

Synthesis and Characterization of Oligomer from 1-Decene Catalyzed by $\text{AlCl}_3/\text{TiCl}_4/\text{SiO}_2/\text{Et}_2\text{AlCl}$

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ABSTRACT: Oligomer of 1-decene was synthesized with Ziegler-Natta catalyst consisting of TiCl_4 , AlCl_3 , Et_2AlCl , and SiO_2 used as support. The effects of temperature, time, ratio of Al/Ti, and concentration of Ti on oligomerization behaviors were investigated. The results showed that the catalyst system was desirable for oligomerization of 1-decene with good catalytic activity, 153.4 kg oligomer/mol Ti h, under typical conditions. The oligomer obtained was characterized with GC-MS, GC, and ^{13}C NMR methods. The

results indicated that the oligomer was of a mixture consisting of di-, tri-, tetra-, and pentamer. The ^{13}C NMR data also implied that chain propagation of this oligomer involved primarily head-to-tail 1, 2-insertions, as well as head-to-head and tail-to-tail 2, 1-insertions. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 584–590, 2006

Key words: supported Ziegler-Natta catalyst; 1-decene; oligomerization; characterization

INTRODUCTION

Many efforts to improve upon the performance of natural mineral oil based lubricants by the synthesis of oligomers from linear superior α -olefins, for example 1-decene, have been the subject of important research and development in the petroleum industry for decades and have resulted in the relatively recent market introduction of a number of polyalpha-olefin (PAO) synthetic lubricants. Synthetic lubricant from 1-decene features stable viscosity over a wide range of temperature, chemical stability, and low pour point when compared with mineral oil. The synthetic lubricant exhibits lower friction and hence increases mechanical efficiency across the full spectrum of mechanical loads from worm gears to traction drives and does so over a wider range of operating conditions. It also features excellent compatibility with mineral oil and/or grease and nontoxic to human being.

Largely because of investigations^{1–3} on the polymerization of propylene and vinyl monomers, the mechanism of the polymerization of α -olefins and the effect of that mechanism on polymer structure is reasonably well understood, providing a strong resource for targeting on potentially useful oligomerization methods

and oligomer structures. Commercially useful synthetic lubricants have been prepared from 1-decene prompted by either cationic or Ziegler catalysts and others.

Oligomerization of 1-decene is usually performed in the presence of a Lewis Acid catalyst such as boron trifluoride (BF_3)⁴ or aluminum chloride,⁵ coupling with higher conversion of greater than 90% to monomer.

Novel high viscosity index (VI) lubricant comprising PAOs have been synthesized with reduced chromium oligomerization catalyst on porous silica support.^{6,7} This lubricant obtained has branch ratio less than 0.19, not only comprising the product of an essentially regular head-to-tail PAO but also providing an oligomer with large pendant alkyl groups on the recurring polymeric unit.

One characteristic of the molecular structure of 1-alkene oligomers that has been found to correlate with improved lubricant properties in commercial synthetic lubricants is the ratio of methyl to methylene groups in the oligomer. The ratio is called the branch ratio and is calculated from infrared data. Herein branch means that methyl side groups are methyl groups which occupy positions other than the terminal positions of the first and last (i.e., α and ω) carbon atoms of the longest carbon chain. This longest carbon chain is also referred to herein as the carbon backbone chain of the olefin.^{8–10}

Oligomers prepared from 1-decene by cationic polymerization have branch ratios of greater than 0.20.

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But those prepared by chromium or Ziegler catalyst have lower branch ratios. Whether by rearrangement or isomerization, it is clear that synthetic lubricant with branch ratio leads to the limits of achievable properties, particularly with respect to viscosity index and pour point obviously. Viscosity index was found to increase with lower branch ratio, but pour point was decreased.^{11,12}

The treatment of BF_3 remained in oligomers is difficult. In factory, a special equipment is required to handle it. Not only is BF_3 harmful to vessel and other equipment, but it can result in lung and eye problems.

