ARTICLE

Polymerization Mechanism of α-Linear Olefin

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The density functional theory on the level of B3LYP/6-31G was empolyed to study the chain growth mechanism in polymerization process of α-linear olefin in $TiCl_3$/$AlEt_2Cl$ catalytic system to synthesize drag reduction agent. Full parameter optimization without symmetry restrictions for reactants, products, the possible transition states, and intermediates was calculated. Vibration frequency was analyzed for all of stagnation points on the potential energy surface at the same theoretical level. The internal reaction coordinate was calculated from the transition states to reactants and products respectively. The results showed as floes: (i) Coordination compounds were formed on the optimum configuration of $TiCl_3$/$AlEt_2Cl$. (ii) The transition states were formed. The energy difference between transition states and the coordination compounds was 40.687 kJ/mol. (iii) Double bond opened and Ti−C(4) bond fractured, and the polymerization was completed. The calculation results also showed that the chain growth mechanism did not essentially change with the increase of carbon atom number of α-linear olefin. From the relationship between polymerization activation energy and carbon atom number of the α-linear olefin, it can be seen that the α-linear olefin monomers with $6-10$ carbon atoms had low activation energy and wide range. It was optimum to synthesize drag reduction agent by polymerization.

Key words: Density functional theory, Polymerization mechanism, α-Linear olefin, Drag reduction agent, Ziegler-Natta catalyst

I. INTRODUCTION

Pipelines were one of major forms of transportation in the world. At present, almost all of oil and natural gas produced in the world were transported by pipelines. According to incomplete statistics, there were about 93% of crude and oil products transported by pipelines [1−3]. There were a lot of advantages for pipeline transportation, including fast construction, low cost, and few limitations by geography and weather conditions, *etc*. However, the pipeline transportation also had some shortcomings. The elastic transportation volume of the pipelines was lower than the other transportation systems. Because it was difficult to exactly predict the oil reserves during oil exploration and the foreground of oil fields also had some indeterminate factors. Even if reserves could be accurately estimated, oil fields also had their own development period, high production period and decline period. The requirements of the oil and its products would also be changed because of the economic development. So, the elastic pipeline throughput was deeply demanded. And there was a very obvious phenomenon that the pipelines aged after long-time used. So, the pipelines would be broken at the original design-

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ing transmission pressure. It was the hidden danger for the security of the pipeline network.

The best way to solve these problems was using drag reduction agent (DRA). DRA was the chemical additive to reduce liquid flow friction and to increase flow rate [4−19]. DRA used in crude oil and other correlative products was named oil DRA. The most important requirement for the oil DRA was soluble in the oil. In addition, the oil DRA required high molecular weight (M>10^6 g/mol), shear degradation resistance, and heat, light, chemical, and biological degradation resistant.

The oil DRA mainly had the following several functions. It could reduce the operating pressure of pipelines and improve the running safety coefficient. The oil throughput was improved under the original pipeline operating conditions, so the operating cost was saved. For the above reasons, study on synthesis and properties of oil DRA with α-linear olefin had become the hotspot since 1980s [20−31].

At present, most of the studies were merely on the basis of past research experience to study on the synthesis and properties of DRA. In this work, the polymerization mechanism of the α-linear olefin was deeply investigated on the atom and molecular level in order to get the valuable references to DRA industrial production.

II. DENSITY FUNCTIONAL CALCULATIONS

The monometallic mechanism for Ziegler-Natta olefin polymerization was proposed by Cossee in 1960 [32, 33]. It was believed that α-linear olefin polymerization may be considered as chain growth mechanism [34, 35]. The proposal has been generally accepted [36−38].

The active center in Ziegler-Natta catalyst was the metal-carbon bond of the transition metal complex, which was formed by the interaction between the main catalyst and cocatalyst of the catalytical system. It can be seen from Fig.1 that a vacant coordination site was generated initially, followed by olefin complexation. The migration of the polymer chain occured and the metal-carbon bond was formed through a four-center transition state. The vacant coordination site was recreated at the site originally occupied by the polymer chain and the process continued. The growing polymer chain terminus flips from site to site.

