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ORIGINAL PAPER

Kinetic and microstructural studies of Cp$_2$ZrCl$_2$ and Cp$_2$HfCl$_2$-catalyzed oligomerization of higher α-olefins in mPAO oil base stocks production

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ABSTRACT

Herein a quenched-flow kinetic technique was applied to calculate the rate constants of 1-hexene and 1-octene oligomerization catalyzed by the Cp$_2$ZrCl$_2$ and Cp$_2$HfCl$_2$/MAO catalyst systems, and subsequently a mechanism for the higher α-olefin oligomerization reaction was proposed. The oligomerization results showed that Zr-based catalyst in the oligomerization of 1-octene had the highest activity of 17 in comparison to Hf-based one with an activity value of 15 g (oligomer/(mmol$_{Cat}$.h)). According to the obtained results, increasing monomer length led to a shift in molecular weight and polydispersity index value (M_w/M_n) to lower values. Furthermore, the microstructure-viscosity relationship was followed by the calculation of branching ratio and short-chain branching percentage. The obtained results revealed that, the oligomers synthesized by the Cp$_2$HfCl$_2$ catalyst had lower short chain branching ratio value and short-chain branching percentages. According to the kinetic results, the initiation rate constant (k_i) of Zr-based catalyst was higher than that of Hf-based catalyst, and the order of calculated propagation rate constants was Zr>H$_f$ for both the 1-hexene and 1-octene-based oligomerizations. **Polyolefins J (2021) 8: 31-40**

Keywords: Olefin; oligomerization; metallocene; microstructure; oil.

INTRODUCTION

Higher α-olefin oligomerization with metallocene catalysts is an interesting topic in both academic and industrial research. The mechanism of higher α-olefin oligomerization and the use of oligomers produced were presented in Refs [1-4]. To design a complex structure, obtaining kinetic parameters as well as calculating the rate constants for the oligomerization reac-

tion is so important in rationalizing complex structure-oligomer property dependency, which links the kinetic factors to the complex structure. However, with further experiments, the rate constants of different reactions occurring in oligomerization are calculated. It has been reported that the initiation [5, 6] and propagation [6-8] rate constants are obtained to follow the rate of

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monomer consumption/oligomer production. In the literature, different methods such as: calculating vinyl unsaturated amount [9, 10] and obtaining the degree of oligomerization [6, 11, 12] have been reported to calculate the chain transfer rate value.

Catalyst type, monomer, oligomerization temperature, and the amount of used catalyst and monomer are the most important factors affecting the reaction kinetic [13]. Hadjichristidis and coworkers studied kinetics of higher α-olefins oligomerization, catalyzed by Cs symmetry hafnocene catalyst, by monitoring the M$_n$, PDI, and productivity with the time [13]. According to the authors, polymerization rate strictly depended on the type of monomer used. Kissin studied the chemistry and kinetic of 1-hexene oligomerization with catalysts of Cp$_2$ZrCl$_2$, (CH$_3$-Cp)$_2$ZrCl$_2$, and (n-C$_4$H$_9$-Cp)$_2$ZrCl$_2$, and with using two types of MAO as the activator [14, 15]. Hilty et al. investigated the kinetics and stereochemistry of poly-1-hexene produced by zirconium-based metallocene catalysts using NMR spectroscopy [16]. Landis and coworkers used quenched-flow kinetics, active site counting, polymer microstructure evaluation, and PDI analysis to calculate the kinetic constants of 1-hexene polymerized by the contact ion-pair and [rac-(C$_2$H$_4$(1-indenyl)$_2$)ZrMe][MeB(C$_6$F$_5$)$_3$] [17]. Basset et al. reported silica-supported tantalum hydride catalyst as a catalyst for alkane metathesis. Supported tantalum and tungsten hydrides are highly unsaturated and electron-deficient species that are highly reactive toward the C-H and C-C bonds of alkanes [18].

Despite much of the work reported in the field of mPAOs, which was briefly reviewed above, the viscosity dependence of the oligomer microstructure is still unclear in these lubricants. Herein, we investigated the microstructure of synthesized oligomers with two commercial metallocene catalysts, i.e. Cp$_2$ZrCl$_2$ and Cp$_2$HfCl$_2$/MAO, and studied microstructure-viscosity relationship by employing distortionless enhancement by polarization transfer (DEPT) technique. Furthermore, the kinetic constants of 1-hexene and 1-octene oligomerization reactions were obtained by quenching the oligomerization reaction during different time intervals.

EXPERIMENTAL

Materials

1-Hexene and 1-octene were provided from Merck (Hohenburn, Germany) and dried over sodium/benzophenone under N$_2$ prior to use. Cp$_2$ZrCl$_2$ and Cp$_2$HfCl$_2$, as commercial metallocene catalysts, and MAO (10% in toluene) as a cocatalyst were purchased from Aldrich (Steinheim, Germany). Toluene (Merck) was distilled over CaH$_2$ and sodium metal, consecutively.

