

## CHAPTER 5

### DISCUSSION

#### 5.1 Structure of Zirconocene

According to Table 4.6, the comparison between X-ray structure and B3LYP/DZVP optimized structure of **structure 3** are given, all of bond distances obtained from B3LYP/DZVP longer than the X-ray structure  $< 0.05 \text{ \AA}$ . On the other hand, calculated bond angles are  $\pm 2^\circ$  deviated from the X-ray ones. This deviation in bond angle is in good agreement with experiment. The deviation in bond distance although rather large is still acceptable. The agreement of calculated geometries can probably be improved by employing larger basis set for example TZVP. However, the size of calculation is scaled as  $N^4$  where N is the number of basis function. With this basis (DZVP), the calculation already took very long time. Increasing basis size would make computation time much longer or even become impossible. The long computation time discourage the quantitative structure-property relation (QSPR) to be performed. New techniques which saved time but still retained accuracy are sought. Thus, the B3LYP/LANL2DZ and ONIOM (B3LYP/DZVP:UFF) calculations on this system were carried out.

The average difference as defined in equation (4.1) was used as a mean to measure the "agreement" of the two methods. According to Table 4.7, the small difference of bond distances, bond angles, and torsion angles for B3LYP/LANL2DZ implies that the method yields practically the same optimized geometry as B3LYP/DZVP. The ONIOM (B3LYP/DZVP:UFF) optimized bond distances and bond angles are in good agreement with B3LYP/DZVP whereas the bond torsions obtained from this method are about  $26.6^\circ$  too large, the result is not acceptable. This is probably because the UFF does not have good parameters for

describing bond torsion of metallocene as can be seen from the large deviation of torsion angle of ethylene-bridge in **structure 5** and silano-bridge in **structure 4**.

From the result in Table 4.7, the effective core potential does not reduce the accuracy of the calculation. The Integrated Molecular Orbital and Molecular mechanics (IMOMM) such as ONIOM (B3LYP/DZVP:UFF) could not determine the torsion angle of the bridge accurately. For the former, the computing time that can be saved is minimal while one could save lots of computing resources for the latter. Here, one needs to judge between time-saving and accuracy. Other force fields such as DREIDING and MM3 that better described the bridge bond torsion need to be tried. Apart from bond distances, bond angles, and torsion angles, the agreement of parameters such as distance between Cp planes, angle between Cp planes, gap aperture, obliquity, cavity angle, and cavity angle computed from the other two methods also need to be tested.

As can be seen in Table 4.8, the distance between Cp planes from B3LYP/LANL2DZ are slightly shorter than those from B3LYP/DZVP. Similar trend was also observed for ONIOM (B3LYP/DZVP:UFF) except for **structure 4**, which has too long distance. This is possibly the result of the off-value torsion angle of silano-bridge. According to Table 4.9, the angles from B3LYP/LANL2DZ are slightly smaller than those from B3LYP/DZVP. Similar trend was also observed for ONIOM (B3LYP/DZVP:UFF) except for **structure 4**, where too large angle was reported.. This discrepancy can be explained in similar way to the distance between Cp planes.

From Table 4.10, the gap apertures from B3LYP/LANL2DZ are similar to those from B3LYP/DZVP. For ONIOM (B3LYP/DZVP:UFF), **structure 4** again has large deviation from B3LYP/DZVP, otherwise is in good agreement. This poor description of silano-bridge torsion angle is possibly the cause of such planes discrepancy. Unlike previous parameters, both B3LYP/LANL2DZ and ONIOM (B3LYP/DZVP:UFF) reported similar obliquity to B3LYP/DZVP because the measurement of obliquity does not involve the silano-bridge torsion.

The ONIOM (B3LYP/DZVP:UFF) once again yield too large twisted angle (Table 4.12) for **structure 4**. Otherwise all methods are in good agreement.

According to Table 4.13, the cavity distance from B3LYP/LANL2DZ is less than those from B3LYP/DZVP. Similar trend was also observed from ONIOM (B3LYP/DZVP:UFF) except the **structure 4**, where too long distance was reported. As can be seen from Table 4.14, the cavity angle from B3LYP/LANL2DZ and ONIOM (B3LYP/DZVP:UFF) is slightly smaller than those from B3LYP/DZVP. Again, the same trend was observed for **structure 4**, where too large angle as compared to B3LYP/DZVP was reported. The discrepancy can be explained in the similar way to the distance between Cp plane.

