

A measure of metallocene catalyst shape asymmetry

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Abstract

An asymmetry parameter (AP) is used as a continuous, positive, metrical shape descriptor and applied to *ansa*-bridged metallocene catalysts of the type [(ligand 1)-bridge-(ligand 2)]MX₂ where ligands 1 and 2 are variously substituted cyclopentadienyl, indenyl or fluorenyl groups connected by, e.g. SiMe₂ or C₂H₄; and where M is Ti, Zr or Hf and X, a halogen or alkyl group. It is the ratio of the van der Waals surface area of the larger ligand divided by that of the smaller. A series of syndioregulating catalysts was used to polymerize propylene. As the catalyst AP increases, the polypropylenes produced have successively higher syndiotacticity. A simple, arithmetic formula for calculating APs of new catalysts is presented.

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1. Introduction

In a recent review, Ewen [1] observed that “small molecular machines called metallocene catalysts have revolutionized the industrial synthesis of valuable plastics” and noted the correlation between catalyst symmetry and polymer (particularly polypropylene) tacticity. Horton [2] has tabulated the relationship between pro-catalyst (i.e. the metallocene dihalide or dialkyl prior to activation by some additional reagent such as methylaluminumoxane) point group symmetry and polypropylene stereochemistry. A very large body of research indicates that, qualitatively, the structure and shape (*vide infra*) of metallocene catalysts can profoundly affect the stereochemistry of polymerization [3]. A general method of altering metallocene shape and structure is the introduction of substituents.

However, a problem in drawing more quantitative conclusions arises from difficulties in characterizing catalyst shapes.

Point group symmetry is not completely useful for the task. It is a *discontinuous* function shape and takes no account of the size of substituents used. For example, [fluorenyl-CMe₂-3-RC₅H₄]ZrCl₂ compounds have C₁ symmetry for R = H. Yet, hemiisotactic polypropylene results when R = Me and isotactic polymer when R = *t*-Bu [4]. Neither does point group notation take account of the position of the substituent. It is possible to lower point group symmetry by introduction of substituents, but at positions so remote from the reaction center that their effect on polymer stereoregularity is negligible.

Metallocenes used for olefin polymerization catalysis have rather complicated *shapes*. Their structures can be described in terms of the usual bond distances and angles as well as by dihedral angles between ligand planes [5]. However, these metrical parameters have not been found to correlate with the stereochemistry of the product polymers. Hortman and

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Brintzinger [6] have proposed the use of coordination gap and aperture obliquity angle as (derivative) structural parameters. These parameters can account for trends in polymerization rates and in stereochemistry. Importantly, Brintzinger noted that they can vary due to the substantial librational excursions which are possible even in bridged (*ansa*) metallocenes. Even if structure–stereochemistry correlations could be wrung from catalyst structure, a structure must first be generated by X-ray crystallographic or molecular mechanics methods. Either can be a challenging task.

In this contribution, a new measure of metallocene catalyst shape termed the asymmetry parameter (AP) is presented. This function is *continuous* and always positive. It may be estimated by simple molecular modeling techniques and is equally applicable to existing catalysts and those not yet synthesized. There is an empirical correlation between AP and polypropylene stereoregularity for a series of syndiospecific catalysts.

2. Results and discussion

The *shape* of a molecule, particularly one containing many atoms, is fundamentally different from its *structure*. It operates on a larger length (or mesh) scale and can be approximated by the van der Waals surfaces of the constituent atoms [7–12] (the ideas underlying the concept of the van der Waals radius have been critically reviewed in [8]; for incisive reviews of ideas about molecular shape and shape descriptors, see, for example, [9]). Because stereoregulation in metallocene catalysts is considered to involve non-bonded repulsive interactions among the catalyst, the growing polymer chain and the entering monomer, it appears reasonable to undertake a description of metallocene catalyst shapes in the context of their van der Waals contours. A general class of metallocene catalysts comprises two carbocyclic ligands bonded to the Group IV metals Ti, Zr or Hf. These two ligands may or may not be identical. Zirconocene dichloride, $(C_5H_5)_2ZrCl_2$, is illustrative of the former. We focus on a subset of such metallocenes in which the two ligands are connected by a one- or two-atom bridge such as $SiMe_2-$ or $-C_2H_4-$. In such *ansa* metallocenes, rotation of the carbocyclic ligands about the metal– C_5 ring centroid axes is strongly

inhibited by a bridging moiety connecting them. Thus, such molecules are (relatively) rigid and have persistent shapes that are amenable to further analysis. Constancy of shape is a prerequisite to the use of a single-valued shape descriptor.

Ansa-metallocenes may be generally represented by [(ligand 1)-bridge-(ligand 2)] MCl_2 . An AP is defined as the ratio of the van der Waals area of ligand fragment 1 to that of ligand fragment 2. The ligands are numbered so that the area of ligand 1 is greater than that of ligand 2. The AP must, therefore, be continuous and positive. In reckoning ligand surface areas, substituents more distant than 5 Å from the reaction center are ignored on the ground that, beyond this arbitrary distance, interactions with the growing polymer chain and/or the incoming monomer are too weak to influence polymer stereochemistry. For example, when one of the ligands is fluorenyl, introduction of bulky *p*-tolyl groups at the 2, 7 positions has hardly any effect on stereoregularity even though, of course, these added groups have a dramatic effect on point group symmetry.

