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The Study on the Oligomerization of 1-Decene with Metallocene Catalysts

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Abstract: The oligomerizations of 1-decene have been carried out with zirconocene catalysts ($(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$, **A**; $[\mu, \mu\text{-}(\text{Me}_2\text{Si})_2(\eta^5\text{-C}_5\text{H}_3)_2][(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2]_2$, **B**; $[(\text{C}_6\text{H}_5)\text{C}(\text{Me})_2(\eta^5\text{-C}_5\text{H}_4)]_2\text{ZrCl}_2$, **C**; $t\text{BuNC}(\text{Me})_2(\eta^5\text{-C}_5\text{H}_4)\text{ZrCl}_2$, **D**; $(\eta^5\text{-C}_5\text{H}_4)\text{C}(\text{C}_5\text{H}_{10})(\eta^5\text{-C}_{13}\text{H}_8)\text{ZrCl}_2$, **E**; $(\eta^5\text{-C}_5\text{H}_4)\text{C}(\text{Me})_2(\eta^5\text{-C}_{13}\text{H}_8)\text{ZrCl}_2$, **F**; $(\eta^5\text{-C}_5\text{H}_4)\text{C}(\text{C}_6\text{H}_5)_2(\eta^5\text{-C}_{13}\text{H}_8)\text{ZrCl}_2$, **G**) in combination with MAO and the effects of the dosage of complex **F**, reaction temperature and Al/Zr ratio on oligomerization and properties of oligomers were also investigated. It was found that the structure of ligands with different steric effects and electronic effects affected the catalytic behavior greatly, and determined the oligomer's component and microstructure. Among them, Cp_2ZrCl_2 , silicon bridged binuclear zirconocene complex **B** and sterically hindered complex **C** mainly produced low viscosity oligomers (100 °C Kv: 2 ~ 3 cSt, dimer content about 60%); As expected, constrained geometry configuration zirconocene complex **D** with more open coordination space displayed higher catalytic activity and the kinetics viscosity of oligomer was higher than that of Cp_2ZrCl_2 (100 °C Kv about 3 ~ 4 cSt); It was interested to find that Cs symmetrical zirconocene complexes **E**, **F**, **G** showed higher activity and primarily produced medium-high viscosity oligomers (100 °C Kv > 20 cSt), which was attributed to the special structure of the zirconocene catalysts and different polymerization mechanism. The GC-MS results demonstrated that the oligomer mixture was less isomerization and composed of dimer to pentamer. The optimum reaction conditions involved a dosage of complex **F** 10 μmol , a reaction temperature of 80 °C, and an Al/Zr ratio of 300 : 1.

Key words: metallocene; 1-decene, oligomerization; structure-property relations; properties and characterization

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Poly- α -olefin synthetic oil (PAO) was the desirable synthetic lubricant base oil because it had good flow properties at low temperatures, relatively high thermal and oxidative stability compared with mineral oil, it also showed low evaporation losses at high temperatures, improved viscosity index and low pour point. At present, the synthesis of PAO was mainly catalyzed by Lewis acid catalysts (boron trifluoride and aluminum chloride)^[1]. However a major problem as-

sociated with the process was that the oligomer catalyzed by Lewis acid catalysts had wide molecular weight distributions containing multiple components, and the oligomer mixtures were difficult to separate; Another problem was that the isomerization of α -olefin couldn't be controlled leading to inappropriate lubricant base oil.

Metallocene catalysts exhibited high catalytic activity with regard to α -olefin oligomerization. Because

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of the single-active site and coordination insertion mechanism, the skeletal isomerization of α -olefin could be avoided, therefore it had narrow molecular weight distribution. Further more, polymer structure could be controlled and polymer molecule could be tailored during the oligomerization process^[2]. Thus, the application of metallocene catalysts for lubricant base oil has caused extensive attention. The unbridged metallocene catalysts (η^5 -RC₅H₄)₂MX₂ (M = Zr, Ti, Hf; X = Cl, Me; R = H, Me, *i*Pr, *n*Bu, *t*Bu)^[3-5] mainly produced low-viscosity PAOs with dimers fraction contents larger than 50%, the isolated dimer and 1-decene were further oligomerized in the subsequent step using cationic catalysts for useful lubricant base stock. Kissin et al.^[6] investigated the use of Cp₂ZrCl₂ or BuCp₂ZrCl₂ in conjunction with methylaluminoxane (MAO) as a highly active catalyst for 1-hexene, 4-methyl-1-pentene and 1-decene polymerization, in which the dimers or trimers could be further polymerized through supported AlCl₃/γ-Al₂O₃ catalyst to obtain single-component and multi-component synthetic lubricating base oils. In 2002, Dimaio et al.^[7] has obtained HVI-PAOs using complex **G**, Ph₂C(3-*n*BuCp-9-Flu)ZrCl₂, Ph₂Si(Cp-9-Flu)ZrCl₂ et al in combination with MAO as catalysts, and investigated the effects of polymerization temperature, MAO concentration and hydrogen concentration on the properties of oligomer. High-viscosity PAO have also been prepared in US patent 7 667 064^[8]. Park et al.^[9] disclosed a new ansa-zirconocene catalyst exhibiting high activities and the oligomer distribution was appropriate for the application of lubricant base stocks. It was well known that the development of metallocene catalytic systems for PAOs has attracted more and more interests^[10-12], however, the relationship between the structure of metallocene catalysts and their catalytic activity and oligomer composition were still unclear. In this paper, the metallocene catalysts with different structures were used for 1-decene oligomerization and the influence of metallocene structure on their catalytic activity and oligomer properties were investigated as well, and the optimal polymerization conditions of preparing narrow-distributed oligomers were obtained.

