Theoretical Models of Ethylene Polymerization

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Metallocenes, whether using a cocatalyst or not, act as catalysts in ethylene polymerization. The positive charge on the transition metal of a metallocene might have an important role in polymerization as an active site in our model approach. Using semiempirical calculations in the absence of cocatalyst, we show one of the possibilities that the positive charge on a metallocene might be more easily transferred through the Cp ring of a ligand to the ethylene than to transfer directly from the transition metal to the ethylene. In these calculations, the charge on titanium in an eight C_2H_4 system is transferred and a polymer chain is produced. This reaction takes place only when ethylenes are arranged in a particular direction with respect to the ring, but does not take place for ethylenes near Ti or Cl atoms. The same mechanism is shown for a metallocene ligand which is sterically hindered or where the Cp ring is replaced by fluorenyl. These results suggest an entirely new polymerization mechanism in the absence of a cocatalyst in which the Cp ring is the active site.

Introduction

A lot of research[1-6] has sought to identify and utilize metallocene catalysts since they were discovered as useful reagents for the stereospecific Ziegler-Natta polymerization of oligomers.[7,8] After titanocene dichloride (Cp_2TiCl_2) was used as the catalyst in polymerization reactions by Breslow and Newburg,[9,10] metallocene catalysts have been accepted as having industrial potential since the mid-1980s.[11-13]

Even though many metallocene catalysts and their derivatives have been suggested, metallocenes themselves are not powerful catalysts because of low activity. However, active catalysts can be made from the complexes with cocatalysts such as methylaluminoxane (MAO) or AlR_nCl_{3-n}.[14-17]

Despite more than 30 years of intensive research, the precise nature of the active center and the mechanism of polymerization are still not fully understood. On the basis of experimental evidence, two mechanisms have been suggested for the mechanism of Ziegler-Natta olefin polymerization. The first one is the direct olefin insertion mechanism suggested by Cossee and Arlman.[18-20] In this mechanism, a vacant coordination site is generated initially, and then a metaloalkyl ring-type complex is formed. Studies on the reaction of Cp-$(CH_3)_2(PPh_3)Co$ with C_2H_4,[23] using deuterium labeling experiments, support the direct insertion mechanism. In the second scheme proposed by Green and Rooney,[21,22] there is an α-hydrogen shift from the growing polymer chain to the transition metal to form a metal carbene. Second or third-row transition complexes generally follow the Green-Rooney mechanism. In particular, it has been observed that both $(CHCMe_3)(H)(PMe_3)_3I_2Ta^{24,25}$ and $(\eta^5-C_5Me_5)_2(C_2H_4)(H)Nb^{26}$ insert ethylene via a metathesis-type mechanism. To follow the direct insertion schemes, the catalyst should be activated, or the ligand should be small enough not to cause steric hindrance. In this paper, we will study the polymerization process theoretically using computer calculations of the titanium metallocenes cyclopentadienyl titanium trichloride ($C_5H_5TiCl_3$, $CpTiCl_3$), dicyclopentadienyl titanium dichloride ($C_{10}H_{10}TiCl_2$,

Cp_2TiCl_2), pentamethylcyclopentadienyl titanium trichloride ($C_{10}H_{15}TiCl_3$), and cyclopentadienyl fluorenyl titanium dichloride ($C_{18}H_{14}TiCl_2$). The first two catalysts are simple systems which allow computational investigation of the reaction mechanism. The last two illustrate more sterically hindered systems.

Computational Methods

The calculations that we performed on these systems were of the incomplete neglect of differential overlap by Zerner (ZINDO) type[27-29] which has been successfully applied to complexes including the transition metals.[30-32] Self-consistent field (SCF) calculations were applied to models of complexes made with the metallocene catalyst and ethylenes by using a generalized closed-shell operator described elsewhere.[33-35] Semiempirical ZINDO calculations were done using the program HYPERCHEM 4.5 from Hypercube, Inc. running on PC compatibles. *ab initio* calculations using the 3-21G* basis set included in the program SPARTAN 5.0 were also done to determine the structure of the catalyst.