Stereoregularity index (SRI) is used as a measure of polymer stereoregularity and the stereoregulating properties of a metallocene catalyst. It is defined as the ratio of *rr* or *mm* triads in a polymer, whichever is larger, to *mm* or *rr* triads, whichever is smaller. SRI measures the departure of polymer stereoregularity from random or atactic (where $SRI = 1.00$). It ranges from unity to very high values (>25) for highly stereoregular polymers. SRI does not differentiate between *iso*- and syndioregular polymers (and catalysts), but this could be done by adding the suffix S or I. Here, we are concerned primarily with syndioregular materials, i.e. $rr > mm$.

Propylene has been polymerized with each of a series of 27 different metallocene catalysts, some of them novel. AP values for these catalysts were calculated by the CAChe molecular mechanics program. SRI of the polypropylenes produced was assessed by pentad level ^{13}C NMR analysis. Numerical data are collected in Table 1. A plot of catalyst AP versus polypropylene SRI is shown in Fig. 1. As the metallocene catalyst becomes increasingly asymmetrical as judged by its AP, the product polypropylene becomes increasingly syndioregular. A dashed line through the data points, intended as a guide to the eye, demonstrates a quite nonlinear, seemingly exponential

Table 1
Data for catalysts and propylene polymers

| Compound | AP | SRI | <i>rr/mm</i> | M_w/M_n^a |
|---|------|-------|--------------|----------------------------------|
| 1 (Fluorenyl-C ₂ H ₄ -fluorenyl) ZrCl ₂ | 1.00 | 1.13 | 23/26 | 4.3/1.4 |
| 2 (Fluorenyl-C ₂ H ₄ -3-phenylindenyl)ZrCl ₂ | 1.16 | 1.50 | 36/24 | 6.2 (69), 1.3 (11) ^c |
| 3 (Fluorenyl-C ₂ H ₄ -2-phenylindenyl)ZrCl ₂ | 1.16 | 2.73 | 22/60 | 4.3/1.1 |
| 4 (Fluorenyl-C ₂ H ₄ -2-methyl-4,5-benzoindenyl)ZrCl ₂ | 1.22 | 2.27 | 22/50 | 7.4/1.0 |
| 5 (Fluorenyl-CMe ₂ -cyclopentadienyl)ZrCl ₂ | 2.09 | 27.30 | 82/3 | 6.2/1.7 ^c |
| 6 (Fluorenyl-C ₂ H ₄ -9-methylbenzo[<i>c</i>]fluorenyl)ZrCl ₂ | 1.18 | 1.33 | 24/32 | 2.0/0.5 |
| 7 (Fluorenyl-C ₂ H ₄ -4-phenylfluorenyl)ZrCl ₂ | 1.44 | 1.68 | 22/37 | 8.0/2.5 ^c |
| 8 (Fluorenyl-C ₂ H ₄ -4-(1-naphthyl)-2,7-di- <i>t</i> -butylfluorenyl)ZrCl ₂ | 1.70 | 13.30 | 6/80 | 4.8/1.6 ^c |
| 9 (Fluorenyl-C ₂ H ₄ -3-methylindenyl)ZrCl ₂ | 1.16 | 1.12 | 29/26 | 6.3 (78), 1.6 (18) ^b |
| 10 (fluorenyl-C ₂ H ₄ -3-trimethylsilylindenyl)ZrCl ₂ | 1.30 | 2.19 | 21/46 | 4.3 (50), 0.9 (50) ^b |
| 11 (Fluorenyl-C ₂ H ₄ -trimethylsilylindenyl)HfCl ₂ | 1.30 | 1.44 | 25/36 | 5.1 (50), 0.8 (50) ^b |
| 12 (Fluorenyl-C ₂ H ₄ -2,7-di- <i>p</i> -tolylfluorenyl)ZrCl ₂ | 1.00 | 1.08 | 28/26 | 5.6/1.8 |
| 13 (Fluorenyl-C ₂ H ₄ -2,7-di- <i>t</i> -butylfluorenyl)ZrCl ₂ | 1.00 | 1.26 | 23/29 | 6.5/3.2 |
| 14 (Fluorenyl-C ₂ H ₄ -indenyl)ZrCl ₂ | 1.35 | 1.65 | 43/26 | 7.5 (20), 0.8 (80) ^b |
| 15 (Fluorenyl-CH ₂ SiMe ₂ -fluorenyl)ZrCl ₂ | 1.00 | 1.04 | 25/24 | 4.2/1.1 |
| 16 (Fluorenyl-SiMe ₂ -fluorenyl)ZrCl ₂ | 1.00 | 1.31 | 29/22 | 11.1/2.8 |
| 17 (Fluorenyl-C ₂ H ₄ -cyclopentaphenanthryl) ZrCl ₂ | 1.08 | 1.84 | 35/19 | 7.2/2.4 |
| 18 (Fluorenyl-SiMe ₂ -cyclopentaphenanthryl)ZrCl ₂ | 1.08 | 2.47 | 42/17 | 1.4/0.5 |
| 19 (Fluorenyl-C ₂ H ₄ -4,5-dihydrocyclopentaphenanthryl)ZrCl ₂ | 1.13 | 6.10 | 61/10 | 7.1/2.5 |
| 20 (Fluorenyl-SiMe ₂ -4,5-dihydrocyclopentaphenanthryl)ZrCl ₂ | 1.13 | 5.90 | 59/10 | 6.6/4.1 |
| 21 (Fluorenyl-SiPh ₂ -4,5-dihydrocyclopentaphenanthryl)ZrCl ₂ | 1.13 | 5.09 | 56/11 | 13.5/5.8 |
| 22 (Perhydrocyclopentaphenanthryl-C ₂ H ₄ -perhydrofluorenyl)ZrCl ₂ | 1.10 | 3.92 | 51/13 | 5.5/0.6 |
| 23 (Fluorenyl-C ₂ H ₄ -4-methylfluorenyl)ZrCl ₂ | 1.11 | 1.03 | 38/37 | 5.3/2.1 |
| 24 (Cyclopentaphenanthryl-SiMe ₂ -indenyl)ZrCl ₂ | 1.46 | 6.36 | 11/70 | 3.2/1.2 |
| 25 (3,4-Dimethylfluorenyl-SiMe ₂ -3,4-dimethylfluorenyl)ZrCl ₂ | 1.00 | 1.28 | 32/25 | 8.5/1.3 |
| 26 (Fluorenyl-SiMe ₂ -indenyl)ZrCl ₂ | 1.35 | 1.88 | 24/45 | 3.5 (15), 1.00 (85) ^b |
| 27 (Fluorenyl-SiPh ₂ -indenyl)ZrCl ₂ | 1.35 | 1.23 | 37/30 | 5.8 (76), 1.0 (24) ^b |
| 28 (Fluorenyl-C ₂ H ₄ -4,5-dimethylfluorenyl)ZrCl ₂ | 1.23 | 1.68 | 32/19 | 2.2/0.7 |
| 29 (Fluorenyl-C ₂ H ₄ -cyclopentaphenanthryl)HfCl ₂ | 1.08 | 2.94 | 47/16 | 9.1/3.2 |