1 Experimental

1.1 Materials

Toluene (analytically pure) was supplied by ShanghaiLing Feng Chemical CO., LTD., and was distilled over sodium for 48 h prior to use; 1-decene (95.8%) was purchased from Tianjin Haina International Trading CO., LTD., dried over sodium hydride, and subsequently distilled prior to use; Cp₂ZrCl₂ was purchased from Meryer Chemical Technology Co., Ltd. MAO (Methylaluminoxane 10% toluene solution) was obtained from Azo. CO., LTD.; Zirconocene catalysts were prepared by our research group.

1.2 Oligomerization of 1-decene

The oligomerization reaction was performed in a 250 mL glass reactor. After evacuation and flushing with Ar (three times), then 1-decene was injected into the reactor. The reactor temperature was increased to certain temperature and maintained for one hour, MAO and zirconocene catalysts dissolved in toluene were injected sequentially into the reactor, the oligomerization reactions were carried out for 3 h. The reaction was quenched with ethanol and was stirring for one hour, toluene and unreacted monomers were removed from the mixture by distillation in vacuum, then the conversion of 1-decene and the catalytic activity were calculated respectively.

1.3 Oligomer Product Characterization

The kinematic viscosity (Kv, cSt) of the oligomers at 40 °C and 100 °C was measured in centistokes with a calibrated glass capillary viscometer according to the ASTM D445-06 method. VI values were calculated according to the ASTM D 2270 method.

Gas Chromatography-Mass Spectrometry (GC-MS) was carried out with HP-689-5973 MSD, which was Agilent 7890A GC/5975C MSD with a fused silica capillary column HP-5MS (30 m × 250 μm × 0.25 μm), Nitrogen was used as a carrier gas at a rate of 2 mL/min and with a split ratio of 100 : 1. The injection temperature was 200 °C, and increased to 450 °C at a rate of 10 °C per minute.

¹H NMR and ¹³C-NMR analysis of the oligomers

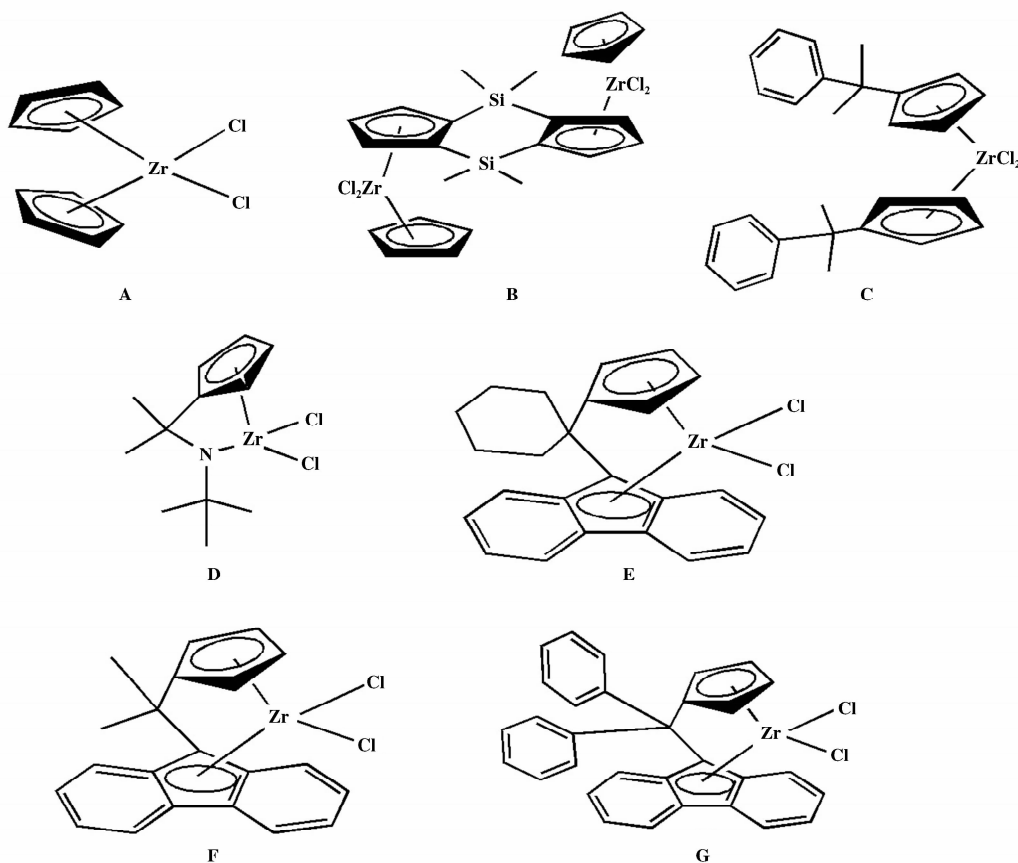
(mass fraction: 15% in CDCl_3) was carried out at 400 MHz and 100.4 MHz respectively on a Bruker AVANCE-400 NMR spectrometer (made in Bruker), it was carried out at room temperature with typical experimental parameters for acquiring quantitative spectra of polyolefins. The pulse angle was 90° , and the pulse delay was 15 s.