Although, in a view foregoing, reduced chromium compound is perfect for oligomerization of 1-alkene, it becomes oxidized when exposed to air. Oxidized chromium is very harmful to human beings and the environment. In addition, chromium compounds can be deposited in animal bodies, fruits, and vegetables, which are essential food to people.

Fortunately, Ziegler-Natta catalyst can resolve those above-mentioned problems. It can not only be a friendly catalyst to human beings and environment, but also shows higher catalytic activity for oligomerization of 1-alkene as well, in addition to commercial attractions, many studies have been done on the oligomerization of 1-alkene and vinyl monomers prompted by Ziegler-Natta catalysts. So far, homogeneous processes predominate because of better catalytic activity shown for oligomerization of 1-alkene. But the work after polymerization is complicated. So heterogeneous processing, which would show higher catalytic activity for oligomerization of 1-alkene, certainly has more attraction to industry because of simple performance after polymerization. Herein we report an efficient heterogeneous processing for oligomerization of 1-decene catalyzed by Ziegler-Natta catalyst. The effects of the oligomerization conditions on the catalytic activity as well as the structure of oligomer obtained are investigated.

EXPERIMENTAL

Materials

All procedures were carried out under nitrogen atmosphere in Schlenk flasks. Toluene and hexane were refluxed from metallic sodium under nitrogen for 12 h and distilled before use. Diethylaluminum chloride (AlEt_2Cl) and triethylaluminum solution in *n*-heptane (400 g/L) was purchased from Aldrich; Silica (Grade 955) was calcinated under nitrogen flow at 200°C for 2 h, 600°C for 4 h prior to use; anhydrous aluminum trichloride (AlCl_3) was purchased from Aldrich and treated under the same conditions as silica; 1-decene was also purchased from Aldrich and was distilled and collected the fraction of 58–62°C under vacuum before use. The other chemicals were purchased commercially and used without further purification.

Preparation of $\text{TiCl}_4/\text{AlCl}_3/\text{SiO}_2$ supported catalyst

Excess TiCl_4 (5.0 mL) was dropped with a syringe for 30 min to the mixture of SiO_2 (5.0 g) and measured amount of AlCl_3 suspended in 50 mL heptane under well-stirred condition at 0°C, then warmed to room temperature. The mixture was stirred overnight. After filtering, the residue was washed with heptane (30 mL \times 5) and dried under vacuum. The supported $\text{TiCl}_4/\text{AlCl}_3/\text{SiO}_2$ catalyst was obtained as beige color. Ti content was 4.22% determined by ICP-AES. About 10 mg of the supported catalyst was dissolved with HF and HNO_3 acid completely. The solution was diluted with distilled water and used for the ICP analysis.

Oligomerization

All performances were carried out in a 200 mL autoclave glass reactor equipped with a mechanical stirrer. After purging out all moisture and oxygen by a high-vacuum pump, the reactor was sealed under nitrogen atmosphere. Fresh required amounts of AlEt_2Cl , supported catalyst and toluene (20 mL) was introduced in this order, and the mixture was stirred for 15 min for preactivation. After that, 20 mL of 1-decene was added. Hydrogen was added as appropriate by syringe. The pressure was maintained at 0.3 MPa throughout the course of the reaction under nitrogen atmosphere. The polymerization was stopped after 1 h at selected temperature and then terminated by addition of acidified alcohol. After filtering, the residue was washed with alcohol. The filtrate was concentrated under constant pressure and then heated under vacuum to remove the remaining monomer. The fraction from 90 to 160°C was collected under vacuum, which was of 1-decene oligomers consisting of di-, tri-, tetra-, and pentamer. The residue after distilling comprised of polymer with higher polymerization degree was stick-like paraffine which was characterized with different methods. We will report the work in other article. The conversion and the catalytic activity of PAO formation was calculated by the weight of fraction distilled and residue to monomer weight, while the conversion and the catalytic activity of oligomer formation was calculated by the weight of fraction distilled to monomer weight.