Results and Discussion

The optimized structure of dicyclopentadienyl titanium dichloride (Cp_2TiCl_2) and cyclopentadienyl titanium trichloride ($CpTiCl_3$) obtained by ZINDO in HYPERCHEM 4.5 which is modified for transition metal complexes is represented in Table 1. We also determined the catalyst structure using *ab initio* methods (Spartan 3-21*G basis set). The two structures agree to within expected differences. These structures agree with experimental studies using electron diffraction,[36] neutron diffraction,[37] and X-ray diffraction.[38-41]

We compare our results with X-ray data in Table 1. The computed structure agrees well with X-ray diffraction experimental results. The structure in Figure 1 is our optimized structure, and we take it as the basic structure in the polymerization processes for subsequent calculations. The struc-

Table 1. Structural Data of CpTiCl₃ and Cp₂TiCl₂

Bond distance (Å)	CpTiCl₃		Cp₂TiCl₂	
	Ours[b]	Exp.[c]	Ours[b]	Exp.[d]
Ti-Cl1	2.34(2.23)	2.30	2.45(2.30)	2.36
Ti-Cl2	2.35(2.23)	2.27	2.46(2.30)	2.37
Ti-Cl3	2.35(2.23)	2.33		
C-C(in Cp ring)[a]	1.43(1.42)	1.43	$\begin{cases} 1.431 \\ 1.431 \ (1.39) \end{cases}$	$\begin{cases} 1.38 \\ 1.39 \end{cases}$
Bond angle(°)				
Cl-Ti-Cl[a]	100.81(103.33)	102.00	91.72(109.47)	94.43
C-C-C(in Cp ring)[a]	108.00(108.00)	108.00	108.00(108.00)	108.00
Cp-Ti-Cp			136.40(135.25)	130.89

[a]average value. [b]ZINDO results using HyperChem 4.5. Values in parentheses are from Spartan 3-21G* *ab initio* calculation. [c]ref. 41. [d]ref. 40.

ture for CpTiCl₃ is in Figure 2. The calculated structure is again in good agreement with experimental data.[41]

Two kinds of ethylene polymerization mechanisms using the Cp₂TiCl₂ catalyst have been proposed by Green *et al*..[21,22] However, the results shown in Figure 1 and Table 1, suggest a difficulty for polymerization according to the mechanisms proposed by Green *et al.* because the Ti atom and cyclopentadienyl ring are too close (2.0-2.4 Å) to either insert an ethylene between them or do the α-hydrogen shift of the metathesis mechanism. The intermediate complexes suggested by Cossee and Arlman would probably be precluded due to high steric hindrance even though the Cossee and Arlman
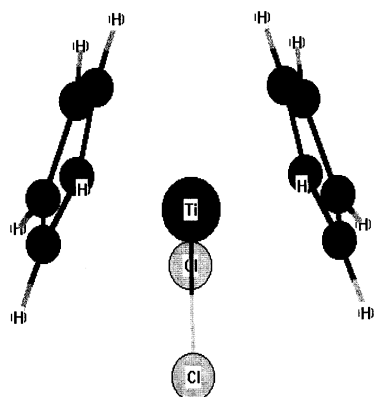
Figure 1. Molecular structure of Cp₂TiCl₂ as determined by ZINDO geometry optimization.
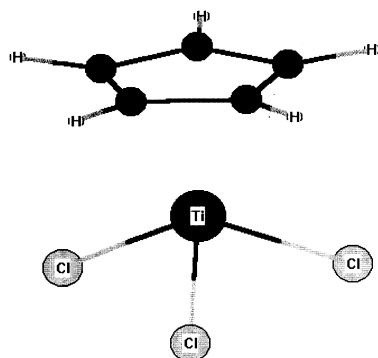
Figure 2. Molecular structure of CpTiCl₃ as determined by ZINDO geometry optimization.

mechanism might be correct for smaller ligands. For the cyclopentadienyl ring or more bulky groups, the structure of Cp₂TiCl₂ would need to be distorted in order to form the intermediate complexes proposed by Cossee and Arlman, or the Cp₂TiCl₂ catalyst should be reacted with a cocatalyst that activates titanium.[14-17,42]

Because of these observations, we calculate and discuss the directional selectivity and the reactivity of Cp₂TiCl₂ without a cocatalyst. But there is no direct experimental observation about the mechanism of ethylene polymerization, so we tried to suggest one of the possibilities by using the computational method. In this research, we did not deal with the process of polymerization under the cationic metallocene catalyst constructed by the assistance of a cocatalyst such as methylaluminoxane (MAO) or AlR_nCl_{3-n}.

Processes of Polymerization under CpTiCl₃ Catalyst. In this section, we study CpTiCl₃ as a catalyst in the polymerization of ethylene because it has the simplest cyclo-organic ligand. We seek the active site where the process of polymerization is initiated. In order to find out the active site of CpTiCl₃, we arbitrarily inserted 14 ethylenes around CpTiCl₃ as shown in Figure 3. The smallest C-C distance between nearest neighbors in the starting structure is 3.0 Å. The ethylene orientations were arbitrary. A ZINDO semi-empirical calculation was begun using this as the starting configuration. This calculation seeks a lower energy configuration. Bond breaking and forming are allowed. The tendency toward polymerization should be revealed by forming polyethylene as a lower energy product.