2 Results and Discussion

2.1 Oligomerization of 1-decene Catalyzed by Zirconocene/MAO

According to the structure of the ligand, metallo-

cene catalysts can be divided into unbridged metallocene, bridged metallocene and constrained geometry configuration metallocene (CGC)^[13]. In this paper, in order to investigate catalytic activity and oligomer microstructure, zirconocene complexes with different structures ligands were prepared: silicon bridged binuclear zirconocene complex **B**, unbridged zirconocene complex **C** with large steric hindrance, constrained geometry configuration zirconocene complex **D**, Cs symmetrical ansa-metallocene complexes **E**, **F** and **G** (shown in Scheme 1).



Scheme 1 Zirconocene complexes used for 1-decene polymerization

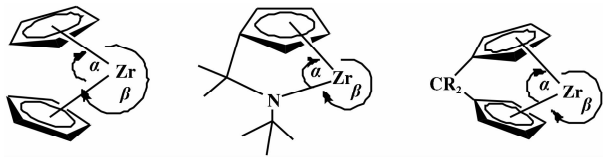
The oligomerization reaction of 1-decene (50 mL) was performed in flash reactor with zirconocene complexes ($8.55 \mu\text{mol}$) in combination with MAO at 100°C for 3 hours, the oligomers was obtained after removing 1-decene from the mixture by distillation in vacuum, the results of oligomers' property and oligomer distribution were shown in Table 1.

It can be seen from Table 1 that zirconocene catalysts all showed superior catalytic activity except complex **B**, **C**, the significant difference of catalytic activity indicated that the ligand structure of zirconocene complexes affected the catalytic properties markedly. $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ showed high activity ($1.2 \times 10^6 \text{ g} \cdot \text{mol Zr}^{-1} \cdot \text{h}^{-1}$). The high activity was due to that two Cp

Table 1 Results of 1-decene Oligomerization Catalyzed by zirconocene Complexes/MAO

Catalyst	Conversion /%	Activity ^a	40 °C Kv/cSt	100 °C Kv/cSt	VI	Oligomer Distribution(wt%)			
						2-mer	3-mer	4-mer	5-mer
A	81.0	11.7	6.32	2.23	195	72.00	21.20	6.50	0.30
B	8.5	1.2	6.84	2.34	186	58.63	27.85	9.56	3.97
C	13.0	1.9	11.25	3.29	178	52.39	32.30	13.22	2.11
D	84.3	12.2	9.29	3.13	237	50.06	33.09	12.29	4.30
E	76.5	11.2	96.79	21.63	252	21.91	33.98	38.94	5.17
F	71.4	10.3	111.14	24.14	250	22.99	32.76	39.20	5.05
G	91.0	13.1	2516.3	239.08	233	7.58	14.37	33.59	44.46

Oligomerization conditions: 1-decene(50 mL), zirconocene complex: 8.55 μmol, Al : Zr = 300 : 1, 100 °C, 3 h;
a. Activity in units of ×10⁵ g · mol Zr⁻¹ · h⁻¹.



Scheme 2 Structure of the bridge in zirconocene complexes

rings could rotate freely, so the steric hindrance was relatively small, which benefited the insertion and coordination of 1-decene. The Si-bridged binuclear zirconocene complex **B**, which was synthesized corresponding to literature^[14], could be seen as a combination of the two Cp₂ZrCl₂ molecules through rigid bridge Me₂Si-, in which Si-bridged Cp₂ZrCl₂ in conjunction with one Cp ring could be seen as a bulky substituent group, which gave the complex **B** relatively limited degree of freedom, so complex **B** had high inserting steric hindrance for olefin monomer, therefore the monomer could only insert from one side of complex **B** and led to the lowest value (1.2×10⁵ g · mol Zr⁻¹ · h⁻¹). Other Si-bridged binuclear zirconocene complex with longer bridge, which were prepared by Wang^[15], showed high activities toward ethylene polymerization, therefore it was considered to be used as catalysts for 1-decene polymerization too. As for complex **C**, which was synthesized corresponding to literature^[16], it contained bulky substituent group so that Cp rings could only make a relative limited rotation, and the steric effects of the bulky ligand was so strong to prevail over any electronic benefits, as a result, the bulky substituent group phC(CH₃)₂ seriously hindered 1-decene from

coordinating to active center, as excepted, its catalytic activity (1.9×10⁵ g · mol Zr⁻¹ · h⁻¹) was much lower than Cp₂ZrCl₂ under similar conditions.
The sp³C bridged CGC complex **D**, which was synthesized corresponding to literature^[17], displayed high catalytic activity(1.2 ×10⁶ g · mol Zr⁻¹ · h⁻¹), even slightly higher than that of Cp₂ZrCl₂, because the constrained bridge in CGC caused the bite angle α (Cp(centroid)-M-N) to be 89.9°^[18], forcing the opening of the supplementary angle β and therefore opening the coordination site. This structural feature benefited 1-decene insertion and coordination to activated metal, which was commonly considered to be responsible for its high catalytic activity.