Characterization

Gas chromatography–mass spectrometry (GC–MS) was performed on HP-6890GC-5973MSD. A fused-silica capillary column DB-5 MS (30 m \times 0.25 mm, 0.25 μm film thickness) was used. Helium and methane were used as the carrier and the reagent gas, respectively, for negative-ion chemical ionization. The following oven temperature program was used. Two minutes at 70°C, then an increase to 100°C at a rate

TABLE I
The Effect of Temperature on the Oligomerization of 1-Decene Promoted by $\text{AlCl}_3/\text{TiCl}_4/\text{SiO}_2/\text{Et}_2\text{AlCl}$

Run	<i>T</i> (°C)	PAO ^a (g)	Oligomer ^b (g)	Conversion ^c (%)	Conversion ^d (%)	Oligomer analysis (%) ^e			
						Di-	Tri-	Tetra-	Penta-
1	30	9.1	3.5	61.5	23.6	9	28	32	31
2	50	12.6	7.7	85.1	52.0	14	36	39	11
3	60	14.5	11.2	98.0	75.7	18	45	31	6
4	70	14.1	10.4	95.3	70.3	25	43	29	3
5	80	13.2	9.6	89.2	64.9	28	44	25	3
6 ^f	60	14.4	11.1	97.3	75.0	19	46	29	6

Oligomerization conditions: catalyst: Ti, 7.3×10^{-2} mmol; 1-decene, 20 mL (14.8 g); solvent: toluene, 20 mL; time: 1 h; Al (AlEt_2Cl)/Ti ratio, 30; $\text{AlCl}_3/\text{SiO}_2$, 5/100 (wt/wt).

^a The total weight of products (g).

^b The weight of oligomers (g).

^c The conversion of PAO to monomer.

^d The conversion of oligomers to monomer.

^e Determined by GC.

^f Solvent: heptane, 20 mL.

10°C/min, followed by an increase to 300°C at a rate of 30°C/min for 1 h. The injection port of the GC was set at 300°C. The energy of 70 eV was used for electron ionization. When solvent comes off the GC column and hits the MS detector, the concentration of the solvent can be so high that it is destructive to the instrument. To prevent this from happening, the detector is programmed to be turned off during the time when the solvent hits the detector. The maximum molecular weight that can be detected by this GC–MS instrument is ~500 Da.

Gas chromatography (GC) was recorded on AGILENT-6890. A fused-silica capillary column DB-5 MS (30 m \times 0.25 mm, 0.25 μm film thickness) was used. Nitrogen was used as the carrier. The column temperature program was set from room temperature to 100°C at a rate 10°C/min, followed by an increase to 300°C at a rate of 30°C/min for 1h. The injection port of the GC was set at 320°C.

Carbon nuclear magnetic resonance, ^{13}C NMR spectra, of oligomer samples were obtained on an INOVA500 MHz instrument. The conditions used for quantitative ^{13}C NMR were 15 wt % sample in benzene- d_6 , at room temperature, 90° pulse angle, inverse-gated decoupling with a 3 s delay between pulses, 1000 scans, tetramethylsilane as internal reference.

RESULTS AND DISCUSSION

Oligomerization temperature

The effect of temperature on 1-decene oligomerization behaviors was investigated and the data is shown in Table I. One can notice that the highest conversion of 98.0% and 75.7% for PAO formation and for oligomer formation were obtained at 60°C, respectively. The conversion of oligomer formation increased with the increase in temperature until 60°C, for instance, the

conversion of 23.6% was obtained at 30°C, the greatest conversion 75.7% obtained at 60°C. However, the temperature was over 60°C, the conversion was slightly decreased, for example, 64.9% obtained at 80°C. Warm heating is possible of benefits to chain propagation to obtain more amount of oligomer and of PAO. But higher temperature usually resulted in species deactivated in coordination polymerization.^{10–12} The percentage of dimer increased with the increase in temperature, but percentage of pentamer decreased (run 1–5 in Table I). It was possible that the chain transfer took place easily at higher temperature. One can find that heptane was also good solvent for this reaction, the conversion of PAO formation and of oligomer formation were not changed obviously when heptane was instead of toluene as solvent (run 6 in Table I) at the same conditions, 97.3% and 75.0% were obtained, respectively.