^a Values in g/mol × 10⁵.

^b Peak molecular weights (%).

^c In 1,2,4-trichlorobenzene.

relationship between the two parameters. An exponential relationship is, in fact, to be expected for enantiomeric site control. Angermund et al. [13] have used molecular modeling to calculate the energy gaps separating the four lowest energy conformers that result when a metallocene coordinates to prochiral propylene. The different conformers lead to different stereochemistries of monomer insertion. The magnitudes of these energy gaps were found to be critical in determining catalyst stereospecificity. The stereochemical outcome of a polymerization is kinetic in nature. It is measured by integration over the stereochemistry of a large number of monomer insertion steps [14]. The Arrhenius equation says that the (relative) rates of *r* and *s* insertions (and the probabilities of their occurrence) are exponentially weighted corresponding

to their activation energies, E_{act} . The AP operates by changing relative values of E_{act} , i.e. Angermund and Fink's energy gaps, for different insertion modes.

Within this set of catalysts studied, there are two subsets that are of especial interest. Symmetrical compounds of the type [(fluorenyl)-bridge-(fluorenyl)] ZrCl₂ (bridge = SiMe₂ or C₂H₄) comprise the first set (fluorenyl-containing metallocenes have recently been reviewed in [15]).¹ AP for these catalysts is 1.0 by definition. The metallocenes have formal C_{2v} symmetry and are predicted to yield atactic polypropylene. The polymers actually produced are substantially atactic but the stereoregularity indices range from 1.08

¹ In this paper, fluorenyl-type ligands are connected to the bridging group at the bridgehead carbon atom C(9).