Three ansa-metallocene complexes containing Cs symmetrical structure have also been tested, and complexes **E**, **F** and **G** were synthesized corresponding to literature^[19]. The nature of substitute on the bridge atom influenced the activity significantly and the influence of the bridge framework on the activity mainly came from steric and electronic effect. As for steric effects, the introduction of (CH₂)₅C, Me₂C and Ph₂C bridge decreased the bite angle α (Cp(centroid)-Zr-Flu) value and increased the supplementary β angle value, It was found that the bite angle α (Cp(centroid)-Zr-Flu) of **F** and **G** were 118.6° and 117.6°, respectively^[20-21], that is, these zirconocene complexes became more open and the catalytic activity was improved as the bite angel decreased. The higher activity was also attributed to favorable electronic charac-

teristics. The metal center of complexes **E**, **F**, **G** were quite electron deficient, and methyl, cyclohexyl, phenyl groups were stronger electron-donating groups, which could push electron cloud to the metal, therefore the electron-donating substituent made the active center more stable, which increased the catalytic activity. The increased stabilities and enlarged reaction space of the metal center are responsible for their high activities, in which complex **E**, **F** exhibited similar catalytic activity, and complex **G** showed the highest catalytic activity ($1.3 \times 10^6 \text{ g} \cdot \text{mol Zr}^{-1} \cdot \text{h}^{-1}$).

It can be found that **A**, **B**, **C**, **D**/MAO primarily produced low viscosity oligomers, while **E**, **F** and **G**/MAO mainly obtained medium-high viscosity oligomers. It turned out that the difference of viscosity was caused by the oligomer distribution and oligomerization mechanism. The oligomer with complex **F** was characterized by GC-MS and the result was shown in Fig 1.

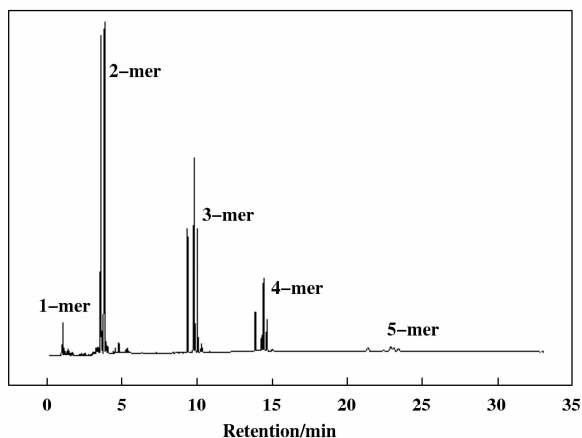


Fig. 1 Oligomer distributions for PAOs prepared using catalyst **F**

It was found that the oligomer was composed of a mixture from the dimer (2-mer) to 5-mer^[22]. The narrow peak distribution of the components suggested there was less isomerization during the chain propagation. The distribution of oligomer catalyzed by zirconocene catalysts **A-G** was shown in Table 1.

The kinetic viscosity at 100 °C of oligomers catalyzed by Cp_2ZrCl_2 was only 2.23 cSt, that's because the dimer content in the oligomer mixture was 72%, and the rest content corresponding to the 3 ~ 5 mers was only 28%. It was well known that the bite angle in

Cp_2ZrCl_2 was 133° ^[23] and the supplementary angle β was 227° , that is, the space of activated center for the monomer coordination and insertion was relative narrow, the result implied that after the formation of dimers, the polymer molecular chain easily terminated through β -H elimination or transferred to co-catalyst, resulting in more and more difficulty in forming multimer (5-mer fraction was only 0.3%, no higher polymer was found). Xu group^[24] has once found that the polymer molecular weights produced by complex **B** were higher than that of Cp_2ZrCl_2 , they ascribed the result to the different electronic environment of the metal sites combined with the double bridged-Cp ligands, that is, the electronic effects were particularly important for the insertion reaction, and caused oligomer molecular weight growth, in which the dimer fraction in oligomers with **B** was 58.63%, slightly lower than that of Cp_2ZrCl_2 , while the fraction of corresponding trimer and tetramer increased slightly. The electronic effects of bulky substituent complex **C**, similar to **B**, stabilized the metal center, which benefited the insertion and propagation of monomers, it turned out that there were also less dimers and more 3 ~ 5 mers compared with that of Cp_2ZrCl_2 .

The dimer fraction in oligomers catalyzed by complex **D** has been found dropped to 50.06%, while the kinetic viscosity at 100 °C increased up to 3.13 cSt, this may be due to **D** had large open space, which offered a relatively open coordination site, and this structural feature was commonly considered to be responsible for the lower dimer fraction and higher 3 ~ 5 mers content than that of Cp_2ZrCl_2 . However, the polymerization reaction was carried out at high temperature and Al : Zr ratio more than 300 : 1, thus, there was large dimer content in the oligomer mixture.