Oligomerization

A 100 mL reactor was equipped with a magnetic stirrer and N$_2$ gas was charged with 5 mL dried toluene and 0.08 mol of the monomer. 3.4 mL of 1.5 M cocatalyst solution (5.25 $\times$ 10^{-3} mol) was introduced into the aforementioned solution. Oligomerization reaction was initiated by injecting of 10 μmol catalyst. After a specific time, oligomerization reaction was terminated by introducing HCl/CH$_3$OH solution into the reaction medium. Then, the oligomer was separated from the unreacted monomer and methanol mixture. The supernatant liquid, which consists of the unreacted monomer and methanol, was separated from the viscous oligomer. The viscous oligomer was diluted with n-hexane and transferred into a separating funnel and the organic layer was washed several times with distilled water followed by sodium bicarbonate and water to remove any traces of alkali. After the work up, the solution was dried with anhydrous sodium sulfate and the solvent was removed in vacuum.

Quenched NMR scale oligomerization of higher α-olefins

1-Hexene and/or 1-octene were injected into a catalyst/cocatalyst mixture in an NMR tube. At the desired reaction progress, the oligomerization was quenched utilizing 0.25 mL of CD$_3$OD. The quenched reaction was characterized according to Refs [4, 19].

Characterization

^{1}H-NMR spectra was performed on a Bruker DRX 400 MHz NMR spectrometer in CDCl$_3$ at 25°C. Standard Bruker pulse DEPT-135 was utilized with the following acquisition conditions: spectral width of 2,0161 Hz, time of domain of 32,769, eight dummy

scans, recycle delay of 2 s, acquisition time of 0.81 s, and 12,288 scans. CDCl$_3$ peak (δc, 22.4 ppm) was employed for chemical shift calibration. The molecular weights of synthesized oligomers and also PDI values were obtained by gel permeation chromatography (GPC Agilent 1100). Kinematic viscosity (KV) contents were analyzed in centistokes (cSt) by using ASTM D445. By employing KV^{40} and KV^{100} values, viscosity index (VI) was calculated by utilizing the method presented in ASTM D2270. Reaction kinetics was followed using the quench-flow method described in the literature [4, 19].

RESULTS AND DISCUSSION

Oligomerization behavior of the catalysts

Cp$_2$ZrCl$_2$ and Cp$_2$HfCl$_2$ catalysts and MAO as cocatalyst were used as the catalytic systems for the oligomerization of 1-hexene and 1-octene at 80°C. The oligomerization results of the catalyst systems used are shown in Table 1. It is obvious that, Cp$_2$ZrCl$_2$ has more catalyst activity, where by adding 10 μmol of the catalyst to pure 1-hexene, 2.90 g of product is obtained after 24 h, which shows an activity of 12 g (oligomer/ (mmol$_{Cat}$.h)). It is 1.13% more than that of Cp$_2$HfCl$_2$ catalyst which is negligible [20]. It was observed that Zr-based metallocene catalysts produce PAOs with low M$_n$ value but with high catalytic activities in comparison to Hf-based ones [21].

In-depth study of the results of Table 1 showed that the type of monomer used has significant influence on the oligomerization activity values. Actually, in the presence of the same catalyst system, 1-octene oligomerization showed higher catalyst activity. It was scientifically accepted that a longer lateral polymer chain opens the π-ligands wider than a shorter α-olefin and