## 5.2 Quantitative Structure-Property Relationships (QSPR)

### 5.2.1 Distance and angle between Cp plane

As can be seen in Table 4.8, the **structure 3** has the largest distance between Cp planes of 4.070 Å. The distance is decreased from **structures 2, 4, and 1** with the value of 4.059 Å, 4.053 Å, and 4.019 Å, respectively. From the Figure 4.6, it was seen that % isotacticity increases as the distance between Cp planes increases. The distance between Cp planes depends on the steric of substituents on Cp ring and increases as this steric increases. In other word, the steric generated by the substituents on Cp ring causes the Cp rings to move apart. The zirconocene with larger distance between Cp planes yielded higher % isotacticity. This relation might seem to conflict with the common understanding that the large distance between Cp planes facilitates the polymer chain to rotate freely and should cause lower % isotacticity. According to Morokuma, the rotation of methyl group of propylene depends on the steric interaction at the transition state. Thus, the steric interaction controls the degree of isotacticity of polypropylene (see Chapter 1). This steric that

controlled the energy difference is the same steric that controlled the distance between Cp ring. It is interesting to note that the **structure 3** which has the highest % isotacticity does not have the highest reactivity (Table 3.1). Thus, the factor that controlled % isotacticity is probably different from that controlled reactivity. The distance between Cp planes controls the size of inner cavity whereas the productivity is controlled by the cavity distance and cavity angle which depend on the substituents group at  $\beta$ -position (sections 5.2.4 and 5.2.5). Thus explained why there is no distance relation between Cp plane and productivity.

The angles between Cp planes described the size of the cavity of the zirconocene similar to those of distance between Cp planes but also includes Cp plane distortion. As shown in Table 4.9, **structure 2** has the largest angle between Cp planes of  $62.08^\circ$ . In decremental order the **structures 3, 4, and 1** have the angle between Cp planes of  $60.99^\circ$ ,  $60.42^\circ$ , and  $58.71^\circ$ . According to the Table 4.9 and Figure 4.7, excluding **structure 2**, the % isotacticity increases as the angle between Cp plane increases. This discrepancy of **structure 2** could be explained. The **structure 2** has too wide angle because the Cp rings are distorted whereas the ring distortion is much less in other compounds. This distortion causes the calculation of the angle between Cp plane to be inaccurate since the planar structure is assumed for the ring in the calculation. This distortion is the result of the large repulsion between *t*Bu groups at  $\beta$ -position. For the **structure 2**, the repulsion is much less at the  $\alpha$ -position since there is no substitution in that position. From Figures 4.8 and 4.9, no angle relation between Cp plane and productivity was observed. The same reason to the case of distance between Cp planes could be used.

### 5.2.2 Gap aperture and obliquity

The gap aperture and obliquity were calculated using program of Hans-Herbert Brintzinger [18]. This program requires parameters such as the centroid of Cp ring, the van der Waals radius of the  $\alpha$  and  $\beta$ -substituents. Here, we

used van der Waals radius of 1.90 Å for methyl group, 1.85 Å for cyclobutyl group, 2.40 Å for *i*Pr group, and 2.45 Å for *t*Bu group [18]. The gap aperture represents the Cp ring openness which includes van der Waals radius of the substituents at the  $\alpha$  and  $\beta$  position. The obliquity was defined by the intersection of the two tangential planes twisted relative to the plane bisecting the centroid-Zr-centroid angle. As shown in Figure 4.10 and Table 4.10, excluding **structure 4**, the % isotacticity increases as the gap aperture increases. The **structure 4** has the largest gap aperture of 62°. In decremental order, **structure 3**, **2**, and **1** have gap aperture of 60°, 42°, and 31°. Interestingly, the **structure 4** which has the smaller bulky group at  $\beta$ -position has larger gap aperture than **structure 3**. This is possibly due to the van der Waals radius chosen for *i*Pr that causes the calculated gap aperture to be overestimated. We found that the calculated gap aperture is sensitive to the choice of van der Waals radius. There are no clear criteria for selecting van der Waals radius. From literature, the van der Waals radius quoted for *i*Pr is between 1.5 – 2.5 Å but generally the value of 2.40 Å was chosen. From Figure 4.12, productivity increase as the gap aperture increase. This relation is similar to that of distance between Cp plane. The gap aperture is calculated from cross product of the tangential line that originated from the center of each Cp ring. So if groups which substitute at the  $\alpha$  and  $\beta$  positions are very bulk, it will narrow the gap aperture.