We noted the important structural changes during the energy minimization process. Some ethylenes near the cyclopentadienyl ring change their C-C bond length from 1.34 Å to around 1.54 Å and H-C-H bond angle from 120° to around 110°. These phenomena mean that the orbital configuration on carbon atoms of ethylene is changed to sp³ type from sp² type. However, other ethylenes near TiCl₃ do not show any change in their bond length and bond angle. The cyclopentadienyl ring itself also shows structural changes as ethylene approaches the Cp ring: out-of-plane distortion of the Cp ring is increased, and aromaticity is broken. If the energy minimization process is continued, an entirely different struc-
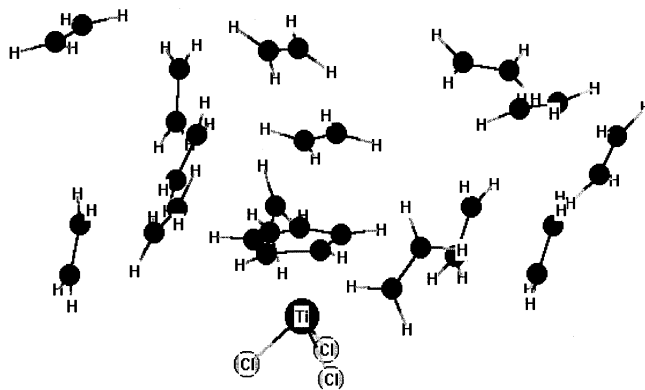
Figure 3. Starting model for energy minimization process of CpTiCl₃ + 14C₂H₄. Ethylenes are arbitrarily distributed keeping the minimum C-C distance as 3.0 Å

ture is obtained, but we generally stopped after 500-1000 iterations of the conjugate gradient geometry optimization algorithm. The intermediate configuration ontained during the optimization illustrates the possibility that polymerization can be modeled using this method. Structural changes in ethylenes are of two types. Some which are close to TiCl₃ do not show any change in their structure. Others move 1-1.5 Å toward the Cp ring, gradually show the indications of polymerization as mentioned above, and finally participate in the polymerization processes together with other ethylenes near the Cp ring. In addition, all of the ethylenes placed around the edge of Cp ring near TiCl₃ show structural changes as they move toward the Cp ring. Among the 14 ethylenes, eight ethylenes show significant out-of-plane distortion and the remaining 6 are farther away from CpTiCl₃ catalyst and show little structural distortion.

Although we did not use a cocatalyst in our calculation, many researchers[14-17] have suggested that TiCl₃ acts as an active site during the polymerization after making a complex with a cocatalyst such as MAO or AIR$_n$Cl$_{3-n}$. Our results, which do not include a cocatalyst, tell us that the TiCl₃ site is not an active site in this case; rather, the polymerization process is initiated from the cyclopentadienyl ring. In future work, we will investigate the role of the cocatalyst in the activation and the mechanism of ethylene polymerization by the activated metallocene catalyst.

Metallocenes are known to act as catalysts in polymerization and can polymerize ethylene in the absence of cocatalyst, although the activity is very low[43,44] compared to cocatalyst activated metallocene. In addition, in the absence of a cocatalyst, the product ethylene chains are short -8 to 10 ethylenes in length. The question we wish to answer is: Why doesn't the metallocene itself keep polymerizing ethylene continuously? and why is there such a big difference in the degree of polymerization between normal and cocatalyst activated metallocene? When one of the ligands in a metallocene is removed by the cocatalyst, the titanium atom develops a positive charge. This positive ion is a seed to initiate the process of polymerization. In such a case, others have suggested that the transition metal itself is an active site.[14-17,42] Catalytic activity is reduced when the charge on titanium is reduced by dispersing the charge through the ethylene chain. But in the presence of the cocatalyst, the metallocene can be active as the catalyst in the process of polymerization by being reactivated continuously by the cocatalyst. In the absence of the cocatalyst, the positive charge on the metallocene might be easier to transfer through the Cp ring to an ethylene than transferred directly from the titanium metal to the ethylene because the Cp ring is more electron rich than ethylene. The positive charge in this case may not be as strong as the charge produced by the cocatalyst. To show the ability of the Cp ring to transfer charge from Ti to ethylenes, we arranged ethylenes in chains of different lengths as shown in Figure 7 for n = 4. The charges on atomic centers were estimated using Mulliken population analysis at typical intermediate steps in the minimization. Without ethylenes (n = 0) the charge on Ti is 0.955, whereas the average charge of carbon atoms