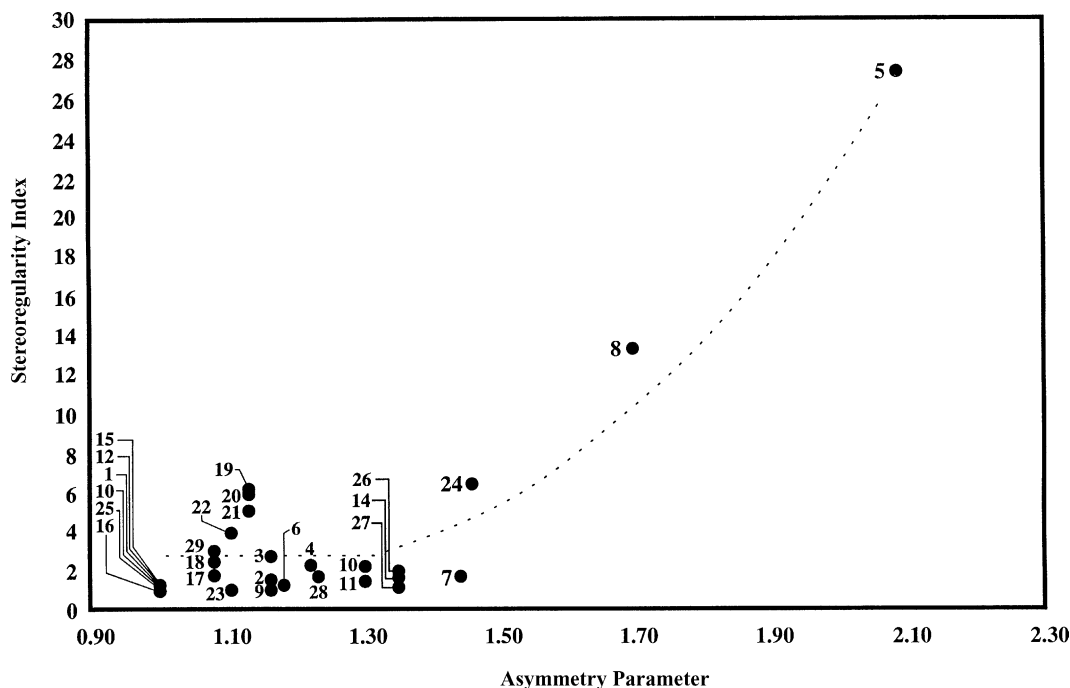


Fig. 1. Plot of catalyst asymmetry parameter vs. polypropylene stereoregularity index for the metallocene catalysts listed in Table 1. The dotted line is only a guide to the eye.

to 1.31. Deviations from the anticipated SRI value of 1.00 are attributed to the effects of chain end control, as was found (at low temperatures) for the C_{2v} catalyst $(C_5H_5)_2TiPh_2$ [16]. That the deviations are small indicates that enantiomorphic site control is the predominant mechanism determining stereoregularity. Introduction of *t*-butyl or *p*-tolyl substituents into the 2, 7 positions in one fluorenyl ring lowers point group symmetry to C_s , but SRI values for the polymers, 1.28 and 1.07, respectively, are within the stated range.

Members of the second subset of catalysts have the general formula [(fluorenyl)-bridge-(R_2 fluorenyl)] $ZrCl_2$ (bridge = $SiMe_2$, $SiPh_2$ or C_2H_4). Half of the ligand is a fluorenyl group. In the other half, R_2 denotes a $-CH=CH-$ group connecting the 4, 5 positions of a fluorenyl ring (compounds **A-bridge**); or a $-CH_2-CH_2-$ group connecting these same two positions (compounds **B-bridge**). **C-bridge** compounds have CH_3 groups at the 4, 5 positions in one part of the ligand. The purpose of the $(CH_3)_2$, CH_2-CH_2 and $CH=CH$ substituents is to incrementally increase the steric bulk of one of the ligands in the critical region

near the zirconium atom and thus produce a gradual increase in the APs of the catalysts.

Fig. 2 shows atomic positions and chemical bonds in **A- C_2H_4** , **B- C_2H_4** and **C- C_2H_4** in their optimized calculated structures. The shapes of these same three molecules, i.e. the contours of their solvent-accessible surfaces, are depicted in Fig. 3. Solvent-accessible surfaces are similar to van der Waals surfaces, but niches smaller than any potential solvent molecule are filled in, thus producing a “shrink wrap” appearance. Fig. 3 clearly demonstrates how the $-CH=CH-$ group spanning the C (4, 5) positions increases the steric bulk of one of the fluorenyl moieties. The AP for this metallocene is 1.08 and it is somewhat syndioregulating for it produces polypropylene with a SRI of 1.84.

When this $-CH=CH-$ group is hydrogenated to produce a $-CH_2-CH_2-$ group as in **B- C_2H_4** , the AP increases slightly to 1.13. Note that two of the methylene hydrogen atoms now protrude above the plane of the fluorenyl rings and into the region adjacent to the zirconium atom as shown in Fig. 3. Addition of only two hydrogen atoms significantly increases the