Al/Ti ratio

The effects of Al (alkyl aluminum)/Ti ratio on oligomerization behaviors of 1-decene are shown in Table II. The supported catalyst exhibited the highest catalytic activity, 153.4 kg oligomer/mol Ti h for oligomer formation and 198.6 kg PAO/mol Ti hr for PAO formation at Al (alkyl aluminum)/Ti = 30 (mol/mol) (run 3 in Table II). The catalytic activities, however, were decreased regardless of the increase or decrease in Al/Ti ratio (runs 7, 8, 9 and 10 in Table II). But the catalytic activity did not decrease sharply when Al/Ti was even up to 50 (run 10 in Table II). It was possible that β -hydrogen elimination was predominated as the pathway of chain transfer rather than alkyl aluminum for 1-decene oligomerization.

It was found that the amount of AlCl_3 obviously influenced 1-decene oligomerization (runs 11, 12, 3

TABLE II
The Effects of Al/Ti Ratio and the Amount of AlCl₃ on 1-Decene Oligomerization Catalyzed by AlCl₃/TiCl₄/SiO₂/Et₂AlCl

Run	Al/Ti (mol/mol)	AlCl ₃ ^a (wt %)	PAO (g)	Oligomer (g)	Activity ^b (kg PAO/(mol Ti h))	Activity ^c (kg olig/(mol Ti h))	Oligomer analysis ^d (%)			
							di-	tri-	tetra-	penta-
7	10	5	9.21	6.81	126.2	93.3	12	20	31	37
8	20	5	11.9	8.53	163.0	116.8	16	26	35	23
3	30	5	14.5	11.2	198.6	153.4	18	45	31	6
9	40	5	13.6	10.5	186.3	143.8	19	48	29	4
10	50	5	12.6	9.32	172.6	127.7	25	40	29	6
11	30	3	13.1	9.70	179.4	132.9	15	40	36	9
12	30	4	14.0	10.8	191.8	147.9	14	42	35	9
13	30	6	14.4	11.0	197.3	150.7	16	40	29	15

Oligomerization conditions: catalyst: Ti, 7.3×10^{-2} mmol; *T*, 60°C; 1-decene, 20 mL (14.8 g); solvent: toluene, 20 mL; time: 1 h.

^a The percentage of AlCl₃ to SiO₂ (wt/wt).

^b The catalytic activity for PAO.

^c The catalytic activity for oligomers formation.

^d Determined by GC.

and 13 in Table II). It was possible that TiCl₃ with γ -crystal formation resulted from TiCl₄ treated with AlCl₃. γ -TiCl₃ was favorable for oligomerization of 1-decene; on the other hand, AlCl₃, lewis acid, withdrew partially charge from Ti—C and C—H bond, which favored oligomerization of olefins and led to regiostructure of oligomer or polymer obtained.¹³

Ti concentration

The effects of Ti concentration on 1-decene oligomerization are shown in Figure 1. The catalytic activity for 1-decene polymerization decreased obviously with the increase in Ti concentration (curve a in Fig. 1). The

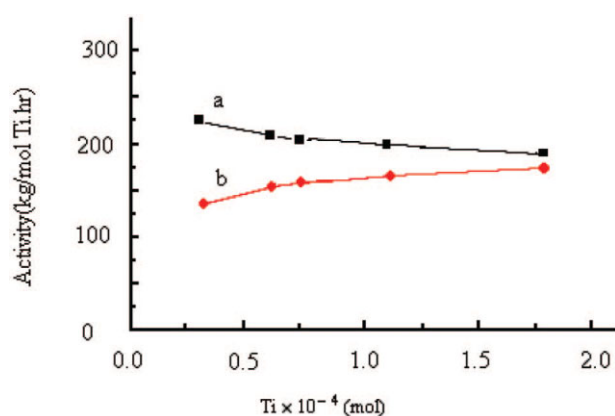


Figure 1 The effect of Ti concentration on catalytic activity of 1-decene oligomerization catalyzed by AlCl₃/TiCl₄/SiO₂/Et₂AlCl. Oligomerization conditions: Al/Ti ratio, 30; AlCl₃/SiO₂, 5/100 (wt %); *T*, 60°C; 1-decene, 20 mL; solvent, toluene (20 mL); time, 1 h. (a) The catalytic activity for PAO; (b) the catalytic activity for oligomer of 1-decene. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