facilitates the insertion of the longer α-olefin [22]. Molecular weight information of mPAOs is another significant factor in evaluating oligomers. The data collected in Table 1 show that M$_n$ obtained from the oils produced depends on the metal center used and shows the trend of H$_f$>Z$_r$, however for Cp$_2$HfCl$_2$ and Cp$_2$ZrCl$_2$ catalysts in the case of 1-hexene, M$_n$ values are 1816 and 692 g/mol, respectively (Figure 1) [21]. In the next step, PDI values were studied to explore the effect of used catalyst systems on molecular weight distribution. According to the results, the obtained distributions were monomodal, and recorded values have been determined to be in the range of
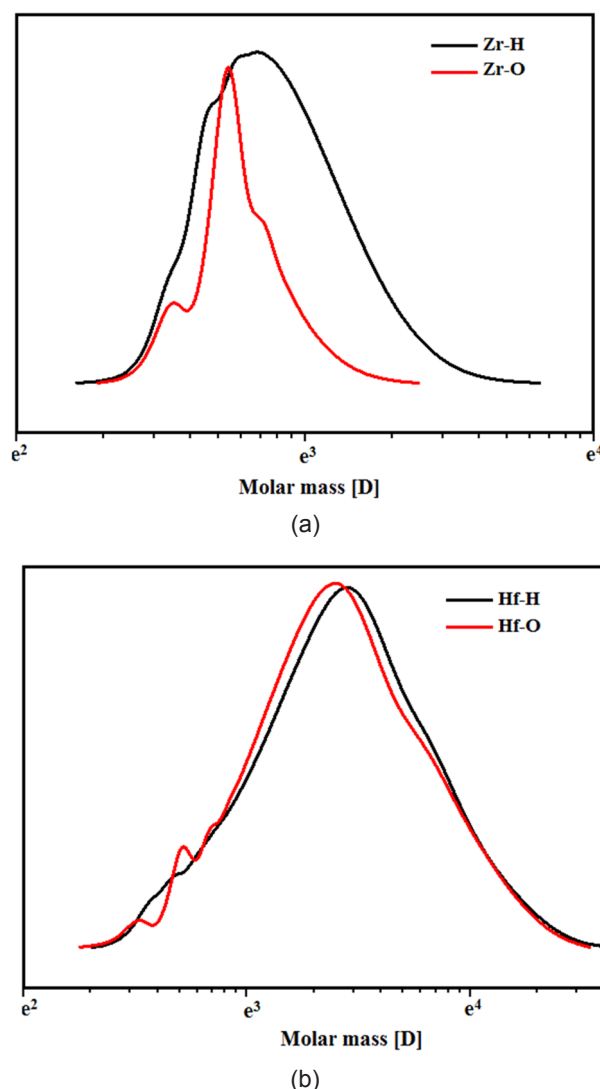

(a)

(b)

Figure 1. GPC curves of the obtained oligomers from (a) [Cp$_2$ZrCl$_2$]= 10 μmol, [monomer]= 0.08 mol, t=24 h, Al/M= 500, T=80°C, 1-hexene oligomer (black), 1-octene oligomer (red); (b) [Cp$_2$HfCl$_2$]= 10 μmol, [monomer]= 0.08 mol, t=24 h, Al/M= 500, T=80°C, 1-hexene oligomer (black), 1-octene oligomer (red).

Table 1. Oligomerization results using the two catalyst systems used.[a]

Sample	Cat	Monomer	Yield (g)	Activity[b]	M$_n$ (g/mol)	PDI
Zr-H	Zr	1-hexene	2.90	12	692	1.33
Zr-O	Zr	1-octene	4.09	17	631	1.23
Hf-H	Hf	1-hexene	2.57	11	1816	2.19
Hf-O	Hf	1-octene	3.67	15	1775	2.13

[a] Oligomerization conditions: [Cat]= 10 μmol, and Al/M=500, [Monomer] =0.08 mol, t=24h, T= 80°C; [b]g (oligomer/(mmol$_{Cat}$.h).

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1.23-2.19. It must be mentioned that, two employed catalyst systems oligomerized 1-hexene/1-octene with moderate activity and produced oligomers with narrow PDI values, meanwhile this behavior revealed the order of H$_f$>Z$_r$ (Table 1).

Furthermore, according to the GPC curves shown, decreasing the monomer length shifted the PDI to higher values. For 1-hexene and 1-octene monomers, the obtained PDI values were 1.33 and 1.23 in the case of Zr-based catalyst, respectively. In fact, the obtained PDI values are very narrow. It should be noted that, in the literature catalyst systems with Ti or other metal centers have been reported which can lead to oligomers with very narrow PDIs but low molecular weight [23].

Kinematic viscosity (KV) of the synthesized oligomers
As mentioned above, oligomers of higher α-olefins which known as PAOs can be used as engine oil. Most important physical characteristics of engine oils are viscosity index (VI), KV[40] and KV[100]. According to academic and industrial reports, oils produced using the application of engine oil should have a temperate KV and high viscosity index values [2, 4, 19]. The viscosity results of the oils produced are listed in Table 2. According to the results, oligomers from Hf-based catalysts showed high-viscosity oils in comparison with the oils obtained by Zr-based catalyst (KV100 = 65 and 64 cSt compared to 4.2 and 3.5 cSt). However, the oils produced by using the two catalyst systems showed a comparable VIs (in the range of 114-139). The above results may be confirmed by NMR analysis, which indicates that the produced mPAOs have branch ratio contents in a close range (Figure 2) [24]. The VI values of the produced oils also increased with increasing the utilized monomer length. It was scientifically accepted that longer α-olefins produce PAOs with higher viscosity index values in comparison to

shorter α-olefins [25]. Branching ratio and short-chain branching values of this type of oils are two critical micro-structural parameters which affect the viscosity properties. Equations of 1 and 2 illustrate the calculation methods of branching ratio and short-chain branching values, respectively [26, 27]. For determining the presence of primary, secondary and tertiary carbon atoms in the oligomeric chains, distortionless enhancement by polarization transfer (DEPT-135) technique was employed. The DEPT-135 spectra of synthesized oligomers in the ranges of 10-50 ppm are depicted in Figure 2, in which the peaks at the underline are attributed to the CH$_2$ groups, and the peaks above the baseline are related to the CH and CH$_3$ groups in the oligomer chain. (The DEPT-135 spectra of all produced oils are represented in Fig S1-S4 of the supporting information).