The C-bridge in ansa-metallocene **E**, **F**, **G** caused its $\alpha(\text{Cp}(\text{centroid})-\text{Zr}-\text{Flu})$ to be lower than that of Cp_2ZrCl_2 , this meant these complexes had more open coordination space, which was conducive to the insertion of 1-decene, therefore these complexes formed oligomers with large molecular weight. What's more, the ansa-metallocene complexes had highly symmetric structure which made 1-decene insert alternate-

ly. More important was that the cyclohexyl, methyl, phenyl with strong electronic effects, especially the phenyl, stabilized the metal center which was electron deficient. These three factors were considered to be responsible for the high oligomer molecular weight, which led to high viscosity. For example, the kinetic viscosity at 100 °C of oligomer with **F** was up to 24.24 cSt, and the kinetic viscosity at 100 °C of oligomer with **G** has reached alarming 239.08 cSt.

It can be seen from the above discussion that **A**, **B**, **C** and **D** primarily produced low viscosity oligomers and showed high catalytic activity, except **B** and **C** slightly lower. complexes **E**, **F** exhibited suitable properties and the oligomer with them could be used as ideal medium-viscosity lubricant base oil (suitable viscosity, high viscosity index). Although complex **G** displayed high catalytic activity and high viscosity index, the kinetic viscosity was too high to be used as lubricant base oil.

2.2 Characterization of PAOs

The oligomer structure was characterized by ¹H NMR and ¹³C NMR, the ¹H NMR spectra of oligomers produced by **F** was shown in Fig. 2.

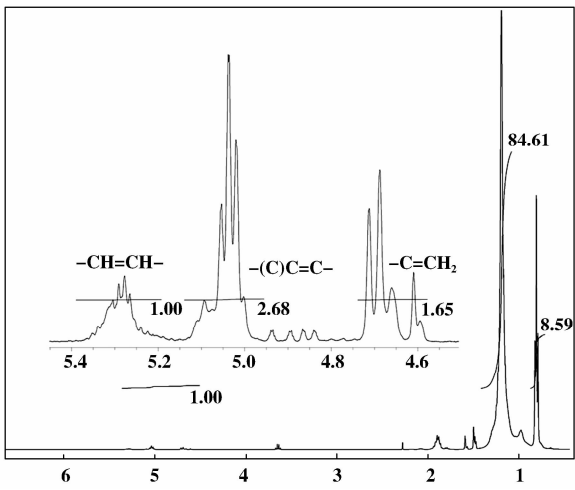
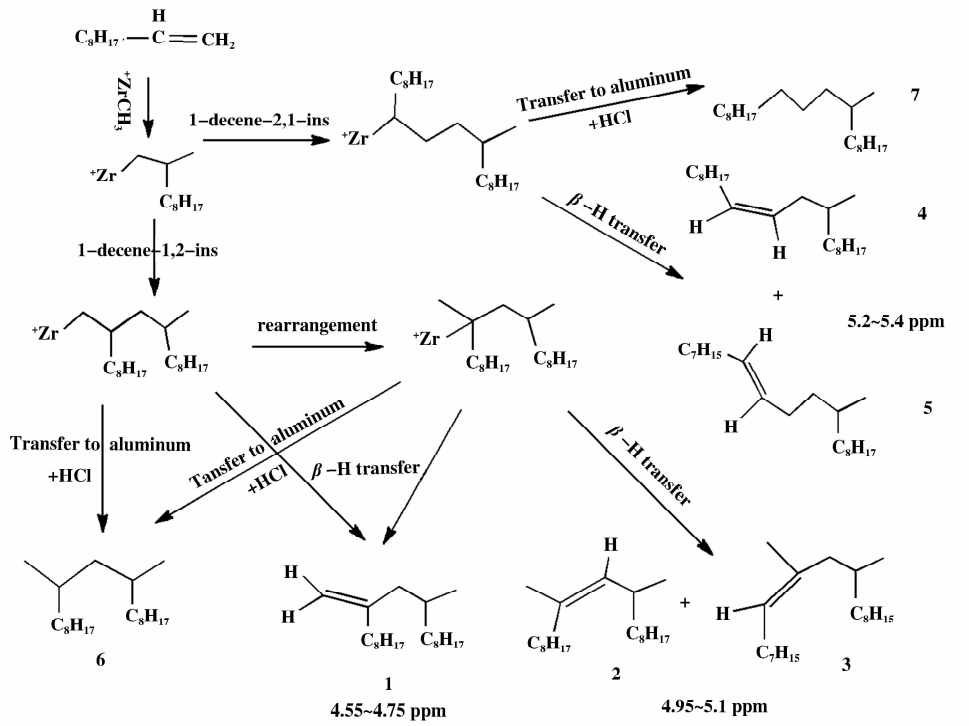


Fig. 2 ¹H NMR spectra of oligomers produced by **F**

It can be seen from Fig. 2 that the saturated hydrogen signal of methyl(0.7 ~ 0.9 ppm) and methylene(0.9 ~ 1.4 ppm) groups was pretty strong, while the unsaturated hydrogen signal(4.5 ~ 5.5 ppm) was very weak, suggesting that there was little unsaturated double bonds fragment in the oligomer carbon frame. The explanation for the reasons of the production of unsaturated bonds and saturated bonds was shown in Scheme 3. It was reported that the unsaturated end