Table 2. Atomic Charge and Electronic Energy of CpTiCl₃ + nC₂H₄

Molecular System	Atomic Charge			(LUMO, HOMO)[c]
	Ti	C₁[a]	Cp ring[b]	
CpTiCl₃	0.955	-0.045	-0.042	(0.878, -9.738)
CpTiCl₃ + C₂H₄	0.932	-0.063	-0.049	(1.000, -7.620)
CpTiCl₃ + 2C₂H₄	0.918	-0.082	-0.054	(1.128, -4.790)
CpTiCl₃ + 3C₂H₄	0.899	-0.086	-0.056	(1.393, -3.275)
CpTiCl₃ + 4C₂H₄	0.849	-0.083	-0.061	(1.495, -2.433)
CpTiCl₃ + 5C₂H₄	0.704	-0.071	-0.065	(1.504, -1.786)
CpTiCl₃ + 6C₂H₄	0.575	-0.059	-0.066	(1.464, -1.098)
CpTiCl₃ + 7C₂H₄	0.513	-0.053	-0.066	(1.483, -0.558)
CpTiCl₃ + 8C₂H₄	0.386	-0.042	-0.056	(1.568, 0.032)

atomic charges are calculated by the ZINDO method using Mulliken population analysis (implemented in HyperChem 4.5). [a]first carbon atom in Cp ring. [b]average charge of carbon atom in Cp ring. [c]eV.

in Cp ring is -0.42. If ethylenes are added, the Ti charge drops showing charge transfer to ethylene. For n = 8, the Ti charge drops to 0.386, but the average charge of carbon atoms in Cp ring has not changed appreciably. The decrease of positive charge on the titanium as determined by Mulliken population analysis is as shown in Table 2. The process of polymerization might be terminated around the seventh ethylene because the charge is reduced to one third of the original one and there is no cocatalyst to reactivate it. The positive charge on the titanium metal is steeply decreased as shown in Table 2. In the case of a complex composed of seven or eight ethylenes, the charge on titanium is reduced to half or one third of the charge with only one ethylene, even though the charges of the carbon atoms in the Cp ring are similar to the charges before ethylene is added. In other words, the positive charge of titanium is spread through the ethylenes without changing the charge of Cp ring. When more than eight ethylenes are complexed, the charge of titanium is less than one third of the charge when there is only one ethylene. This might be thought as insufficient to continue the polymerization. Furthermore, the ethylenes after the eighth show only slight structural changes in their bond length and bond angle. These structural changes are too small to indicate the polymerization process is taking place when more than eight ethylenes are added to the system. According to our calculational model without a cocatalyst, a metallocene can polymerize only about seven ethylene molecules in one chain in agreement with experimental results.[43,44]

The energy diagram of the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) of the complexes listed in Table 2 is depicted in Figure 4. The energy of the LUMO for all complexes is almost the same, but the energy of the HOMO increases, and the energy gap between the HOMO and the LUMO decreases as the number of ethylenes increases. This fact means that the complex can be easily excited and reacted to be polymerized as the degree of polymerization is increased. But even though the energy gap is small, the polymerization might not continue because the decreasing charge on the metal atom discussed previously decreases the driving force to withdraw
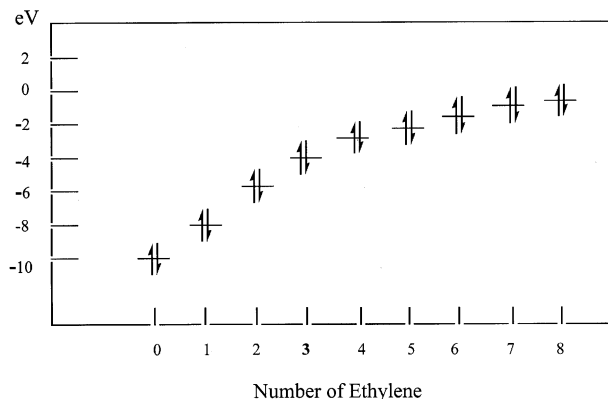
Figure 4. HOMO and LUMO energies from SCF ZINDO calculation. The occupied states are HOMO and the unoccupied states are LUMO.
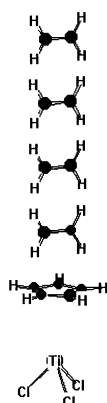

Figure 6. Starting model for energy minimization process of $CpTiCl_3$ + $4C_2H_4$. Four ethylenes are arranged parallel to Cp ring keeping the C-C distance between the ethylene carbons 3.0 Å.