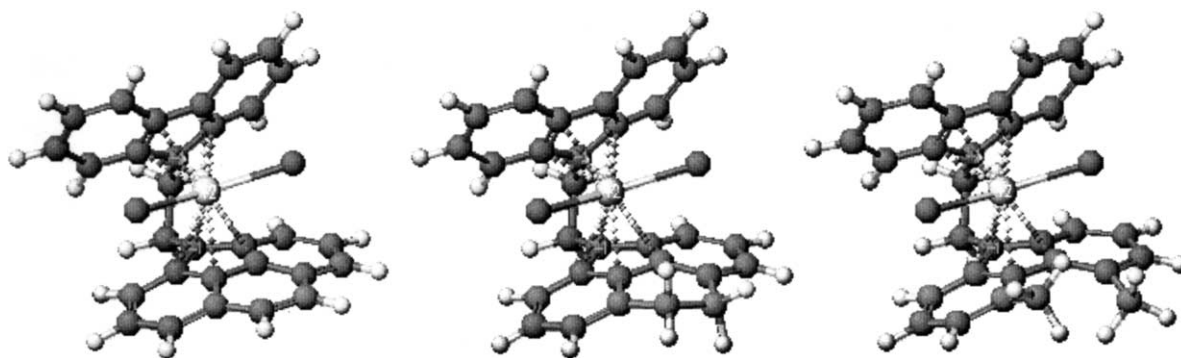


Fig. 2. Molecular structures for [fluorenyl- C_2H_4 -cyclopentaphenanthryl]ZrCl₂ (left); [fluorenyl- C_2H_4 -dihydrocyclopentaphenanthryl]ZrCl₂ (middle) and [fluorenyl- C_2H_4 -4,5-dimethylfluorenyl]ZrCl₂ (right).

syndioregulating ability of the catalyst and it produces polypropylene having a SRI of 6.10. We think it remarkable that the stereoregulating properties of metallocene catalysts are so sensitive to deceptively minor structural variations.

Conceptual hydrogenolysis of the bridge C–C bond in **B-C₂H₄** produces **C-C₂H₄** in which the two CH₂ groups are converted to CH₃ groups. As a result, the molecule becomes even more asymmetrical and AP increases to 1.23. However, the stereoregulating ability of the catalyst actually drops and the polypropylene produced has an SRI value of only 1.68. We surmise that this unanticipated result may stem from the fact that, *relative* to its **A** and **B** analogues, **C-C₂H₄** lacks a persistent shape. In addition to rotation of the CH₃ groups, low frequency vibrations can cause these CH₃ groups to bend away from one another and out of the plane of the fluorenyl moiety to which they are attached. Thus, this part of the metallocene molecule is more plastic than rigid and it can deform to accommodate incoming monomer and/or the growing polymer chain in a way that is not possible when the 4,5 substituents are linked together to form part of a six-membered ring.

The nature of the bridge connecting the two ligand fragments of a metallocene catalyst was ignored in defining an AP. This is at best an approximation that has only the merit of convenience and which offers ground for future improvement. For the metallocenes **B-C₂H₄**, **B-SiMe₂** and **B-SiPh₂**, the respective polypropylene SRI values are 6.10, 5.90 and 4.75. All three catalysts are syndioregulating and the structural

nature of the bridge can be viewed as a second-order perturbation. It accounts for much of the vertical scatter seen in Fig. 1. Asymmetry in the bridging moiety alone is insufficient to affect stereoselectivity. This is evidenced by [fluorenyl-CH₂-SiMe₂-fluorenyl]ZrCl₂ which produces polypropylene with an SRI of 1.04.

Exhaustive hydrogenation of **A-C₂H₄** produces [(decahydrocyclopentaphenanthryl)- C_2H_4 -(decahydrofluorenyl)]ZrCl₂, entry 22 in Table 1. The –CH=CH– group connecting the 4, 5 positions of one of the fluorenyl rings is transformed, as before, to a –CH₂–CH₂– moiety. In addition, the four benzo groups are converted to (CH₂)₄ tetramethylene substituents. As a result of this reduction, both fluorenyl groups become cyclopentadienyl groups, each bearing two tetramethylene rings. Both halves of the ligand have larger van der Waals surfaces because =CH– has been replaced by –CH₂–. However, the ratio of the van der Waals areas of the two ligand fragments, AP does not change. The SRI of the polypropylene produced by this hydrogenated catalyst is 3.92; it is still syndioregulating, but less so than its aromatic precursor. This result indicates that the shape parameter is applicable to cyclopentadienyl- as well as fluorenyl-containing ligands. It is still catalyst shape that determines stereoregulation.

Disorder tends to increase with temperature and so an increase in propylene polymerization temperature is expected to decrease stereoregularity. Temperature can effect a significant perturbation on the stereoregulating effect of metallocene structure. Thus, when **A-C₂H₄** was used as a polymerization

catalyst at 65 °C, polymer SRI decreased to 3.0 as compared to 6.1 at 25 °C. Comparisons of metallocene stereospecificity are thus best made at similar temperatures.

The idea of using van der Waals surface areas to calculate metallocene catalyst APs can be used in a general way. The surface areas of cyclopentadienyl, indenyl and fluorenyl groups are given in [Table 2](#). This