So, the full parameter optimization without symmetry restrictions for reactants, products, the possible transition states and intermediates was calculated on the level of B3LYP/6-31G by the density functional theory in this work. Vibration frequency was analyzed for all of stagnation points on the potential energy surface at the same theoretical level. The internal reaction coordinate (IRC) was calculated from the transition states to reactants and products respectively. All calculations were completed by Gaussian 03 package on the shenteng server.

III. RESULTS AND DISCUSSION

A. Configuration of TiCl$_3$/AlEt$_2$Cl catalyst

Ziegler-Natta catalytic system had developed to the fifth generation product at present. It was universally accepted that the second-generation, TiCl$_3$/AlEt$_2$Cl, was suitable for the polymerization of olefin [39, 40]. In this work, the polymerization mechanism of the α-linear olefin in TiCl$_3$/AlEt$_2$Cl catalytic system was discussed using the density functional theory in order to get the valuable references to synthesis of DRA. The polymer-
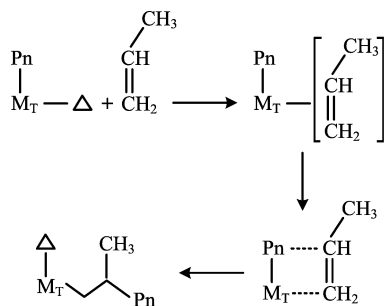
ization mechanism of α-linear olefin can be attributed to the chain growth mechanism. So, it was assumed that the catalyst contained one methyl, and this methyl was the growth chain. How the methyl moved to the α-linear olefin and achieved the chain growth was deeply studied.

Given TiCl$_3$/AlEt$_2$Cl combined one methyl, the catalyst containing growth chain was optimized. Figure 2 (a) and (b) give the two similar energy structures and their energy difference was only 2.969 kJ/mol. Consequently, the two structures could appear in the reaction.

B. The coordination compound formed on the optimization configuration of catalyst

Propylene was representative of the α-linear olefins, it was selected as the example to study the polymer-
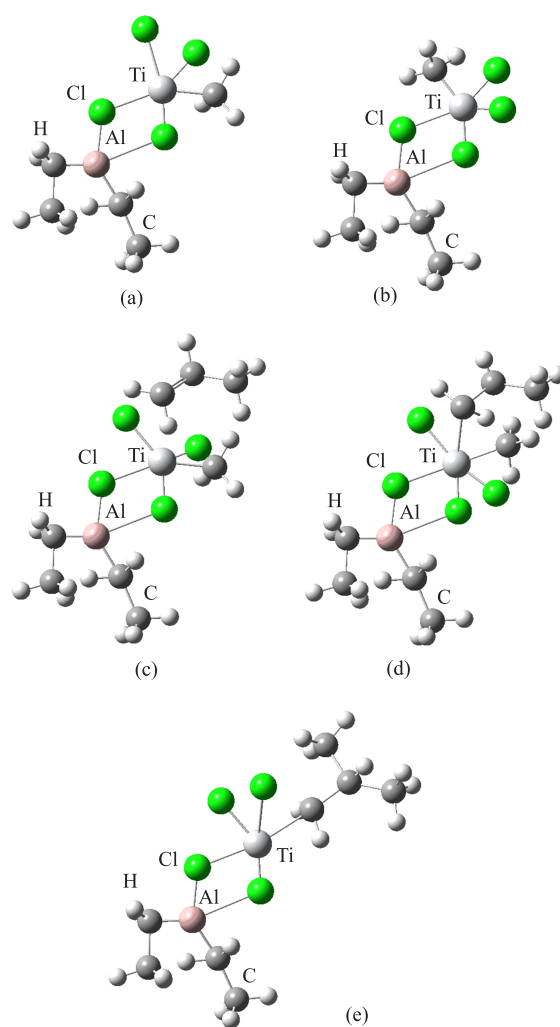

FIG. 2 Optimized structures of TiCH$_3$Cl$_3$/Al(Et)$_2$Cl ((a), (b)), coordination compound (c), transient state (d), and complex compound with new growing long chain (e) obtained by density functional theory calculations.