$$\text{branching ratio} = [15 \times \sum_{k=0}^{n} (\text{C integral for } CH_3 \text{ groups})] /$$

$$[15 \times \sum_{k=0}^{n} (\text{C integral for } CH_3 \text{ groups}) + 14 \times$$

$$\sum_{k=0}^{n} (\text{C integral for } CH \text{ and } CH_2 \text{ groups})]$$

$$(1)$$

Short-chain branching percentage

$$= [\sum_{k=0}^{n} (\text{C integral short-chain methyl}) /$$

$$\sum_{k=0}^{n} (C \text{ integral all methyl})] \times 100 \quad (2)$$

The results calculated in Table 2 showed that not only the kinetic viscosity values but also the viscosity index contents were affected by the microstructures of the synthesized oligomers which have been manifested in the form of branching ratio and short-chain branching percentage. According to Table 2, the oligomers obtained by the hafnocene catalyst showed a very low branching ratio in comparison to the oligomers which synthesized by zirconocene one, which is an evidence that the synthesized oligomer had an extremely regular structure. Furthermore, the oligomers obtained by the Cp$_2$HfCl$_2$ catalyst demonstrated low value of short-chain branching percentages, meaning

Table 2. Viscosity results of the synthesized oligomers.

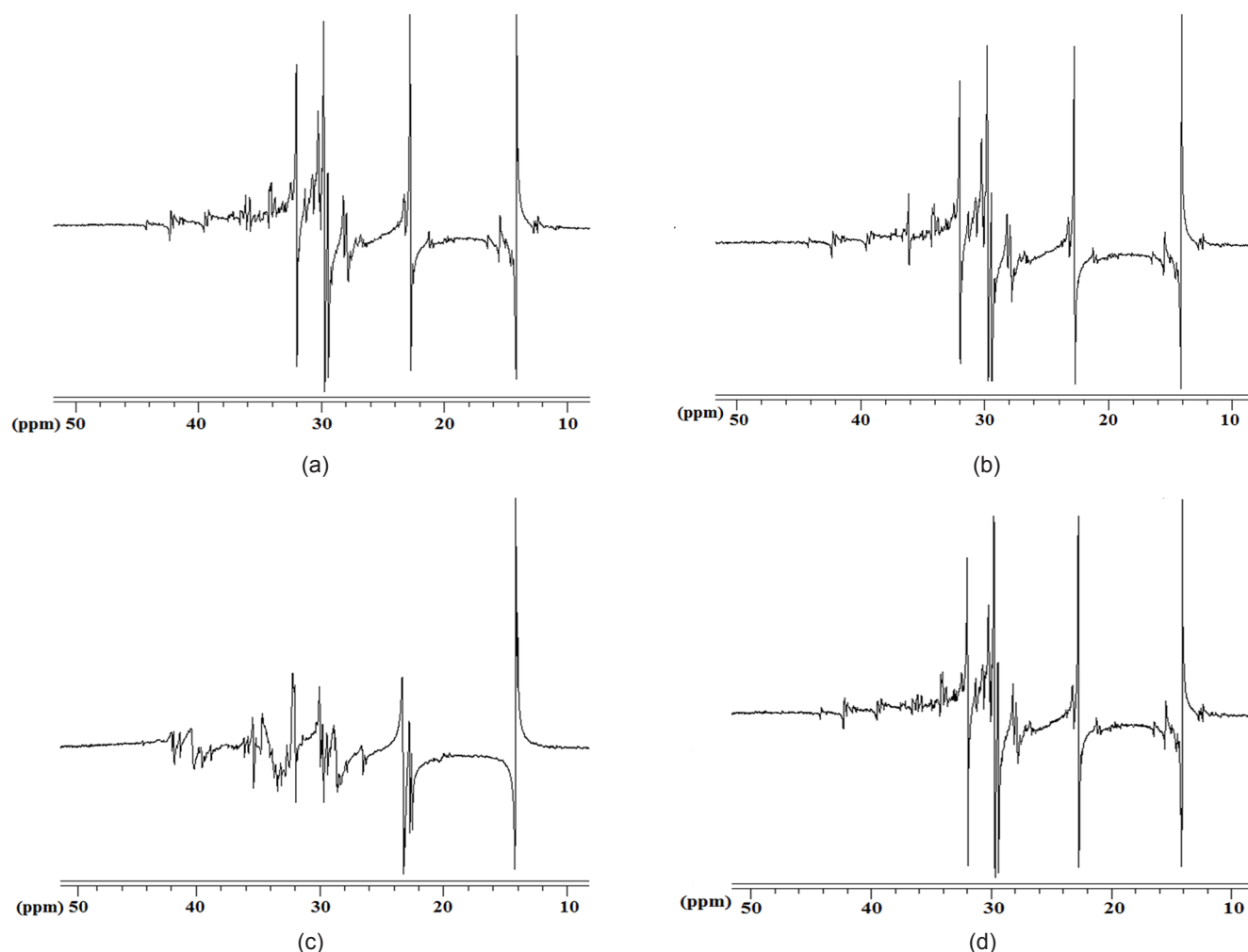| Sample	KV[100] (cSt)	KV[40] (cSt)	VI	Branching ratio	Short-chain branching (%)
Zr-H	4.2	20.3	114	1.18	55.6
Zr-O	3.5	14.5	126	1.17	54.1
Hf-H	65	354	136	1.14	38.0
Hf-O	64	275	139	1.13	35.7