catalytic activity of 225 kg PAO/mol Ti h was obtained at Ti being 2.6×10^{-5} mol, however, 180 kg PAO/mol Ti h obtained when Ti concentration was up to 1.8×10^{-4} mol.

But the catalytic activity for oligomerization of 1-decene was slightly increased with increase in Ti concentration (curve b in Fig. 1). The catalytic activity of 125 kg oligomer/mol Ti h was obtained at Ti being 2.6×10^{-5} mol, and it was increased to 168 kg oligomer/mol Ti h when Ti concentration was up to 1.8×10^{-4} mol.

Oligomerization time

The effect of oligomerization time on catalytic activity is shown in Figure 2. It can be noted that the catalytic activity for PAO decreases with increase in oligomerization time. The catalytic activity for PAO was reduced from 207.3 kg PAO/mol Ti h in 20 min to 198.6 kg PAO/mol Ti h in 60 min and to 170.1 kg PAO/mol Ti h in 150 min (curve a in Fig. 2). But the catalytic activity for oligomer of 1-decene obviously decreased with increase in time. It was reduced from 171.3 kg oligomer/mol Ti h in time 20 min to 153.4 kg oligomer/mol Ti h in 60 min and to 90.8 kg oligomer/mol Ti h in 150 min (curve b in Fig. 2).

Oligomer component

The GC–MS results of oligomer (run 3 in Table I) were shown in Figure 3. One noted that the oligomer was of a mixture consisting of four fractions that the elution time were 17.5 min, 30.2 min, 33.4 min and 41.3 min, respectively. The MS analysis confirmed that the first fraction, elution time about 17.5 min was dimer because of $M^+ = 281 [M + H]$, the molecular weight was

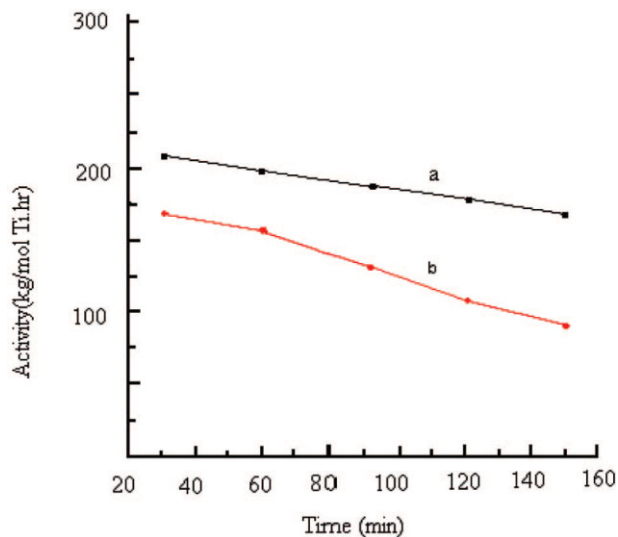


Figure 2 The effect of oligomerization time on catalytic activity of 1-decene oligomerization catalyzed by $\text{AlCl}_3/\text{TiCl}_4/\text{SiO}_2/\text{Et}_2\text{AlCl}$. Oligomerization conditions: catalyst (Ti), 7.3×10^{-2} mmol; Al/Ti ratio, 30; T , 60°C ; $\text{AlCl}_3/\text{SiO}_2$, 5/100 (wt %); 1-decene, 20 mL; solvent, toluene (20 mL). (a) The catalytic activity for PAO; (b) the catalytic activity for oligomer of 1-decene. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

just two times as that of 1-decene. The second fraction, $M^+ = 421$ [$M + H$], was trimer. The tetramer and pentamer M^+ was not obtained because of the maximum molecular weight of the GC-MS instrument is 500 Da. By deducing, the third and the fourth fraction, elution time about 33.4 and 41.3 min, were tetra- and