Scheme 3 Chain transfer and chemical shift

groups (structures: 1 ~ 5) and saturated end groups (structures 6, 7) of these oligomers originated mainly through β -hydride eliminations and chain transfers to the co-catalyst, respectively^[25]. The signal of chemical shift 4.4 ~ 5.5 ppm was amplified, and there were mainly three vinyl end group signals emerged at 4.55 ~ 4.75 ppm, 4.8 ~ 5.15 ppm and 5.2 ~ 5.4 ppm, which were assigned to vinylidene ($-\text{C}=\text{CH}_2$), trisubstituted vinylene ($-(\text{C})\text{C}=\text{CH}-$), and disubstituted vinylene ($-\text{C}=\text{CH}-$) respectively^[26-27], and the integration ratios of the three signals were 1.65 : 2.66 : 1.00. The vinylidene ($-\text{C}=\text{CH}_2$) was produced through

1, 2-insertion and then terminated through β -H elimination, and the chain transfer reactions via 1, 2-insertion was facilitated after rearrangement and subsequently generated many trisubstituted vinylene ($-(\text{C})\text{C}=\text{CH}-$) end groups, while disubstituted vinylene ($-\text{C}=\text{CH}-$) was formed through 2, 1-insertion and β -hydride eliminations. Thus, most of the chain transfer reactions occurred via 1, 2-insertion and the isomer via 2, 1-misinsertion contributed only 23.2% when **F** was used as catalyst.

The ^{13}C NMR spectra of oligomers produced by **F** was displayed in Fig. 3.

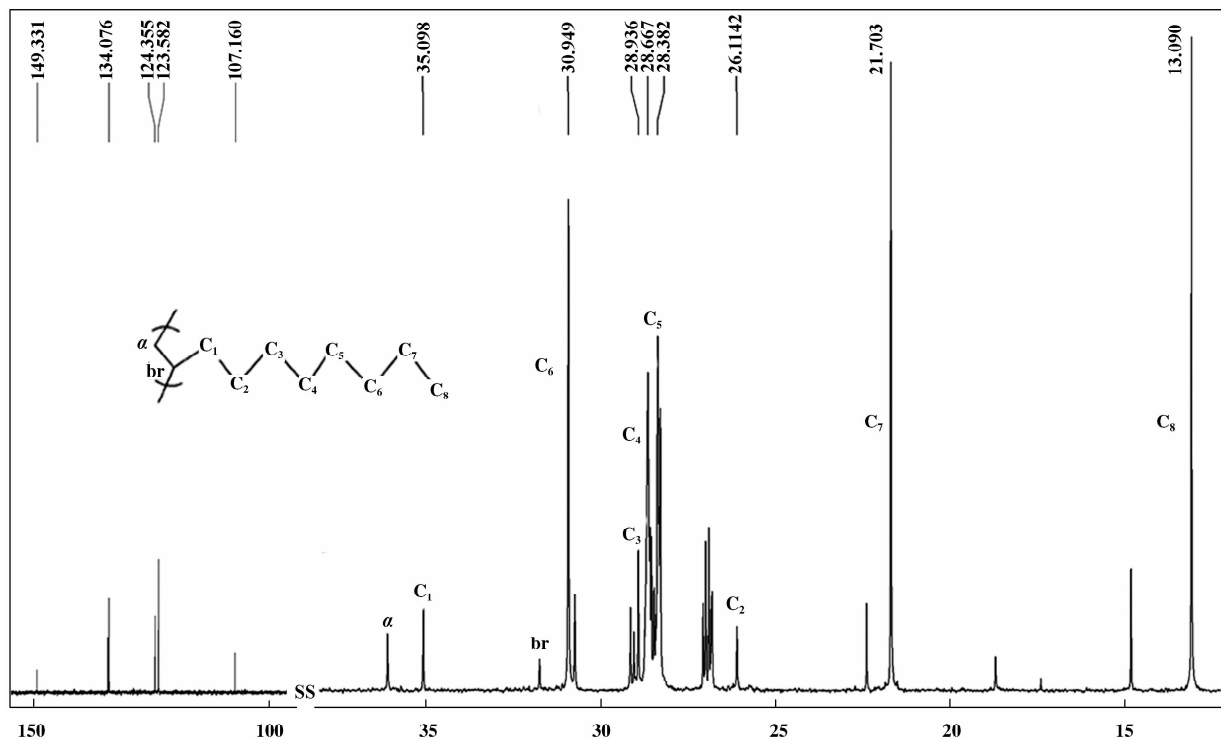


Fig. 3 ^{13}C NMR spectra of oligomers produced by **F**

According to Carman and Wilkes' nomenclature^[28-29], the chemical shifts of oligomers could be distributed as followings: C1:35.10 ppm, C2:26.11 ppm, C3:28.94 ppm, C4:28.67 ppm; C5:28.38 ppm; C6:30.95 ppm; C7:21.70 ppm; C8:13.09 ppm, 120 ~ 140 ppm was for the double bond^[30-32]. Although the oligomers containing unstable carbon bonds should be saturated through hydrogenation, the investigating of the properties of such oligomers with unsaturated bond could provide significant information for the preparation for lu-

bricants base oil, since there was little difference between the kinetic viscosity and viscosity index of unsaturated and saturated lubricant oils^[33]. Due to the atactic structure, the ^{13}C NMR signals in the aliphatic carbon region (13 ~ 42 ppm) were very complicated, which were different from that of isotactic or syndiotactic structures^[27, 34], however, the atactic PAO has been previously reported to be better used as lubricant base oil because it exhibited lower pour point than the isotactic- or syndiotactic-rich analogs^[35].