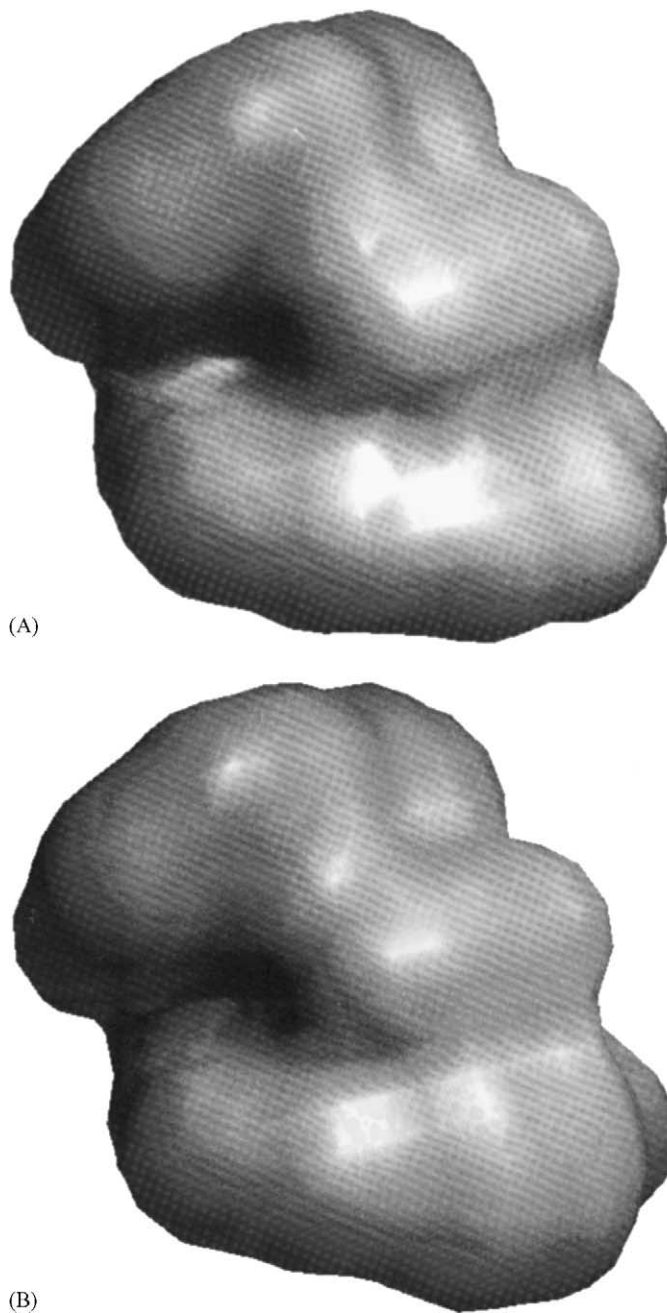


Fig. 3. Solvent-accessible surfaces for the metallocene catalysts shown in [Fig. 2](#).

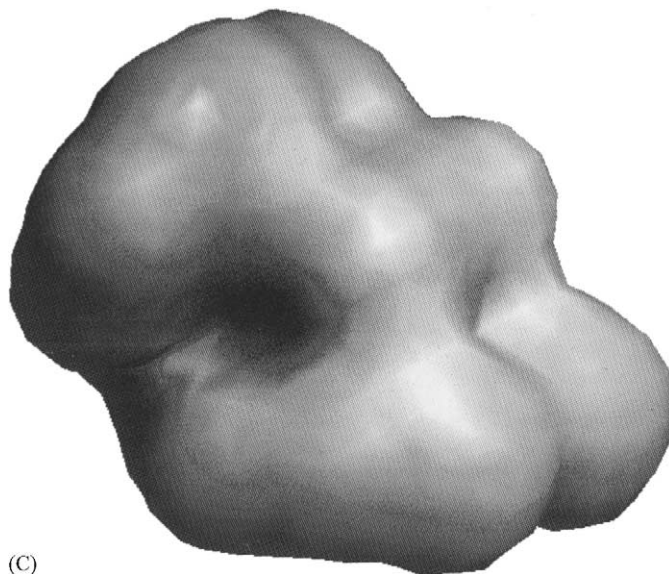


Fig. 3. (Continued).

Table 2
Surface areas of molecular fragments

| Fragment | Surface area (\AA^2) |
|-----------------------------------|---------------------------------|
| C_6H_5 | 66 |
| C_5H_5 | 76 |
| Indenyl | 121 |
| Fluorenyl | 151 |
| CH_3 | 18 |
| C_2H_5 | 35 |
| <i>i</i> - C_3H_7 | 52 |
| <i>t</i> - C_4H_9 | 68 |
| CF_3 | 29 |

table also shows the absolute increase in surface area when H in C_6H_6 is replaced by various alkyl or aryl groups or by CF_3 . These increments comprise group additivity contributions to molecular surface areas. Thus, AP values for a wide variety of metallocenes, even ones that have yet to be made, can be calculated by simple arithmetic. For example, the surface area increment for the *t*-butyl group is 65\AA^2 ; and 151\AA^2 for the fluorenyl group. Thus, the AP for the metallocene [(fluorenyl)- SiMe_2 -(4,5-*t*-Bu₂fluorenyl)] ZrCl_2 is calculated to be $[151 + 2(68)]/151$ or 1.90. This value is so high that it is quite probable, based on the data in Fig. 1, that if this highly congested

metallocene were made, it would prove to be quite highly syndioregulating just as Ewen proposed [17].

3. Conclusions

A simple, approximate method of describing the degree of asymmetry in *ansa*-bridged metallocene olefin polymerization catalysts is presented. There is an empirical relationship between catalyst asymmetry and its stereoregulating tendency. This relationship may have predictive value for new catalysts in which enantiomeric site control predominates over chain end stereocontrol.