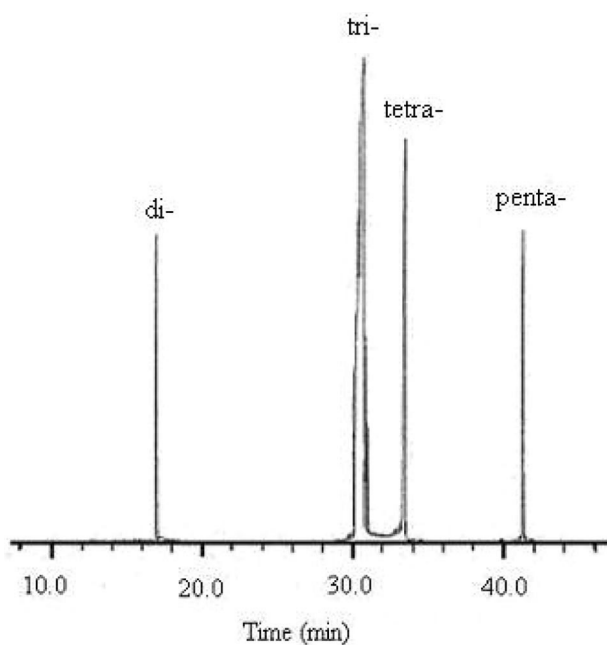


Figure 3 The GC spectrum of oligomer of 1-decene (run 3 in Table 1).