Figure 2. Expanded ^{13}C-NMR spectra of the synthesized oligomers using DEPT-135 technique; (a) Zr-H, (b) Zr-O, (c) Hf-H, and (d) Hf-O ([cat]= 10 µmol, [monomer]= 0.08 mol, t=24 h, Al/M= 500, T=80 C).

that oligomer with the low branching ratio and low short-chain branching content have high viscosity index values [26, 28]. On the other hand, the results of Table 1 and Table 2 show that the viscosity index has a direct relationship with the molecular weight of the oligomers, so that the higher the molecular weight, the larger the VI values [2].

Kinetic studies of oligomerization reactions

In this part of our investigation, the kinetic of 1-hexene, and 1-octene oligomerization utilizing two employed metallocene catalysts were considered. The method which we used to obtain the kinetic model was according to Refs [4, 19]. For each catalyst system, we determined a kinetic modeling method analyzing (1) monomer consumption, (2) active site contents, and (3) unsaturated end group contents during the oligomerization time. Scheme 1 shows the essential reac-

tion involved in the kinetic model considered in our study.

Initiation rate constant (k_i) is attributed to the active complex in the oligomerization media. According to the pervious kinetic studies up to 30°C, k_i has a direct relationship with [monomer] [4, 19]:

$$\frac{\partial [1^*]}{\partial t} = k_i[1][\text{Monomer}] \qquad (3)$$

Where, [1] is the concentration of primary catalyst and [1*] is the concentration of the primary active catalyst. The catalyst participation value was calculated by employing active site counting technique (quenching with CD3OD) examined with ^{2}H-NMR. An in-depth review of the data in Table 3 shows that ki is higher for Zr-based catalysts than for Hf-based catalysts. It has been previously reported that a stronger sigma bond
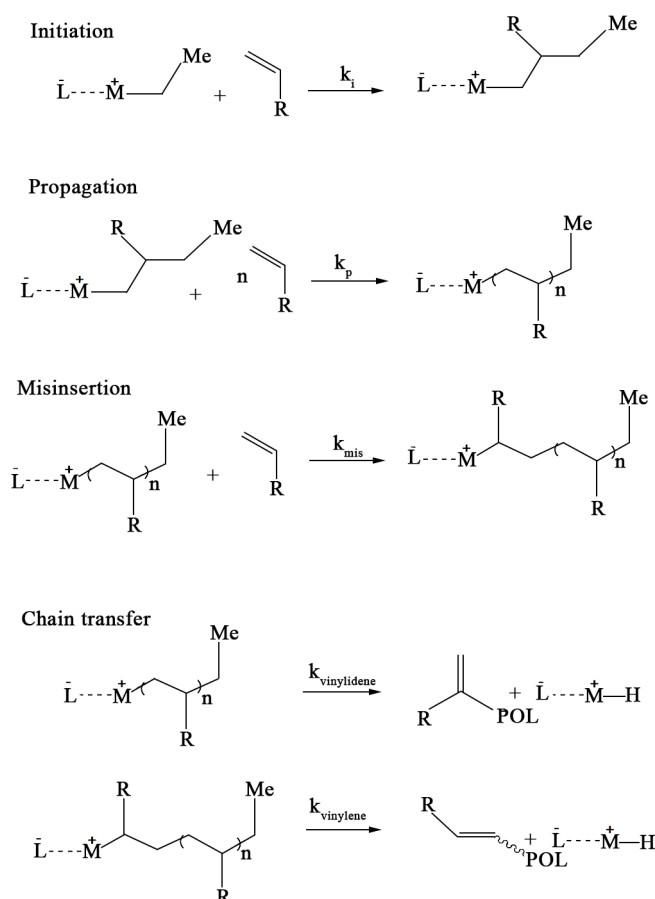
Scheme 1. Elementary kinetic steps for oligomerization reaction (R= C4 or/and C6 branches in the case of 1-hexene, and 1-octene, respectively; M= Zr or Hf for the Cp$_2$ZrCl$_2$ and Cp$_2$HfCl$_2$ catalysts).