FIG. 1 Cossee mechanism for Ziegler-Natta olefin polymerization. M$_T$: transition metal, Pn: polymer chain, $\triangle$: vacant coordination site.

TABLE I The contrast of the structural parameters between coordination compound and transient state.

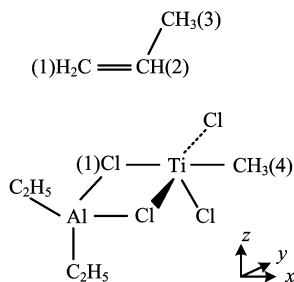| State	Bond length/Å				Angle/(°)	
	C(1)−Ti	C(1)−C(2)	Ti−C(4)	C(2)−C(4)	∠C(3)−C(2)−C(1)−Ti	∠Cl−Ti−Cl
Coordination compound	2.901	1.348	2.059		−102.27	
Transient state	2.185	1.417	2.193	2.152	−116.16	191.83
Product	2.036	1.534		1.535		101.96

FIG. 3 The election of the atom labels and the coordinates.
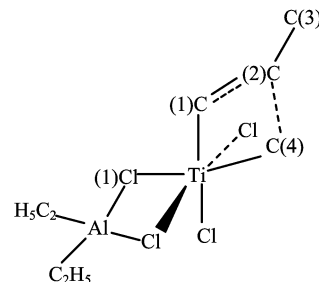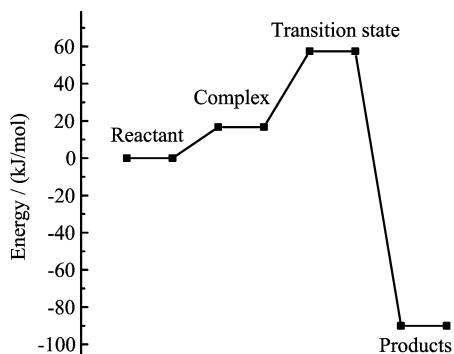

FIG. 5 The reacting trend of IRC computation.

FIG. 4 Schematic of the energy of transition states.

tor corresponds to the opening of double bond, rupture of Ti−C(4) bond, and generation of C(2)−C(4) bond. Structural change between transient state and coordination compound was given in Table I. It can be seen from Fig.4 that the activation energy of the polymerization was the energy of transition states.

D. The chain growth process and the configuration with new growing long chain

The IRC computation was made from the transition state, and the reacting trend can be obtained after 200 steps calculations. The reacting trend of IRC computation was shown in Fig.5.

The process of chain growth was actually a migration process of the long growing chain ($-CH_3$). And during this migration from Ti to C(2), changes of system configuration have also taken place. Under the strong effect between C(2) and C(4), Ti−C(4) bond ruptured and C(2)−C(4) bond gradually came into being. The length of C(1)−C(2) double bond has been elongated in the formation of the C(2)−C(4) bond and Ti−C(1) bond. That was to say, Ti−C(1) bond was generated during C(4) migration to C(2). At the same time, the growing long chain, $-CH_3$, changed into $-CH_2CH(CH_3)_2$. Obviously, the number of carbon atoms in growing long chain increased. The configuration of coordination compound with new growing long chain was shown in Fig.2(d). Due to the effect of the carbon number in growing long chain, the energy was lower than that of transient state by 137.370 kJ/mol, the distance between catalyst center Ti and co-catalyst center Al was elongated from 3.562 Å to 3.585 Å. The structural parameters of coordination compound in transient state and chain growth state were given in Table I and II.

ization mechanism. The configuration and structural parameters of the coordination compound composed of propylene and configuration (Fig.2(a)) were calculated. It can be seen from Fig.3 that the atom labels and the coordinates were established. In the process of propylene closing to Ti atom, the energy of this system was improved gradually. After surpassing a small barrier energy, the stable coordination compound was formed. Figure 2(c) give the configuration of the coordination compound. The distance of Ti−C(1) was 2.901 Å.