According to Figure 4.13, no relation between obliquity and the productivity was found but one can divide the result into 2 groups. The **structures 1** and **2**, which have the obliquity of  $-33^\circ$  and  $-34^\circ$ , respectively, have low productivity (85 and 355 kg(PP).(h mol(Zr) p), respectively). The **structures 3** and **4**, which have the obliquity of  $-16^\circ$  and  $-17^\circ$ , respectively, have high productivity (505 and 3000 kg (PP).(h mol(Zr) p), respectively). Thus, zirconocene with less negative obliquity are more reactive.

### 5.2.3 Twisted angle

The repulsion of the bulky-substituents causes the centroid of two Cp rings in zirconocene to become unaligned or moving out of each other. This property can be measured using the twisted angle. The twisted angle reflects the steric of the bulky groups. The positive value means the upper Cp ring move to the left and the negative value means the upper Cp rings moves to right hand (Figure 5.1).

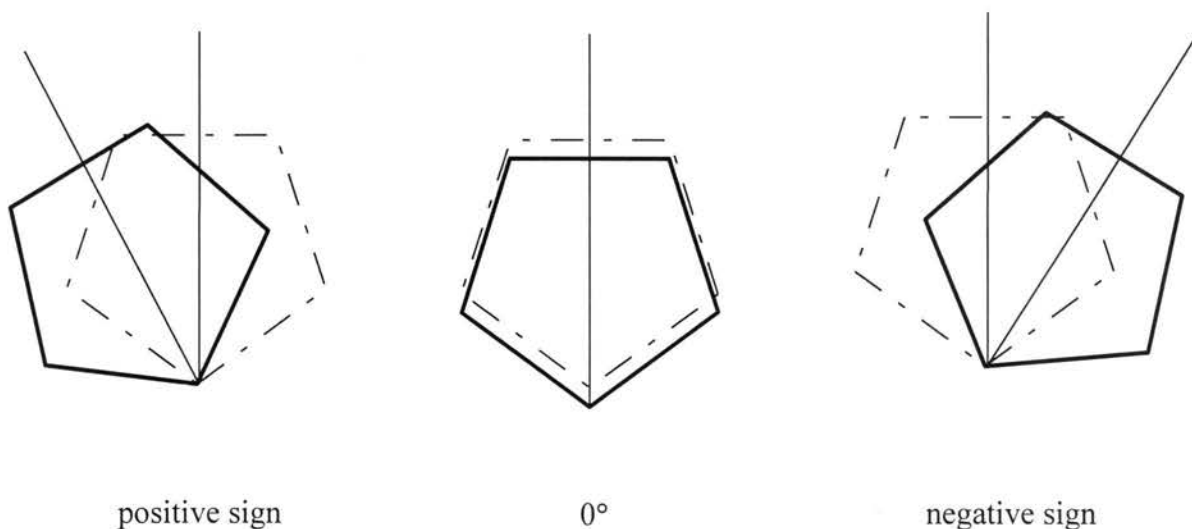


Figure 5.1 The definition of positive and negative signs of twisted angle.

According to Table 4.12, **structures 1** and **5**, which contained the ethylene-bridge have large and positive twisted angle of  $22.24^\circ$  and  $20.62^\circ$ , respectively. Whereas, the **structures 2, 3, and 4**, which contained the silano-bridge, have small positive or negative twisted angle of  $0.10^\circ$ ,  $-9.98^\circ$ ,  $-9.24^\circ$ , respectively. This is probably because, the silano-bridge is more strained than the ethylene-bridge. Therefore, Cp rings of the zirconocene structures with the silano-bridge are more difficult to move. Since, the repulsion of the  $\alpha$ -substituents (H atom) of **structure 2** is much less than the methyl group of **structure 3** and **4**, therefore, within the silano-bridge series only the **structure 2** has the positive twisted angle. From Figure 4.14, the zirconocene with negative or small positive twisted angle seemed to yield polypropylene with high % isotacticity. Similar to % isotacticity, the zirconocene

structures with the negative twisted angle also have high productivity. It is noticed that the zirconocene with negative twisted angle has the methyl group as  $\alpha$ -substituents. This agrees with the proposal that methyl group at  $\alpha$  position of Cp ring increases the productivity of the catalyst [17].