between Hf and C is responsible for low ki value of Hf-based catalysts [3].

By comparing the results Table 1 and Table 3 it can be understood that the catalyst with high ki value yields oligomer chains with low molecular weight, in other words, the high content of active centers in the reaction mixture causes more chains with low M_n value [19].

Oligomerization was conducted at 3, 6, 12, 18, 24 h with a constant [monomer]. A traditional set of data
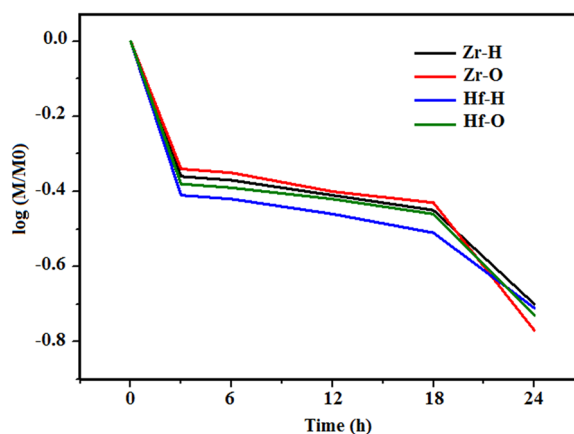

Figure 3. Monomer consumption data of the 1-hexene/1-octene oligomerization reaction catalyzed by the two metallocene systems ([monomer]=16 M; [catalyst]=5 mM; Al/M=500; T=80°C).

is displayed in Figure 3, with monomer consumption curves versus oligomerization time for each catalyst system. We assumed that the propagation rate was independent of the cocatalyst concentration, so we established equation 4 to calculate the propagation rate constant (k$_p$) [4, 19].

$$\frac{\partial [1-\text{monomer}]}{\partial t} = k_p [1^*][1-\text{monomer}] \qquad (4)$$

Examination of the obtained rate constants showed that, the k$_i$ values are less than k$_p$ ones for the two catalysts used. Furthermore, the obtained k$_p$ values followed the trend of Zirconocene>Hafnocene in both 1-hexene and 1-octene oligomerizations. In fact, the difference in the kp values of the two used complexes is related to the electronic nature of the metal centers used [19, 29, 30]. The curves shown in Figure 3 and data recorded in Table 3 show that the propagation rate constant of 1-hexene oligomerization with the two catalyst systems used is low in all the reaction times [21].

Table 3. Optimal kinetic parameters of the two catalyst systems used.

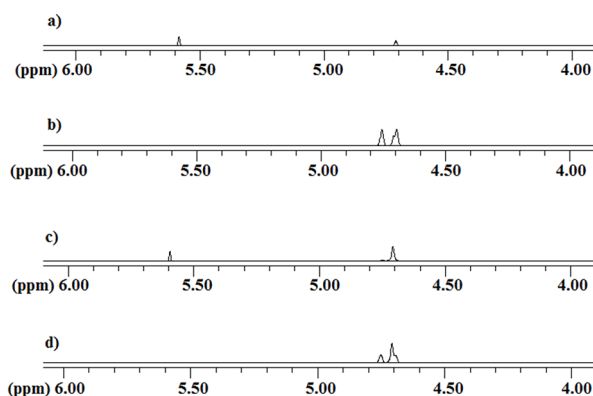| Parameter	Zr-H	Zr-O	Hf-H	Hf-O
$10^6 k_i$ (M^{-1} s^{-1})	6.571±0.07	6.708±0.01	6.012±0.04	6.460±0.03
$10^2 k_p$ (M^{-1} s^{-1})	0.049± 0.02	0.065±0.01	0.068±0.02	0.074±0.06
$10^6 k_{vinylidene}$ (s^{-1})	≅0.00	0.035±0.02	≅0.00	0.021±0.01
$10^6 k_{vinylene}$ (s^{-1})	0.014±0.01	≅0.00	0.027±0.01	≅0.00
$10^2 k_{mis}$ (M^{-1} s^{-1})	0.017±0.01	0.020±0.01	0.033±0.01	0.035±0.02
$10^{-4} k_p/k_{vinylidene}$	(a)	1.857±0.05	(a)	3.523±0.01

(a) Not determined

Figure 4. ¹H-NMR spectra of the unsaturation region of synthesized oligomers: a) Zr-H, b) Zr-O, c) Hf-H, and d) Hf-O.