4. Experimental

Molecular surface area calculations were performed with CAChe Mechanics (to optimize ligand fragment geometries so as to minimize non-bonded repulsions and torsional strain) and Project Leader (to compute surface areas) molecular mechanics programs (all version 3.8, from Oxford Molecular Ltd., Oxford, UK), run on a Macintosh computer. Isodensity surfaces were calculated at $0.01 \text{ e}/\text{\AA}^3$ to provide a computationally

reproducible surface that closely approximates the van der Waals surface. Metallocene catalyst molecules are actually three dimensional objects and so molecular volumes of various catalysts were calculated with the same program. There was obtained an excellent linear correlation between molecular areas and molecular volumes. Therefore, use of surface areas is appropriate. Molecular surface areas were calculated as well with the AMPAC program (as implemented in Spartan 4pc). This latter methodology views molecules and atoms as being bounded by exponentially decreasing electron density function rather than as hard spheres. The absolute surface areas of ligand fragments (fluorenyl, cyclopentadienyl etc.) differ somewhat from those obtained using CACHe. However, the ratios of surface areas of the ligands, the AP values, are not significantly different from those obtained using CACHe. Dr. Shih-Hung Chou has found the surface areas of the groups listed in Table 2, determined by the CACHe program correlate linearly ($r^2 = 0.998$) with surface area parameters calculated with use of the program Cerius2. The results indicate that a set of valid, internally consistent APs can be developed with several different modeling programs because the area ratios of the various ligands modeled remain essentially the same.

The catalyst structures shown in Fig. 2 were obtained using WebLab Pro 3.0 from Molecular Simulations Inc. The solvent-accessible surfaces represented in Fig. 3 were computed by this program and are shaded by electrostatic potential.

Metallocene catalysts were prepared by literature methods [18].

Propylene was polymerized at $25 \pm 10^\circ\text{C}$. Typically, a 20 ± 1 mg quantity of metallocene catalyst was dissolved under nitrogen in 16 ml methylaluminoxane solution in toluene (Albermarle Corp., $[\text{Al}] = 1.7 \text{ M}$). After 1 h, the solution was diluted with 10 ml toluene and transferred to a 100 ml stainless steel cylinder fitted with a valve. The cylinder was pressurized to about 800 psi with nitrogen, inverted and then attached to a stainless steel reactor containing about 1800 gm propylene (Matheson Gas Products polymerization grade, passed through two Matheson model 6406A purifiers connected in series) at a temperature of ca. 8°C . This reactor had a volume of 8 l and was equipped with a thermocouple, an agitator and a jacket through which coolant (dry ice–isopropanol) could

be circulated as needed to control the reaction temperature. It was evacuated with a mechanical pump then backfilled with nitrogen prior to being charged with propylene. Upon opening the cylinder valve, the catalyst solution was injected into the reactor. Polymerization was carried out at $25 \pm 10^\circ\text{C}$ for 4 h then terminated by venting the unreacted monomer. Characterization data for the polymers are given in Table 1. The quantities of the catalysts were adjusted within the indicated range so as to aid in maintenance of reaction temperature with smaller amounts of the more active catalysts being used.

^{13}C NMR analyses to determine microstructure at the pentad level were conducted at 100°C using *o*-dichlorobenzene solutions of the polymers and a Varian XL-500 spectrometer [19]. Weight average (M_w) and number average (M_n) molecular weights were determined by gel phase chromatography (GPC) on filtered solutions using a Waters 150C system equipped with Jordi Associates Inc. 500A and mixed bed columns which were calibrated with polystyrene standards. Toluene at 25° was used as solvent unless otherwise noted. Some catalysts, particularly those of the type [(fluorenyl)-bridge-(Rindenyl)]ZrCl₂, produced polymers whose GPC curves were bimodal. In these instances, peak molecular weights are given along with estimated area percentages in parentheses.

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References

- [1] J.A. Ewen, *Sci. Am.* 276 (1997) 86–91.
- [2] A.D. Horton, *Trends Polym. Sci.* 2 (1994) 158–167.
- [3] (a) W.J. Kaminsky, *Chem. Soc. Dalton Trans.* (1996) 255–170;
(b) H.H. Brintzinger, D. Fischer, R. Mulhaupt, B. Rieger, R.M. Waymouth, *Angew Chem. Int. Ed. Engl.* 34 (1995) 1143–1170;
(c) J.B.P. Soares, A.E. Hamilec, *Polym. React. Eng.* 3 (1995) 131–200;