Figure 5. Starting model for energy minimization process of $CpTiCl_3$ − $4C_2H_4$. Four ethylenes are arranged perpendicular to Cp ring keeping the C-C distance between ethylene carbons 3.0 Å.

Figure 7. Energy minimization process of $CpTiCl_3$ − $4C_2H_4$. Four ethylenes are arranged oblique to Cp ring keeping the C-C distance between ethylene carbons 3.0 Å. Structure a is the starting model, and b is an intermediate structure obtained during the optimization.

an electron from the HOMO. In other words, without the cocatalyst to propagate positive charge to the metal atom, the polymerization can not continue further than about 7 ethylene units.

Next, we investigate the effect of changing the direction of ethylene placement with respect to the cyclopentadienyl ring. Using the starting structure in Figure 5 where the ethylene planes are perpendicular to the Cp ring, no structural changes are observed during the optimization process. When the ethylene planes are parallel to the Cp ring as shown in Figure 6 with the C–C axis aligned with Cp reflection plane, no structural changes are observed either. However, the polymerization of ethylene is shown clearly in Figure 7b where the initial structure as shown in Figure 7a has the C–C axis of the ethylenes aligned obliquely to the C_2 axis of the Cp ring about 55°, and the projection of C–C axis of ethylene to the Cp ring is coincident with a C_2 axis of the Cp ring. Any arrangement where the oblique angle is changed more than a few degrees from 55° is unsuccessful. On the basis of these three results, we conclude that ethylene can be polymerized not only on the specific site of the $CpTiCl_3$ catalyst, but also along a specific orientation with respect to the catalyst.

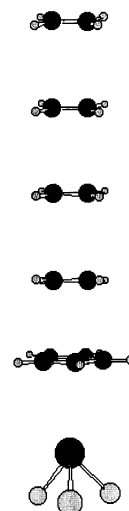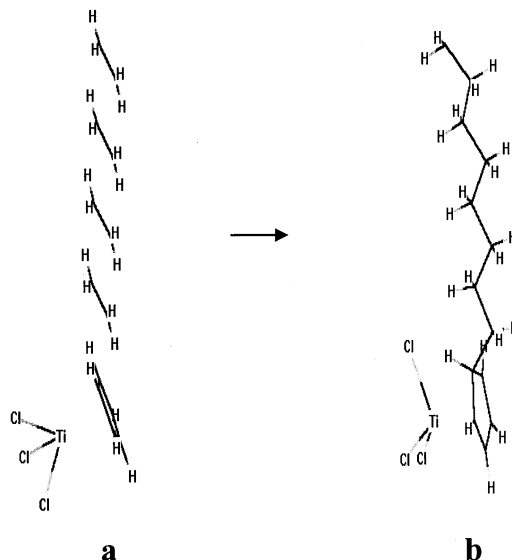Using the ideas and methods used in the above calcula-

tions, we now seek to explain whether ethylenes can be polymerized at other sites near the Cp ring. The model of 2-chain and 3-chain systems depicted in Figure 8 and 9, show that ethylenes can be polymerized at any carbon site of the Cp ring during the structure optimization. They can even be polymerized simultaneously at all five sites as long as they are aligned in the proper direction.