Chain transfer reactions are crucial in coordinative polymerization since the propagation reaction must be ended by hydrogen or monomer transfer reactions

[1, 2, 19, 31]. A variety of unsaturated structures can be produced via termination reactions: vinylidene, $CH_2=CRR'$ (Vd, between 4.7 and 4.8 ppm); vinyl, $CH_2=CHR$ (Vn, 4.9 and 5.6 ppm); trisubstituted vinylene, $RCH=CR'R''$ (3Vn, 5.2 ppm); and disubstituted vinylene, $RCH=CHR'$ (2Vn, between 5.3 and 5.5 ppm) [1, 2]. The ¹H-NMR spectra of the synthesized oils showed the unsaturated end groups peaks (Figure 4). In the case of 1-hexene-based oligomers, there was no the chemical shift of vinylidene groups (Spectra a and c in Figure 4), and surprisingly 1-octene-based oligomers showed only vinylidene unsaturated structures (Spectra b and d in Figure 4, ¹H-NMR spectra of the synthesized oligomers are depicted in Figures S5-S8 in Supporting Information) [1, 32].
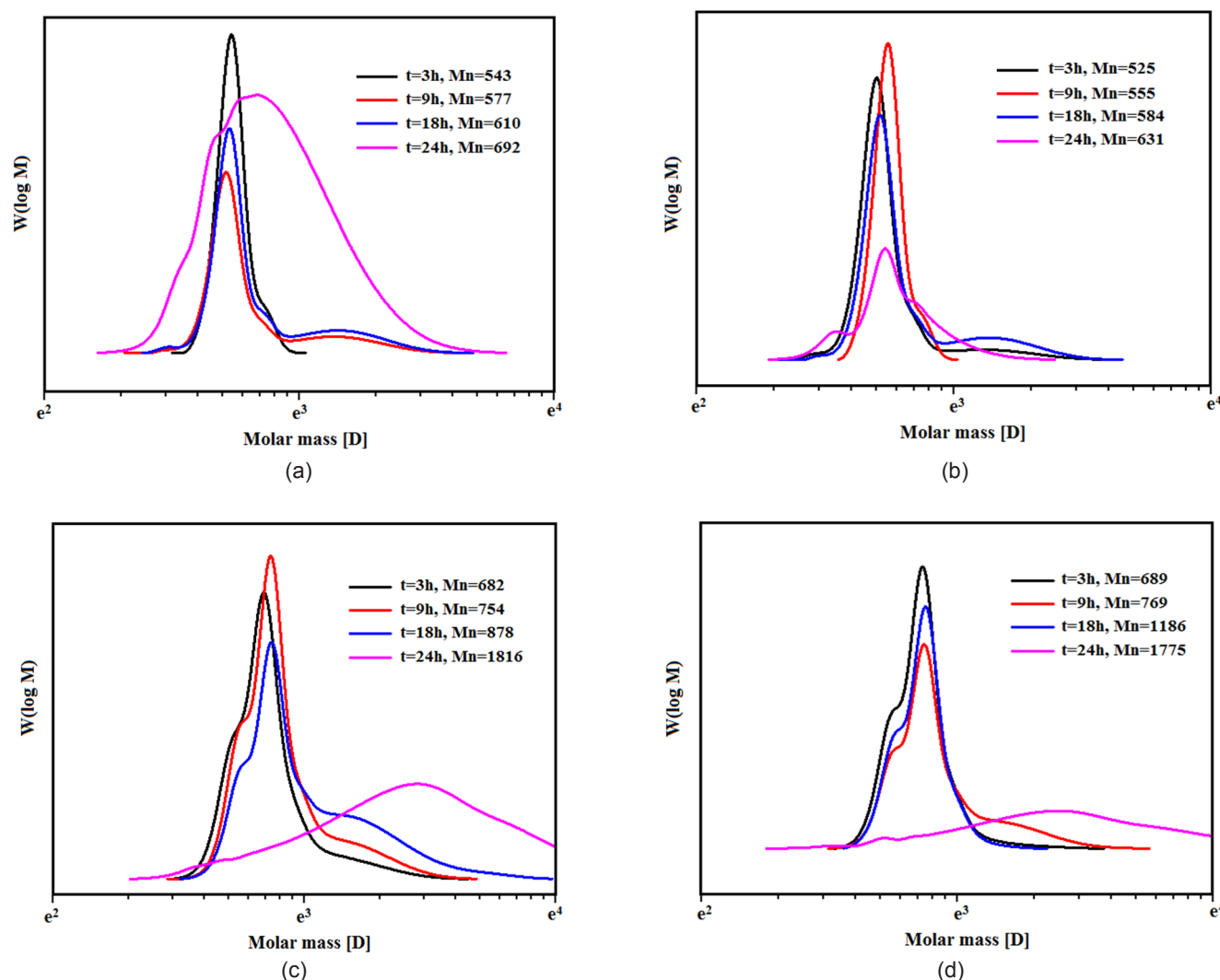