- (d) M.J. Bochman, Chem. Soc. Dalton Trans. (1996) 255–270;
(e) V.K. Gupta, S. Satish, I.S.J. Bhardwaj, Macromol. Sci. Macromol. Chem. Phys. C43 (1994) 439–514;
(f) W. Kaminsky, Macromol. Chem. Phys. 197 (1996) 3907–3945;
(g) M. Baumert, H. Frey, M. Holdera, J. Kressler, F. Senertz, R. Mulhaupt, Macromol. Symp. 121 (1997) 53–74;
(h) W. Kaminsky, M. Arndt, Adv. Polym. Sci. 127 (1997) 144–187;
(i) K. Soga, T. Shiono, Prog. Polym. Sci. 22 (1997) 1503–1546.
- [4] (a) J.A. Ewen, M.J. Elder, R.L. Jones, L. Haspeglagh, J.L. Atwood, S.G. Bott, K. Robinson, Makromol. Chem. Macromol. Symp. 48/49 (1991) 253–295;
(b) J.A. Ewen, Macromol. Symp. (1995) 181–196.
- [5] (a) A. Razavi, L. Peters, Nafpliotis, J. Mol. Catal. 115A (1997) 129–154;
(b) L. Resoni, R.L. Jones, A.L. Rheingold, G.P.A. Yap, Organometallics 15 (1996) 998–1005;
(c) F. Piemontesi, I. Camurati, L. Resoni, D. Balboni, A. Sironi, M. Moret, Organometallics 14 (1995) 1251–1266;
(d) S. Harder, M. Lutz, A.W.G. Straub, Organometallics 16 (1997) 107–113;
(e) U. Stehling, J. Diebold, R. Kirsten, W. Roll, S. Jungling, R. Mulhaupt, Organometallics 13 (1994) 964–970;
(f) W. Spaleck, F. Kuber, A. Winter, J. Rohrman, B. Bachman, M. Antberg, V. Dolle, E.F. Paulus, Organometallics 13 (1994) 154–963;
(g) L. Resconi, F. Piemontesi, I. Camurati, O. Sudmeijer, I.E. Nifantev, P.V. Ivchenko, L.J. Kuzmina, Am. Chem. Soc. 120 (1998) 2308–2321;
(h) A. Razavi, J.L. Atwood, Organometal. Chem. 520 (1996) 115–120.
- [6] K. Hortman, H.H. Brintzinger, N. J. Chem. 16 (1992) 51–55.
- [7] (a) M. Pinsky, D. Avnir, Inorg. Chem. 37 (1998) 5575–5582 (and previous papers in that series);
(b) R.S. Rowland, R.J. Taylor, Phys. Chem. 100 (1996) 7384–7391;
(c) A.G. Orpen, Chem. Soc. Rev. 21 (1993) 191–197.
- [8] (a) A.Y. Meyer, Chem. Soc. Rev. 15 (1986) 449–474;
(b) R.S. Rowland, R.J. Taylor, Phys. Chem. 100 (1996) 7384–7391.
- [9] (a) P.G. Mezey, Rev. Comput. Chem. 1 (1993) 265–294;
(b) P.G. Mezey, Shape in Chemistry: An Introduction to Molecular Shape and Topology, VCH, New York, NY, 1993;
(c) S. Hyde, S. Andersson, K. Larsson, Z. Blum, T. Landh, S. Lidin, B.W. Ninham, The Language of Shape, Elsevier, Amsterdam, 1997.
- [10] C.A. Tolman, Chem. Rev. 77 (1997) 313–348 (this important review describes use of van der Waals surfaces of tertiary phosphines to describe the steric properties of such ligands in terms of cone angles).
- [11] (a) J.J. McKinnon, A.S. Mitchell, M.A. Spackman, J. Chem. Soc. Chem. Commun. 1998, 2071–2072;
(b) M.A. Spackman, P.G. Byrom, Chem. Phys. Lett. 267 (1997) 215–220;
(c) J.J. McKinnon, A.S. Mitchell, M.A. Spackman, Chem. Eur. J. 4 (1998) 2136–2141.
- [12] D. White, N.J. Coville, Adv. Organometal. Chem. 36 (1994) 95–158.
- [13] (a) Y. van der Leek, K. Angermund, M. Reffke, R. Kleinschmidt, R. Goretzki, G. Fink, Chem. Eur. J. 3 (1997) 585–591;
(b) K. Angermund, G. Fink, V.R. Jensen, R. Kleinschmidt, Chem. Rev. 100 (2000) 1457–1470.
- [14] V. Busico, R. Cipullo, Prog. Polym. Sci. 26 (2001) 443–533.
- [15] (a) H.G. Alt, E. Samuel, Chem. Soc. Rev. 27 (1998) 323–329;
(b) H.G. Alt, A. Koppl, Chem. Rev. 100 (2000) 1205–1221.
- [16] J.A. Ewen, J. Am. Chem. Soc. 106 (1984) 6355–6364.
- [17] J.A. Ewen, US Patent 4,892,851.
- [18] (a) A.R. Siedle, D.K. Misemer, V.V. Kolpe, B.F. Duerr, US Patent 6,265,512;
(b) A.R. Siedle, D.K. Misemer, V.V. Kolpe, B.F. Duerr, US Patent 6,323,151;
(c) A.R. Siedle, D.K. Misemer, V.V. Kolpe, B.F. Duerr, WO 99/20664.
- [19] A. Tonelli, NMR Spectroscopy and Polymer Microstructure: The Conformational Connection, VCH, Deerfield Beach, FL, 1989.