Processes of Polymerization under Cp_2TiCl_2 Catalyst. The polymerization activity of Cp_2TiCl_2 without cocatalyst might be very low due to the structural hindrance as discussed before. To polymerize according to the mechanism proposed by Cossee or Green, the ethylene should combine with Cp_2TiCl_2 as shown in Figure 10. In this case, the two Cp rings would need to be distorted to where they are almost
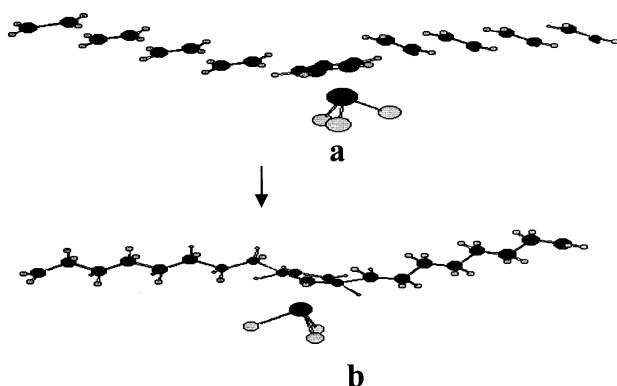
Figure 8. Energy minimization process of CpTiCl₃ + 8C₂H₄(2-chain). Eight ethylenes in two 4-membered chains are arranged oblique to Cp ring keeping the C-C distance between ethylene carbons 3.0 Å. Structure a is the starting model, and b is an intermediate structure obtained during the optimization.
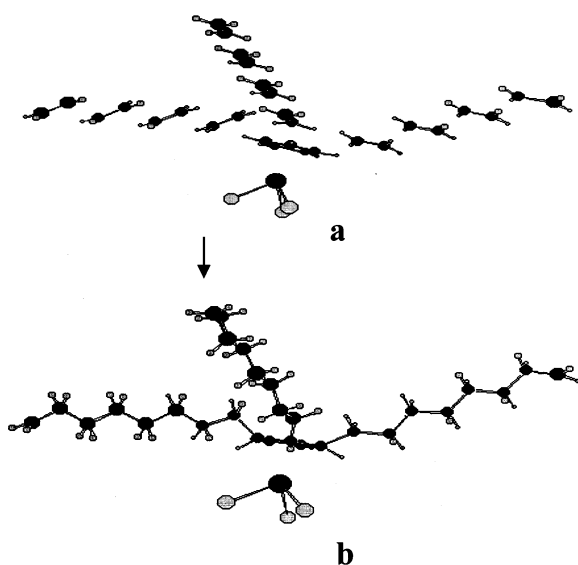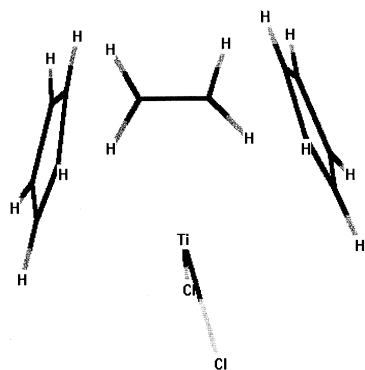
parallel to each other. This is an energetically unfavorable arrangement, and the complex's original molecular properties may be significantly altered. Hortmann and Brintzinger[45] have pointed out this steric effect for the metallocene catalysts and argued the importance of the steric effect on reactivity and stereoselectivity trends. Several researchers[46-49] have addressed the influence of varying the ring-ligand substituents. The electronic energy of the complex in Figure 10 and the complex having only one ethylene nearest to Cp ring by removing three ethylenes in Figure 11a is -7974.348 eV and -8015.807 eV, respectively. The complex shown in Figure 10 is less stable by about 41.459 eV. The HOMO and LUMO of the above complexes are -4.174 and -4.482 eV, 3.884 and -0.548 eV, respectively. These energy values include the implication that the metallocene complex in Figure 11 is more easily excited and reactive than that of Figure
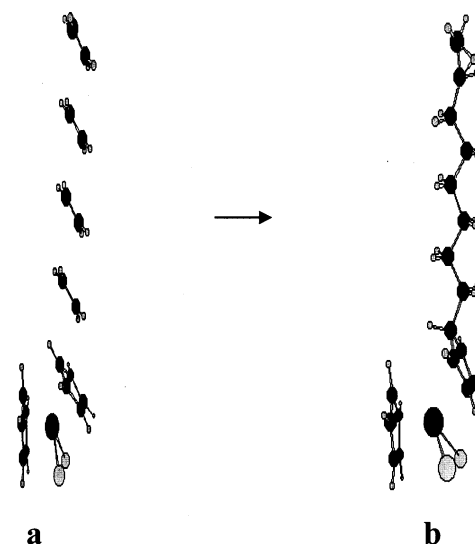

Figure 9. Energy minimization process of CpTiCl₃ + 12C₂H₄(3-chain). Twelve ethylenes in three 4-membered chains are arranged oblique to Cp ring keeping the C-C distance between ethylene carbons 3.0 Å. Structure a is the starting model, and b is an intermediate structure obtained during the optimization.

Figure 11. Energy minimization process of Cp₂TiCl₂ + 4C₂H₄. Four ethylenes are arranged oblique to Cp ring keeping the C-C distance between the ethylene carbons 3.0 Å. Structure a is the starting model, and b is an intermediate structure obtained during the optimization.

Figure 10. The molecular structure of Cp₂TiCl₂ + C₂H₄. Ethylene is directly combined with the titanium atom through a charge-transfer complex. The bond distances between titanium and two carbon atoms of ethylene are 2.15 Å and 2.15 Å.