C. Calculated results and discussion of transition state

C(1) further closed to Ti atom, and when the distance was 2.185 Å, transient state can be gained. Figure 2(d) showed the configuration of the transient state.

The energy difference between transient state and coordination compound was 40.687 kJ/mol. The unique virtual vibration frequency of transition state was 305.29i cm^{-1}. The virtual vibration mode of eigenvec-

TABLE II The change of Mulliken charges in the polymerization reaction.

State	Ti	C(1)	C(2)	C(4)
Monomer		−0.374	−0.164	
Coordination compound	0.555	−0.396	−0.059	−0.696
Transient state	0.413	−0.467	−0.060	−0.640
Product	0.638	−0.533	−0.068	−0.455

TABLE III The change of Mulliken charges from the coordination compounds to the transient states with different α-linear olefin.

α-Linear olefin	Ti	C(1)	C(2)	C(4)
Ethylene	−0.152	0.125	−0.064	−0.068
Propylene	−0.142	0.071	0.001	−0.056
1-butylene	−0.138	0.077	0.003	0.053
1-pentene	−0.138	0.075	−0.001	0.054
1-hexene	−0.139	0.078	0.002	0.053
1-heptene	−0.138	0.077	0.003	0.054
1-octene	−0.137	0.079	0.003	0.053
1-nonene	−0.138	0.076	0.001	0.054
1-decene	−0.138	0.075	0.002	0.053
1-undecene	−0.139	0.078	−0.001	0.054
1-dodecene	−0.138	0.078	−0.001	0.054
1-tridecene	−0.137	0.077	0.002	0.054
1-tetradecene	−0.138	0.075	0.001	0.053
1-pentadecene	−0.138	0.075	0.001	0.054
1-hexadecene	−0.138	0.076	0.002	0.054

E. The effect of the carbon atom numbers of α-linear olefin on polymerization

The carbon number of α-linear olefin widely used in industrial production was from 2 to 22. Taken the representative α-linear olefin, propylene, as starting point of calculation, the chain growth reaction of α-linear olefin was calculated. The results suggest that chain growing mechanism has not changed with the increase of carbon atom numbers in α-linear olefin. The calculation results of α-linear olefin with different carbon atom numbers were shown in Table III, IV, and V.

In the reaction of propylene, the energy of coordination compound, transient state and product relative to monomer was 16.694, 57.381, and −90.059 kJ/mol respectively, and the virtual vibration frequency of transient state was 305.29i cm^{-1}. The relationship between activation energy and carbon number of α-linear olefin can be gained from the changes of energy and virtual vibration frequency in the reaction. Figure 6 gave the relationship between activation energy and the carbon atom numbers of α-olefin.

From Fig.6, it can be known that with the change of α-linear olefin carbon atom number, the activation energy increased at first, then decreased, and then increased again. Ethylene had the lowest activation en-
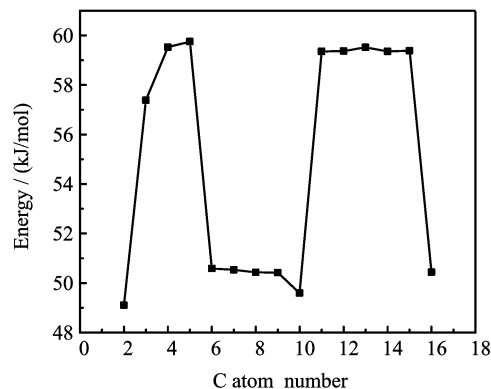
FIG. 6 The relation between activation energy and the carbon atom number of α-olefin.

ergy, so it was optimum selection to synthesis DRA in TiCl$_3$/AlEt$_2$Cl catalytic system. But it was well-known that polyethylene was very difficult to dissolve in oil. The most important requirement for the oil DRA was soluble in the oil. It was expensive and not easy to get when the carbon atom number of α-olefin was above 16. So it was not suitable for the industrial production. As for the industrial production, the α-linear olefin monomers with 6−10 carbon atoms was the first choice to synthesize the DRA because it had a relative fluctuation range and low activation energy.