2.3 Effects of reaction conditions on 1-decene oligomerization

It was found that reaction conditions affected catalytic activity and properties of the oligomers markedly.

Table 2 reveals the influence of complex **F** dosage on catalytic activity and properties of the resulting oligomers.

Table 2 The influence of complex **F** dosage on catalytic activity and properties of the resulting oligomers

complex F μmol	Activity ^a	Conversion /%	40 °C Kv/cSt	100 °C Kv/cSt	VI
5	7.6	30.8	184.9	41.00	274
7.5	10.2	61.6	167.1	36.38	265
10	8.7	70.8	118.2	27.00	265
12.5	7.1	71.5	116.7	25.30	251
15	6.2	74.9	87.54	18.64	236

Oligomerization conditions: 1-decene(50 mL), Al : Zr = 300 : 1, 100 °C, 3 h;

a. Activity in units of $\times 10^5 \text{ g} \cdot \text{mol Zr}^{-1} \cdot \text{h}^{-1}$

The results indicated that the highest catalytic activity ($1.0 \times 10^6 \text{ g} \cdot \text{mol Zr}^{-1} \cdot \text{h}^{-1}$) occurred when 7.5 μmol **F** was used, and then the activity decreased slightly, which could be attributed to the difficulty of 1-decene diffusion in high viscosity oligomer system. It was found that the viscosity at 40 and 100 °C decreased as the dosage of **F** increased, which was attributed to

this reason; certain monomers were initiated by more coordination centers and produced more oligomers with low molecular weight. Therefore, 10 μmol complex **F** was used. Table 3 reveals the influence of Al/Zr ratio on catalytic activity and properties of the resulting oligomers with complex **F**.

Table 3 The influence of Al/Zr ratio on catalytic activity and properties of the resulting oligomers

Al/Zr ratio	Activity ^a	Conversion /%	40 °C Kv/cSt	100 °C Kv/cSt	VI
100;1	2.3	18.7	211.45	42.65	257
200;1	6.7	54.3	191.67	38.77	254
300 : 1	8.9	70.8	120.48	25.78	250
400;1	7.9	64.0	114.91	24.36	246
500;1	7.4	60.2	109.00	22.65	239

Oligomerization conditions: 1-decene(50 mL), Complex **F**: 10 μmol, 100 °C, 3 h;

a. Activity in units of $\times 10^5 \text{ g} \cdot \text{mol Zr}^{-1} \cdot \text{h}^{-1}$.

It was found from Table 3 that the catalytic activity increased as the Al/Zr ratio augmented until Al/Zr ratio was 300 : 1, and then decreased slowly, but the viscosity at 40 and 100 °C steadily decreased as the Al/Zr ratio increased. It was well known that the co-catalyst MAO played an important role in the process of

1-decene oligomerization, such as removing the harmful substances from the polymerization system, methylating the zirconocene complex to promote the formation of alkylated active center, eliminating CH_3^- from the active center to form a alkyl cation with 14 electrons, which stabilized by the anion formed by MAO with

CH_3^- . It was easy to understand that the quantity of active center increased as the dosage of MAO augmented, which in turn promoted the activity of the catalyst and led to a reduction of polymer molecular weight. These factor reflected in the nature of the polymer was that the kinetic viscosity at 40 and 100 °C of oligomers decreased upon increasing Al/Zr ratio. It was well known that there was always residual of trimethylaluminum (TMA) in MAO, and the reaction between active species and TMA^[36] also affected the catalytic activity. The results showed that the catalytic activity increased as the ratio of Al/Zr ratio augmented to 300 : 1 (the highest catalytic activity: $8.9 \times 10^5 \text{ g} \cdot \text{mol Zr}^{-1} \cdot$

h^{-1}) and then decreased, which may be caused by the excess of MAO interfering the formation of the coordination sites through the over-reduction of Zr species with TMA^[37]. Further more, MAO itself was a chain transfer agent and the chain terminations through transferring to the co-catalyst are favored at higher Al/Zr ratio, so the excess MAO would lower the molecular weight of the polymer, that is, the experimental result was due to the above two factors. Therefore, Al/Zr ratio of 300 : 1 was used.

Table 4 reveals the influence of reaction temperature on catalytic activity and properties of the resulting oligomers with complex **F**.

Table 4 The influence of reaction temperature on catalytic activity and properties of the resulting oligomers

Temperature °C	Activity ^a	Conversion /%	40 °C Kv/cSt	100 °C Kv/cSt	VI
60	9.2	74.7	427.92	78.37	265
80	9.7	78.6	176.85	36.90	258
100	8.8	71.3	125.09	26.39	248
120	7.3	58.7	117.16	23.66	235
140	4.0	32.1	76.58	16.18	228

Oligomerization conditions: 1-decene (50 mL), complex **F**; 10 μmol , Al : Zr = 300 : 1, 3 h;

a. Activity in units of $\times 10^5 \text{ g} \cdot \text{mol Zr}^{-1} \cdot \text{h}^{-1}$.