Figure 12. Energy minimization process of Cp₂TiCl₂ + 8C₂H₄(2-chain). Eight ethylenes in two 4-membered chains are arranged oblique to Cp ring keeping the C-C distance between ethylene carbons 3.0 Å. Structure a is the starting model, and b is an intermediate structure obtained during the optimization.
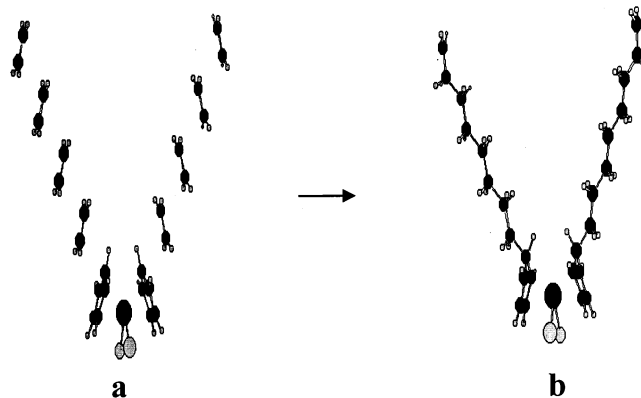
10, but that type of complex in Figure 10 is also plausible if unsaturated "cation-like" active centers are formed by the cocatalyst.[50-53]

Using the ideas and methods applied to the polymerization with the $CpTiCl_3$ catalyst of the previous section, typical computational results for polymerization processes of Cp_2TiCl_2 + $4C_2H_4$ (1-chain) and Cp_2TiCl_2 – $8C_2H_4$ (2-chain) are depicted in Figure 11 and 12.

From our results, we propose another ethylene polymerization mechanism under the titanocene catalyst, which is a different polymerization mechanism than those suggested by Cossee and Arlman[18-20] or Green and Rooney.[21,22] This mechanism can explain the ethylene polymerization process well and also explain the activity of polymerization.

Polymerization Mechanism using $C_{10}H_{15}TiCl_3$ and $C_{18}H_{14}TiCl_2$ Catalysts. Using the same ideas and procedures applied to the previous cases, we now try to show how ethylenes can be polymerized even though the catalyst has bulky ligands such as pentamethylcyclopentadienyl titanium trichloride ($C_{10}H_{15}TiCl_3$) and cyclopentadienylfluorenyl titanium dichloride ($C_{18}H_{14}TiCl_2$). The initial structure of $C_{10}H_{15}$-$TiCl_3$ and $C_{18}H_{14}TiCl_2$ in Figure 13 and 14, respectively, are the optimized structure, and their structural data obtained by ZINDO optimization are represented in Table 3. The fluorenyl ring in the optimized structure of $C_{18}H_{14}TiCl_2$ is inclined slightly backward while still maintaining aromaticity. Ethylenes arranged stereospecifically as in Figure 15a and 16a are polymerized as shown in Figure 15b and 16b. Due to the
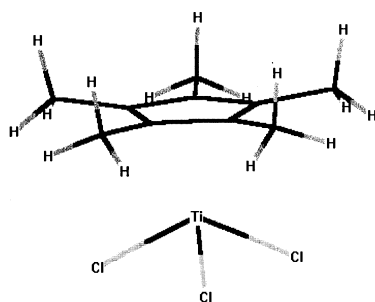
Table 3. Structural Data of $C_{10}H_{15}TiCl_3$ and $C_{18}H_{14}TiCl_2$

	$C_{10}H_{15}TiCl_3$	$C_{18}H_{14}TiCl_2$
Bond distance (Å)		
Ti-Cl1	2.37	2.47
Ti-Cl2	2.37	2.45
Ti-Cl3	2.37	
C-C(in Cp ring)[a]	1.45	
C(in Cp ring)-C(in CH₃)[a]	1.40	
C-C of benzyl ring(in fluorene)[a]		{ 1.41 ; 1.41
C-C of Cp ring(in fluorene)[a]		1.43
Bond angle(°)		
Cl-Ti-Cl[a]	101.03	
C-C-C(in Cp ring)[a]	107.89	93.55
Cp-Ti-Cp		
C(in CH₃)-C-C[a]	125.95	
C-C-C of benzyl ring(in fluorene)[a]		{ 119.92 ; 120.00
C-C-C(in Cp ring)[a]		108.00

[a] average values. Values are obtained by ZINDO optimization.

side chains of the ring in Figure 15 and the size of ring in Figure 16, ethylenes must be oriented more stereospecifically than in $CpTiCl_3$ and Cp_2TiCl_2, in agreement with the priciples discussed by Hortmann and Brintzinger.[15] Namely, the steric hindrance caused by the methyl groups and fluorenyl ring of $C_{10}H_{15}TiCl_3$ and $C_{18}H_{14}TiCl_2$ catalysts can make the ethylene polymerize only in a stereospecific direction and at a specified position as shown in Figure 15a and Figure 16a. The projection of the C–C axis onto the Cp ring is coincident with a C_2 axis of the Cp ring as shown in Figure 15a, and ethylenes are aligned obliquely upward from the Cp ring so that the methyl groups attached to the Cp ring do not hinder the ethylene. Ethylenes which satisfy the above conditions can be polymerized as illustrated in the cases $CpTiCl_3$ or Cp_2TiCl_2. Furthermore, one polymer chain restricts the propagation of other chains because of steric hindrance. In