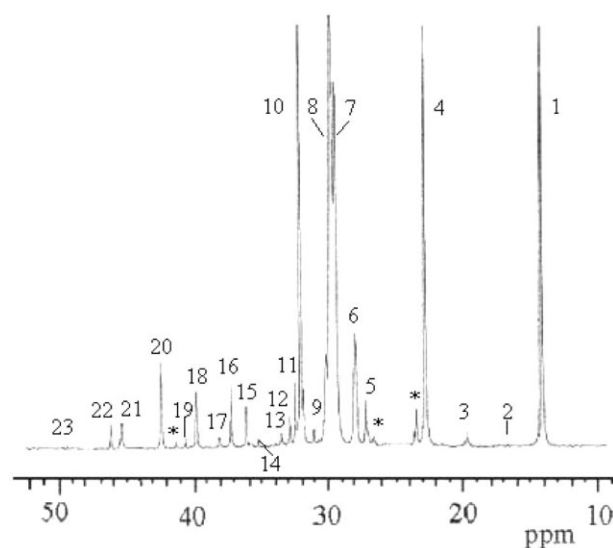


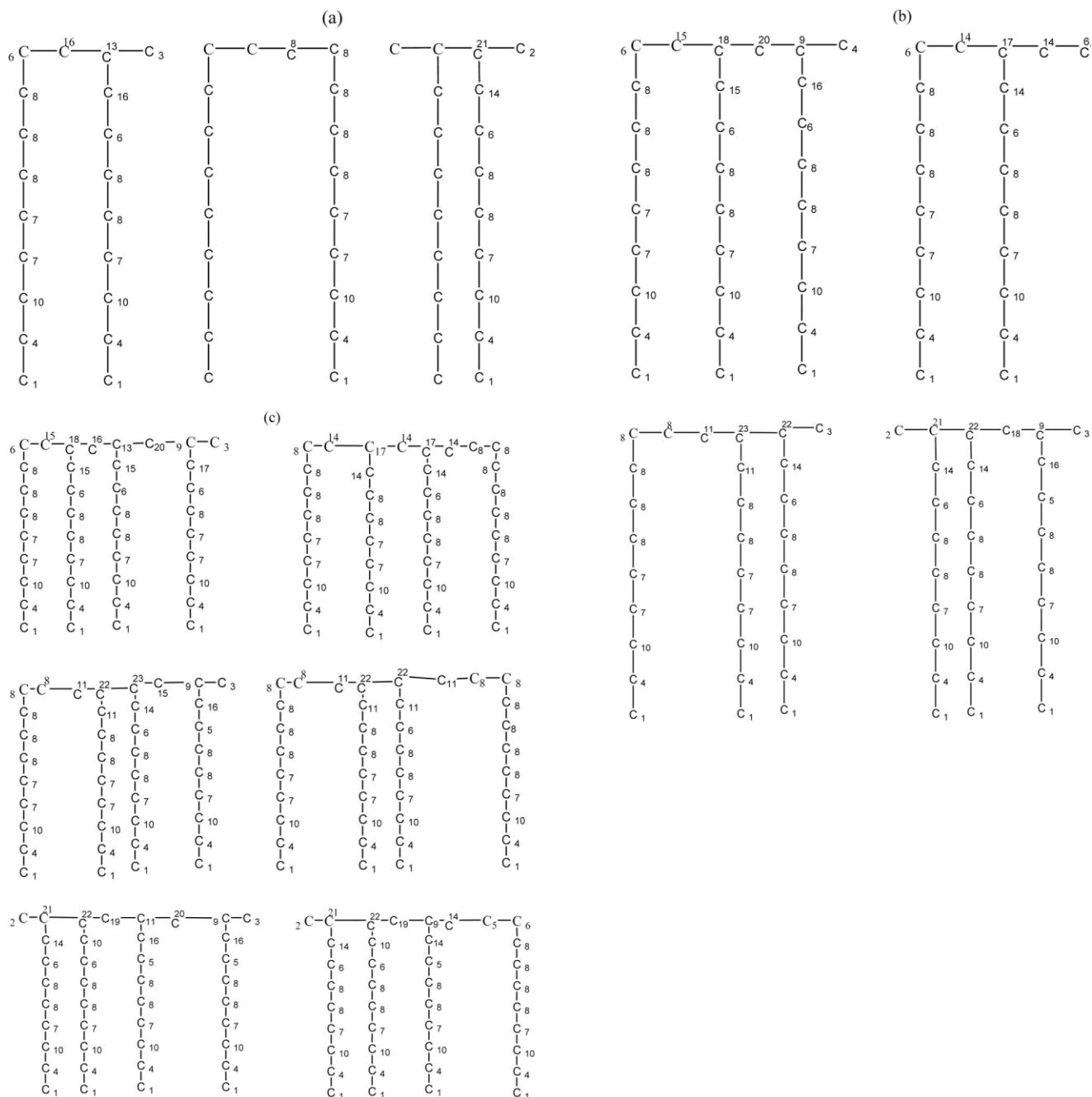
Figure 4 The ^{13}C NMR spectrum of oligomer of 1-decene (run 3 in Table 1).

pentamer, respectively. By contrast, the elution time of the monomer, 1-decene was 13.2 min. The amount of oligomers of 1-decene obtained was determined by GC instrument.

Microstructure

The microstructures of oligomers obtained with catalyst $\text{AlCl}_3/\text{TiCl}_4/\text{SiO}_2/\text{AlEt}_2\text{Cl}$ were analyzed by ^{13}C NMR (Fig. 4). From Figure 4 one can note that the ^{13}C NMR results confirmed that the oligomer contained regioirregular structures and a nonnegligible proportion of 1-decene units arranged in tail-to-tail and head-to-head sequences was observed. Any signals of residue from cocatalyst and of double bond in oligomer were not observed from ^{13}C NMR spectra. The result indicated that the chain transfer to hydrogen was predominated, while the chain transfer to cocatalyst and β -hydrogen elimination were negligible.