#### 5.2.4 Cavity distance and cavity angle

The cavity distance is the closest distance between 2 hydrogen atoms of the bulky group at  $\beta$ -substituents. The van der Waals radius was not taken into account for the measurement of the cavity distance. The cavity distance related to the size of the entrance channel of the zirconocene cavity. The cavity angle is the angle of H-Zr-H where H is hydrogen atom of the bulky group at  $\beta$ -position in each cyclopentadienyl rings (also not taken into account of van der Waals radius). Again this cavity angle represents the openness of zirconocene outer cavity.

According to the Table 4.13, the **structure 3** has the highest cavity distance of 5.713 Å and in the decremental order the cavity distances of the **structures 4, 2, and 1** are 5.665 Å, 5.563 Å, and 5.126 Å. From Table 4.14, the **structure 3** also has the highest cavity angle of 96.91°. Similarly, the cavity angle in the decremental order of the **structures 4, 2, and 1** are 95.01°, 94.79°, and 87.80°.

As seen in Figures 4.16 and 4.18, no linear relation was found between the cavity distance and cavity angle and % isotacticity, although both parameters produced the same trend. Whereas there exists some relation between these parameters and the productivity except for the **structure 4**. As mentioned in 4.1.4, there are 2 conformation for the **structure 4**. These 2 conformations can be switched between each other since their energy is only 2.96 kcal/mol different. It is possible, during the course of reaction, the form which has lower energy, can switch to the form of higher energy. From Tables 4.13 and 4.14, the conformer with has the higher energy also has larger cavity distance and cavity angle. If we interchange the

cavity distances and angle of conformer I with those of conformer II, relation could be observed between cavity distance and cavity angle and productivity. So the productivity increases as the cavity distance and cavity angle increase. This relation could be explained. The entrance of the cavity measured by cavity distance and angle, control the rate in which propylene entering the zirconocene cavity thus controls the rate in which propylene insertion to the zirconium center. The cavity distance and angle are the good parameters for describing both selectivity and reactivity of the catalyst.

### 5.2.5 Atomic charges

According to Table 4.15 and Figure 4.20, we could not find the relation between charge of Cp ring and zirconium taken from neutral zirconocene and productivity. However, for the ion form (Table 4.16 and Figure 4.21) if we consider only compound with the silano-bridge (the **structures 2, 3, and 4**) one can see that the productivity increases as the charge of zirconium increases. Similar trend was also observed for the charge of cyclopentadienyl. In the ion form, both of ethylene bridge and silano-bridge are the electron donating group whereas, in neutral form, the ethylene bridge is the electron withdrawing group. In the ion form, the *t*Bu and *i*Pr are a good electron donating groups as compared with the neutral form. Also the charge of zirconium in the ion form is larger than in the neutral form for the **structures 4 and 5**. This is possibly the reason that the **structure 4 and 5** has higher productivity than other zirconocenes. The fact that we can observed relation between zirconium and Cp charge and the productivity only where zirconocene is in the ion form is very interesting. This guides us to identify the rate determining step (RDS) of the reaction. There are 3 main step which controlled the reactivity of catalyst *i.e.* (1) the formation of zirconocene ion by the help of MAO co-catalyst; (2) the insertion of first propylene to zirconium center; (3) The next insertion of propylene to zirconium center. From this result, it appears that (2) is the RDS since the insertion at the zirconium center is more favorable for zirconocene ion with more positive zirconium charge. Thus, zirconocene ion with more positive charge at zirconium center trends



to be more reactive. This agrees very well with the observed relation between productivity and cavity distance and angle. As can be seen from the Table 4.16, for the ion form, both of the bulky group at  $\alpha$  and  $\beta$ -position must be the good electron donating group for the catalyst to be highly reactive.