Figure 13. Molecular structure of $C_{10}H_{15}TiCl_3$ as determined by ZINDO geometry optimization.
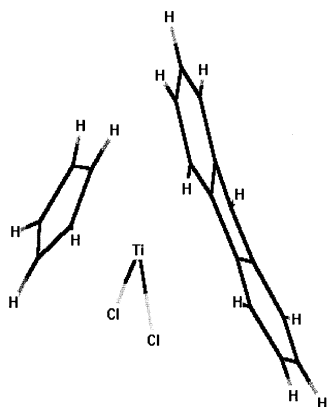
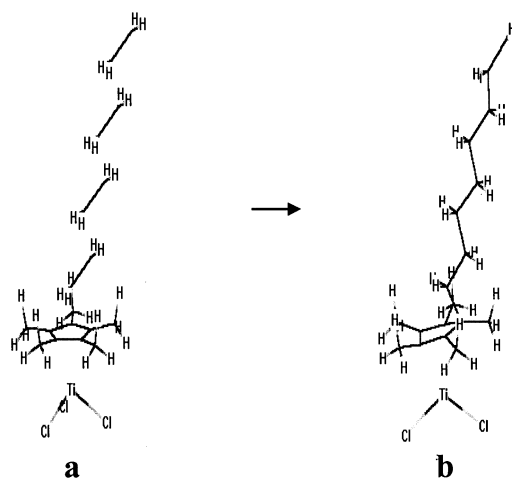**Figure 14.** Molecular structure of $C_{18}H_{14}TiCl_2$ as determined by ZINDO geometry optimization

a   b

Figure 15. Energy minimization process of $C_{10}H_{15}TiCl_3$ + $4C_2H_4$. Four ethylenes are arranged in a linear chain obliquely and inclined in relation to Cp ring keeping the C-C distance between ethylene carbons 3.0 Å. Structure a is the starting model, and b is an intermediate structure obtained during the optimization.

a   **b**

Figure 16. Energy minimization process of $C_{18}H_{14}TiCl_2 + 4C_2H_4$. Four ethylenes are arranged in a linear chain obliquely and inclined in relation to fluorenyl ring keeping the C-C distance between ethylene carbons 3.0 Å. Structure a is the starting model, and b is an intermediate structure obtained during the optimization.
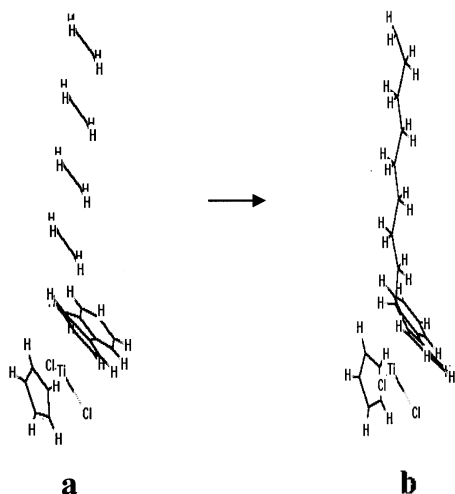
the case of $C_{10}H_{15}TiCl_3$ catalyst, a maximum of two chains can be polymerized due to the steric hindrance between methyl groups of the Cp ring, or between ethylenes of one chain and ethylenes of another chain. Three polymeric chains are possible on the fluorenyl ring due to the steric hindrance between ethylene chains in the $C_{18}H_{14}TiCl_2$ catalytic complex.

The trends and the mechanism of polymerization under these two catalysts as shown in Figure 15 and Figure 16 are similar to the results using of $CpTiCl_3$ and Cp_2TiCl_2 catalysts as shown in Figure 7 and Figure 11.

Conclusion

We have demonstrated a new polymerization mechanism by calculating various types of polymerizing processes where metallocene catalysts such as $C_5H_5TiCl_3$, $C_{10}H_{10}TiCl_2$, $C_{10}H_{15}$-$TiCl_3$, and $C_{18}H_{14}TiCl_2$ react with ethylene in the absence of a cocatalyst, even though it is one of the possibilities. Using this mechanism, the degree of polymerization is limited about seven or eight in our model calculations, and the active site for polymerization is not the transition metal but the Cp ring. In particular, ethylene can be polymerized only when the ethylenes are arranged in particular orientation with respect to the Cp ring.

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