. Jones, A. Razavi, J.J. Ferrara, *J. Am. Chem. Soc.* 110 (1988) 6255.
- [4] L. Cavallo, G. Guerra, M. Vacatello, P. Corradini, *Macromolecules* 24 (1991) 1784.
- [5] (a) W.E. Piers, J.E. Bercaw, *J. Am. Chem. Soc.* 112 (1990) 9406; (b) H.H. Brintzinger, H. Krauledat, *Angew. Chem. Int. Ed. Engl.* 29 (1990) 1412; (c) H.H. Brintzinger, M.L. Leclerc, *J. Am. Chem. Soc.* 117 (1995) 1651; (d) B.J. Burger, W.D. Cotter, E.B. Coughlin, S.T. Chascon, S. Hajela, T.A. Herzog, R.O. Koehn, J.P. Mitchell, W.E. Piers, P.J. Shapiro, J.E. Bercaw, in: G. Fink, R.H. Muehlaupt, H.H. Brintzinger (Eds.), *Ziegler Catalyst*, Springer-Verlag, Berlin, 1995; (e) R.H. Grubbs, G.W. Goates, *Acc. Chem. Res.* 29 (1996) 85.

- [6] (a) P. Cossee, *J. Catal.* 3 (1964) 99;
(b) E.J. Arlman, *J. Catal.* 3 (1964) 89;
(c) E.J. Arlman, P. Cossee, *J. Catal.* 3 (1964) 99.
- [7] Isomerization in these systems is referred to ligands with unsubstituted cyclopentadienyl and epimerization to substituted cyclopentadienyl group, however, for the sake of simplicity we employed the term epimerization in general.
- [8] A. Razavi, L. Peters, L. Nafpliotis, D. Vereecke, K. Den Daw, *Makromol. Symp.* 89 (1995) 345.
- [9] A. Razavi, J.L. Atwood, *J. Organomet. Chem.* 520 (1996) 115.
- [10] (a) R. Kleinschmidt, M. Reffke, G. Fink, *Macromol. Rapid Commun.* 20 (1999) 284;
(b) A. Razavi, D. Vereecke, L. Peters, K. Den Daw, L. Nafpliotis, J.L. Atwood, in: G. Fink, R. Muehlaupt, H.H. Brintzinger (Eds.), *Ziegler Catalysts*, Springer-Verlag, Berlin, 1993;
(c) V. Busico, R. Cipullo, G. Talarico, *Macromolecules* 30 (1997) 4787;
(d) A. Razavi, *C.R. Acad. Sci. Paris Ser. IIc Chem./Chem.* 3 (2000) 615.
- [11] (a) T.A. Herztog, L. Zubris, J.E. Bercaw, *J. Am. Chem. Soc.* 118 (1996) 11988;
(b) D. Veghini, J.E. Bercaw, *Polymer Reprints* 39 (1998) 210.
- [12] (a) A. Razavi, U. Thewalt, *J. Organomet. Chem.* 621 (2001) 267;
(b) A. Razavi, European patent application no. 96111127,5 and international patent application PCT/EP97/03649(WO 98/02469).
- [13] (a) V. Busico, R. Cupillo, F. Cutillo, G. Talarico, A. Razavi, *Macromol. Chem. Phys.*, submitted for publication.;
(b) In liquid monomer and comparatively low temperature ($T < 30\text{ }^{\circ}\text{C}$). The stereo regularity, however, suffers with decreasing monomer concentration and/or increasing polymerization temperature, mainly as a result of an increased probability of consecutive monomer insertion at the same active site (site epimerization) with the corresponding formation of m-type stereodeflects. Since in the chain end control mechanism the formation of m defects is independent of monomer concentration, which means the fraction of m defects is not sensitive to such variable; conversely, in the case of enantio-sites control, the fraction of m-defects (i.e. that of site epimerization) increases with decreasing monomer concentration.
- [14] (a) A. Razavi, V. Bellia, Y. De Brauwer, K. Hortmann, M. Lambrecht, O. Miseque, L. Peters, S. Van Belle, in: W. Kaminsky (Ed.), *Metalorganic Catalysts for Synthesis and Polymerization*, Springer, Berlin, 1999;
(b) H.G. Alt, M. Jung, G. Kehr, *J. Organomet. Chem.* 562 (1998) 153;
(c) D. Drago, P.S. Pergosin, A. Razavi, *Organometallics.* 19 (2000) 1802;
(d) A.K. Dash, A. Razavi, A. Mortreux, C. Lehmann, J.F. Carpentier, *Organometallic* 21 (2002) 3238;
(e) E. Kirlov, L. Touquet, A. Razavi, S. Kahlal, J.Y. Saillard, J.F. Carpentier, *Organometallics*, submitted for publication.
- [15] A. Kabi-satpathy, S. Bajgur, K.P. Reddy, J.L. Petersen, *J. Organomet. Chem.* 364 (1989) 105.
- [16] (a) A. Razavi, L. Peters, L. Nafpliotis, *J. Mol. Catal. A* 115 (1997) 129;
(b) There exists no publication on the regioselective behavior of the double bridge system, however, no regio defects have been observed in syndiotactic polymers produced with these catalysts. J.E. Bercaw, Private communication.
- [17] By increasing the number of transients and using a high resolution ^{13}C -NMR spectrum, peaks related to regio defects can be detected in highly regio regular syndiotactic polypropylene and even for isotactic polypropylene made with the highly specific ZN based catalyst. Prof. Busico, Private communication.
- [18] (a) G. Guerra, P. Longo, L. Cavallo, P. Corradini, L. Resconi, *J. Am. Chem. Soc.* 119 (1997) 4394;
(b) G. Guerra, L. Cavallo, G. Moscardi, G. Vacatello, P. Corradini, *J. Am. Chem. Soc.* 116 (1994) 2988;
(c) M. Toto, L. Cavallo, P. Corradini, G. Moscardi, L. Resconi, G. Guerra, *Macromolecules* 31 (1998) 3431.