The regiostructures and assignments of ^{13}C NMR of di-, tri-, and tetra- of 1-decene were compiled in Scheme 1. The subscript numbers in Scheme 1 were referred to Figure 4. The calculation of theoretical chemical shifts was referenced with Grant and Paul¹⁴ and previous works.^{15–17} For dimers of 1-decene, three kinds of sequences, head-to-tail (HT), tail-to-tail (TT) and head-to-head (HH), were possible produced. tertiary carbons $T_{\alpha\omega}$ (HT) and $T_{\alpha\beta}$ (TT) were identified by the presence of the resonances at δ 33.32 and 45.25 ppm, labeled with the number 13 and 21 in Figure 4 and Scheme 1(a). For trimers, four sequences could be obtained [Scheme 1(b)]. One of them, head-to-tail (HTT) sequence existed two kinds of tertiary carbons in backbone, $T_{\beta\beta}$ and $T_{\beta\omega}$ assigned at δ 30.96 and 36.15 ppm and labeled by 9 and 15 in Figure 4 and Scheme 1b.



Scheme 1 (a) Dimers of oligomer from 1-decene; (b) trimers of oligomer from 1-decene; (c) tetramers of oligomer from 1-decene.

$T_{\omega\omega}$ at δ 38.10 ppm was attributed to the tertiary carbon of $\llcorner\llcorner$; $T_{\omega\omega}$ and $T_{\alpha\beta}$ at δ 46.31 and 49.30 ppm to \llcorner ; $T_{\beta\alpha}$, $T'_{\alpha\beta}$, $T'_{\beta\beta}$ at δ 45.25, 46.31 and 30.96 ppm to \llcorner sequences, labeled by 17, 22, 23, and 9, respectively. Six kinds of sequences for tetramers could be obtained (Scheme 1c). Tertiary carbons $T_{\alpha\beta'}$, $T_{\beta\beta'}$ and $T'_{\beta\beta}$ at δ 39.75, 33.32, and 30.95 ppm were attributed to $\llcorner\llcorner\llcorner$ sequence. $T_{\beta\omega}$ at δ 38.10 ppm to $\llcorner\llcorner$, $T_{\alpha\omega'}$, $T_{\alpha\beta'}$ and $T_{\beta\beta}$ at δ 46.31, 49.30, and 30.95 ppm to $\llcorner\llcorner$, $T_{\alpha\omega}$ at δ 46.31 ppm to $\llcorner\llcorner$, $T_{\beta\alpha}$, $T_{\alpha\beta'}$, $T_{\beta\beta'}$ and $T'_{\beta\beta}$ at δ 45.25, 46.31, 32.30, and 30.95 ppm to $\llcorner\llcorner$, $T_{\beta\alpha}$, $T_{\alpha\beta'}$ and $T_{\beta\omega}$ at δ

45.25, 46.31, and 30.95 ppm to $\llcorner\llcorner$ sequences, respectively. Methyl and ethyl carbons were assigned in Figure 4 and labeled in Scheme 1. The regiostructures of pentamer, however, were not listed in Scheme 1, because the same of assignments as that of tetramers were revealed by calculation according to Grant method.¹⁴

CONCLUSIONS

$\text{AlCl}_3/\text{TiCl}_4/\text{SiO}_2/\text{AlEt}_2\text{Cl}$ supported catalyst exhibited higher catalytic activity for 1-decene oligomeriza-

tion. Addition of AlCl_3 , $\text{AlCl}_3/\text{SiO}_2 = 5\%$ (wt/wt), improved the catalytic activity for oligomerization of 1-decene. Other nonpolar solvent, however, heptane was also favorable for oligomerization of 1-decene. Other oligomerization conditions such as temperature, Al/Ti ratio, Ti concentration and time showed considerable effects on catalytic activity and component of oligomers. The activity of 153.4 kg oligomer/mol Ti h for oligomer formation was obtained under the typical conditions of Al/Ti ratio 30, Ti concentration 7.3×10^{-2} mmol/L, temperature 60°C and time 1 h. ^{13}C NMR result confirmed the regiostructures of oligomers from 1-decene catalyzed by $\text{AlCl}_3/\text{TiCl}_4/\text{SiO}_2/\text{AlEt}_2\text{Cl}$ catalyst.

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