### 5.3 Suggestion for New Zirconocene Catalyst

The ideal catalyst, which gives the high % isotacticity should have following properties; large distance and angle between Cp planes large gap aperture, small negative twisted angle, large cavity distance and angle. Except for the twisted angle, all these parameters represent the cavity size of zirconocene. As discussed in 5.2, the selectivity (in this case % isotacticity) is controlled by the steric of the substituents that causes the enlargement of the cavity size. One might notice that substituents which generate enough steric and make these parameters larger are at the  $\beta$ -position on Cp ring. The bulkier substituents creates the larger cavity size and, therefore, higher % isotacticity. The cavity distance as well as cavity angle is not the best representative for the cavity size since they measure the entrance of the cavity not the cavity. The twisted angle represents 2 factors, the steric of substituents at  $\beta$ -position and the strain (the flexibility) of the ethano/silano bridge. If the bridge is flexible such as the ethano bridge, the steric of  $\beta$ -substituents will not cause the enlargement of zirconocene cavity size but instead twisted the Cp rings to move apart. This lowers the steric at the transition state and repulsion resulting in lower % isotacticity as for **structure 1**. On the other hand, for the strained bridge such as silano bridge the steric of  $\beta$ -substituents could not overcome the bridge stiffness and the effect only results in the enlargement of the cavity. Thus, apart from large bulky group at  $\beta$ -position, the very strained bridge would be required for catalyst with high selectivity. The  $\alpha$ -substituents should also be sufficiently bulky to control the stiffness of the bridge.

The ideal catalyst which gives the high productivity should have following properties; obliquity around  $-17^\circ$ , small or negative twisted angle, large

cavity distance and angle, more positive charge on zirconium or more negative charge on Cp ring. As discussed in 5.2, the factor which controls the reactivity in this case the productivity, is the rate of first propylene insertion. This rate of insertion depends on the rate of entering the cavity distance and the charge on zirconocene. The rate of entering can be estimated from the cavity distance and angle which measures the entrance channel to the cavity. The catalyst with larger entrance channel will have faster rate of entering and these faster rates of first propylene insertion. The factor that determined the entrance channel is  $\alpha$ -substituents,  $\beta$ -substituents, and the bridge strain. The large bulky group at  $\beta$ -position causes the entrance channel to be wide open if incorporates with stiff bridge such as silano bridge. The bulkiness of the group at  $\alpha$ -position also helps opening up the entrance channel. The **structure 4** is exceptional. Although *i*Pr is less bulky than *t*Bu, the flexibility of the *i*Pr group that works like a switch to close the channel to improve steric on to open the channel to improve the rate of entering, makes the compound unique and yields highest reactivity. The charge of zirconium could be made positive by attaching electron donating groups at  $\alpha$  and  $\beta$ -position of the Cp ring. However, only the zirconium charge in the ion form not the neutral form is significant and the electronic effect of the substituents in neutral and ion forms is different. This effect could only be determined through quantum calculations. The obliquity and twisted angle control the symmetry of the catalyst. The value of zero for obliquity means the catalyst has perfect  $C_2$  symmetry. Large (negative) deviation from zero makes the catalyst less active. However, small and negative deviation makes the catalyst highly active. It seems that some certain ( $-17^\circ$ ) of this values is required for catalyst with high reactivity. The factors which control the obliquity and twisted angle are the bridge strain and the balance of  $\alpha$  and  $\beta$ -substituents. The zirconocene with less strain bridge like ethano bridge has large obliquity and twisted angle. Thus for catalyst with high reactivity the required feature is not so large but flexible substituents at  $\beta$ -position, the stiff bridge between Cp, and the electron donating substituents at both  $\alpha$  and  $\beta$ -positions.

It can be seen that there are several features that are different between catalysts with high selectivity and reactivity. Too large and bulky  $\beta$ -substituents might not always be good for both selectivity and reactivity. The more clever way is to try the bulk but flexible group at  $\beta$ -position. The balance substituents might not be very good for catalyst with high selectivity but is a must for that with high reactivity. More information is needed to pinpoint the required features for good catalyst.