Figure 5. GPC curves of the obtained oligomers from (a) Cp_2ZrCl_2 catalyst, [cat]= 10 μmol, [1-hexene]= 0.08 mol, Al/M= 500, T=80°C; (b) Cp_2ZrCl_2 catalyst, [cat]= 10 μmol, [1-octene]= 0.08 mol, Al/M= 500, T=80°C; (c) Cp_2HfCl_2 catalyst, [cat]= 10 μmol, [1-hexene]= 0.08 mol, Al/M= 500, T=80°C; (d) Cp_2HfCl_2 catalyst, [cat]= 10 μmol, [1-octene]= 0.08 mol, Al/M= 500, T=80°C.

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It was accepted that the vinylidene production rate is independent of [monomer], and the vinylene production rate is first order with respect to [monomer] [19]. According to Equation 5 and using the calculated values of k_i, the $k_{vinylidene}$ and $k_{vinylene}$ values were obtained. However, these results suggest that $k_{vinylidene}$ is smaller in the case of oligomers produced with the hafnocene-based catalyst than in the oligomers produced with the zirconocene-based one. However, the value of $k_{vinylene}$ is bigger in the case of hafnocene-based catalyst than in the oligomers produced with the zirconocene-based one.

$$\frac{\partial[\text{end group}]}{\partial} \quad (5)$$

$$k\,[1]\,\left(t + \frac{1}{k_i[1-decene]_0}e^{-k\,[1-decene]\,t} - \frac{1}{k_i[1-decene]_0}\right)$$

$$\text{Propvs term}\;\frac{\text{rate}1,2-ins}{\text{rate}1,2-term} \approx \frac{k_p[C^*][M]}{k_{vinylidene}[C^*]} = \frac{k_p[M]}{k_{vinylidene}} \quad (6)$$

Where, [M] = [monomer] and [C*] = concentration of the primary active catalyst.

The tendency of the catalyst systems toward 1-hexene and/or 1-octene oligomerization to produce longer or shorter chains can be obtained by Equation 6. According to this formula, $k_p/k_{vinylidene}$ concept is an indication of the length of the synthesized oligomers (the GPC results of the synthesized oligomers in different oligomerization times are presented in Figures S9-S24 in Supporting Information). Based on the results, it can be concluded that hafnocene catalyst produces longer chains than zirconocene, which is a confirmation of GPC analysis (Figure 5). It can be suggested that the sustainability of the 6s orbital and a stronger sigma bond between Hf and C can be responsible for the observed behavior [3].

In order to estimate mis-inserted monomers amounts, Equation 7 is introduced.

% mis insertion ≈

$$\frac{2,1-ins}{\text{all ins}} \approx \frac{[C^*][M]k_{mis}}{[C^*][M](k_p+k_{mis})} = \frac{k_{mis}}{k_p+k_{mis}} \quad (7)$$

Where, [M] = [monomer], and [C*] = concentration of the primary active catalyst.

The mis-insertion percentages of oils produced by the two catalysts used are listed in Table 3. According to the results, the rates of mis-insertions of the two catalyst systems are lower than their propagation rate. Meanwhile, the zirconocene catalyst showed lower degree of mis-insertions percentage [19]. Pino and coworkers showed that in the oligomerization of α-olefins, monomer insertion reaction usually proceeds by 1,2-insertion pathway in the case of Zr-based one, and subsequently after an occasional 2,1 insertion, the chain growth is terminated by hydrogen with the creation of end group structure [33].

CONCLUSIONS

To better understand the effect of the metallocene type catalysts on the higher α-olefins oligomerization behaviors, a comprehensive kinetic study has been conducted on the 1-hexene and 1-octene systems catalyzed by Cp_2ZrCl_2 and Cp_2HfCl_2/MAO at temperature of 80°C. The correlation between the viscosity measurements and the microstructure of the synthesized oligomers was demonstrated by the branching ratio and short-chain branching percentages data. The obtained kinetic results enabled us to provide a mechanism of 1-hexene/1-octene oligomerization for each catalyst system, which consists of initiation, propagation, monomer mis-insertion and chain transfer steps.

ACKNOWLEDGEMENTS

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