It can be found from table 4 that the catalytic activity presented a downward trend as reaction temperature increased, which implied that higher temperature was harmful for 1-decene oligomerization. Generally the increase of reaction temperature was conducive to the diffusion of 1-decene and increased the propagation rate of 1-decene, but it also increased the deactivation rate of the active sites, therefore the combination of these two effects likely accounted for the above reaction temperature influence. The viscosity decreased upon increasing reaction temperature, indicating that chain propagation was favored at low temperature, whereas chain terminated by β -H elimination and transferred to co-catalyst occurred at higher temperature^[38]. Now, it was easy to understand that both kinetic viscosity at 40 and 100 °C decreased upon increasing reaction temperature. The highest viscosity index occurred at 60 °C,

because the structures of oligomers produced at different reaction temperatures were different, and viscosity index was influenced by the molecular branch ratio as well as the lateral chain length. However, the kinetic viscosity at 100 °C of the oligomer prepared at 60 °C was too high, thus, 80 °C was used as reaction temperature.

3 Conclusions

In this paper, the oligomerization of 1-decene catalyzed with different zirconocene complexes was performed, it can be found that the nature of ligands in zirconium complexes affected the polymerization reaction markedly. **A**, **B**, **C** and **D** mainly produced low viscosity oligomers (100 °C Kv: 2 ~ 4 cSt, dimer content was about 60%), and Cp_2ZrCl_2 and complex **D** showed high catalytic activity (above $10^6 \text{ g} \cdot \text{mol Zr}^{-1} \cdot$

h^{-1}). The oligomers formed by **E**, **F** exhibited suitable properties (suitable viscosity, high viscosity index and high catalytic activity up to $10^6 \text{ g} \cdot \text{mol Zr}^{-1} \cdot \text{h}^{-1}$) and the oligomers could be used as medium-viscosity lubricant base oil. Although complex **G** displayed high catalytic activity and high viscosity index, the viscosity was too high to be used as lubricant base oil. The GC-MS analysis results indicated that the oligomer mixture was mainly composed of dimer to pentamer, and the narrow peak of components suggested that there was less isomerization during the oligomerization. The results of ^1H NMR and ^{13}C NMR indicated that the unsaturated and saturated end groups of these oligomers originated mainly through β -hydride eliminations and chain transfers to the co-catalyst, respectively, most of the chain propagation reactions were carried out via 1, 2-insertion and 2, 1-insertion. This catalytic activity of 1-decene oligomerization increased initially and then decreased upon increasing the dosage of complex **F**, reaction temperature and Al/Zr ratio, while increasing the dosage of complex **F**, Al/Zr ratio and reaction temperature all decreased the viscosity of oligomers. The optimum reaction conditions involved a dosage of complex **F** $10 \mu\text{mol}$, a reaction temperature of 80°C , and an Al/Zr ratio of $300:1$, and complex **F** was applicable to the commercial production of lubricant base oil.

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茂金属催化剂催化 1-癸烯齐聚研究

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摘要: 考察了 1-癸烯和不同结构的茂金属催化剂($(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$, **A**; $[\mu, \mu\text{-}(\text{Me}_2\text{Si})_2(\eta^5\text{-C}_5\text{H}_3)_2][(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2]_2$, **B**; $[(\text{C}_6\text{H}_5)\text{C}(\text{Me})_2(\eta^5\text{-C}_5\text{H}_4)]_2\text{ZrCl}_2$, **C**; $t\text{BuNC}(\text{Me})_2(\eta^5\text{-C}_5\text{H}_4)\text{ZrCl}_2$, **D**; $(\eta^5\text{-C}_5\text{H}_4)\text{C}(\text{C}_5\text{H}_{10})(\eta^5\text{-C}_{13}\text{H}_8)\text{ZrCl}_2$, **E**; $(\eta^5\text{-C}_5\text{H}_4)\text{C}(\text{Me})_2(\eta^5\text{-C}_{13}\text{H}_8)\text{ZrCl}_2$, **F**; $(\eta^5\text{-C}_5\text{H}_4)\text{C}(\text{C}_6\text{H}_5)_2(\eta^5\text{-C}_{13}\text{H}_8)\text{ZrCl}_2$, **G**)/MAO 的齐聚反应, 并探讨了茂金属 **F** 的用量, 聚合温度和 Al/Zr 比对聚合反应和齐聚物性能的影响. 实验结果表明, 由于其不同的位阻效应和电子效应, 不同结构的茂金属对 1-癸烯的催化活性和齐聚物组分分布影响显著. 其中, Cp_2ZrCl_2 , 双核硅桥联的茂金属 **B** 和大位阻的茂金属 **C** 主要合成低粘度的齐聚物 (100 °C Kv: 2 ~ 3 cSt, 二聚体含量约为 60%); 限制构型的茂金属 **D** 因为有更加开放的配位结构呈现出高的催化活性, 齐聚物的粘度也略高 (100 °C Kv: 3 ~ 4 cSt); Cs-对称型茂金属 **E**, **F**, **G** 都有较高的催化活性, 合成的齐聚物粘度也较高 (100 °C Kv > 20 cSt), 主要归因于茂金属的特殊结构和聚合机理. GC-MS 结果表明茂金属催化 1-癸烯合成的齐聚物异构化较少, 主要由二聚体到五聚体的混合物组成. 茂金属 **F** 催化 1-癸烯较优的齐聚条件是催化剂用量 10 μmol , 聚合温度 80 °C, Al/Zr 比 300 : 1.

关键词: 茂金属; 1-癸烯; 齐聚; 结构性能关系; 性能与表征