IV. CONCLUSION

The chain growth mechanism of polymerization process using α-linear olefin in TiCl$_3$/AlEt$_2$Cl catalytic system to synthesis drag reduction agent (DRA) was studied using the density functional theory on the level of B3LYP/6-31G. The calculation results showed as follows. Firstly, coordination compounds was formed on the optimum configuration of the catalyst. Secondly, the transition state was formed, the energy difference between transition state and the coordination compounds was 40.687 kJ/mol. Finally, double bond opened and Ti−C(4) fractured, as a result, the polymerization was completed.

Beginning of propylene which was the simple α-linear olefin, the chain growth reactions of series α-linear olefin were studied systematically. The calculating results preliminarily indicated that chain growth mechanism did not essentially change with the increase of carbon atom number of α-linear olefin. It also can be known that the α-linear olefin monomers with 6−10 carbon atoms was the first choice to synthesize the DRA. It was a very important reference for the production.

V. ACKNOWLEDGMENTS

TABLE IV The bond length (in Å) of coordination compounds with different α-linear olefin.

α-Linear olefin	Bond length of coordination compounds/Å				Bond length of transient states/Å				
	Ti−C(1)	C(1)−C(2)	C(4)−C(2)	Ti−C(4)	Ti−C(1)	C(1)−C(2)	C(4)−C(2)	Ti−C(4)	Ti−H
Ethylene	3.010	1.342	3.642	2.056	2.245	1.397	2.183	2.175	2.057
Propylene	2.901	1.348	3.700	2.059	2.185	1.417	2.152	2.193	2.055
1-butylene	2.899	1.348	3.690	2.059	2.179	1.417	2.167	2.188	2.055
1-pentene	2.885	1.348	3.677	2.059	2.177	1.418	2.165	2.189	2.054
1-hexene	2.878	1.348	3.668	2.059	2.177	1.418	2.164	2.189	2.055
1-heptene	2.872	1.348	3.663	2.059	2.177	1.418	2.164	2.189	2.055
1-octene	2.875	1.348	3.665	2.058	2.178	1.417	2.166	2.188	2.055
1-nonene	2.870	1.348	3.652	2.059	2.177	1.418	2.162	2.189	2.054
1-decene	2.869	1.348	3.648	2.059	2.178	1.417	2.165	2.188	2.055
1-undecene	2.867	1.348	3.646	2.059	2.177	1.417	2.164	2.189	2.055
1-dodecene	2.866	1.349	3.643	2.059	2.178	1.417	2.164	2.188	2.055
1-tridecene	2.866	1.348	3.645	2.059	2.179	1.418	2.163	2.189	2.055
1-tetradecene	2.865	1.348	3.641	2.059	2.178	1.418	2.162	2.187	2.055
1-pentadecene	2.872	1.348	3.658	2.059	2.177	1.417	2.164	2.189	2.055
1-hexadecene	2.871	1.348	3.659	2.059	2.178	1.417	2.163	2.188	2.055

TABLE V The change of energy (relative to monomer) and virtual vibration frequency of transition states in the reacting process with different α-linear olefin.

α-Linear olefin	Change of energy/(kJ/mol)			Frequency/cm^{-1}
	Coordination compounds	Transient states	Products	
Ethylene	21.504	49.105	−101.050	275.38
Propylene	16.694	57.381	−90.059	305.29
1-butylene	16.452	59.527	−75.845	303.02
1-pentene	16.176	59.748	−86.869	302.73
1-hexene	7.034	50.590	−95.864	302.30
1-heptene	7.130	50.535	−95.939	304.37
1-octene	7.034	50.431	−95.843	301.49
1-nonene	6.971	50.422	−95.810	301.48
1-decene	6.164	49.594	−96.592	300.39
1-undecene	15.829	59.355	−86.969	303.17
1-dodecene	15.800	59.368	−86.990	303.42
1-tridecene	15.846	59.514	−86.806	303.59
1-tetradecene	15.821	59.355	−86.940	307.61
1-pentadecene	15.896	59.384	−86.802	304.09
1-hexadecene	7.009	50.439	−95.969	303.82

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