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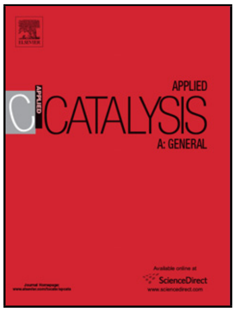

Title: Structurally uniform 1-hexene, 1-octene, and 1-decene oligomers: zirconocene/MAO-catalyzed preparation, characterization, and prospects of their use as low-viscosity low-temperature oil base stocks

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Structurally uniform 1-hexene, 1-octene, and 1-decene oligomers: zirconocene/MAO-catalyzed preparation, characterization, and prospects of their use as low-viscosity low-temperature oil base stocks

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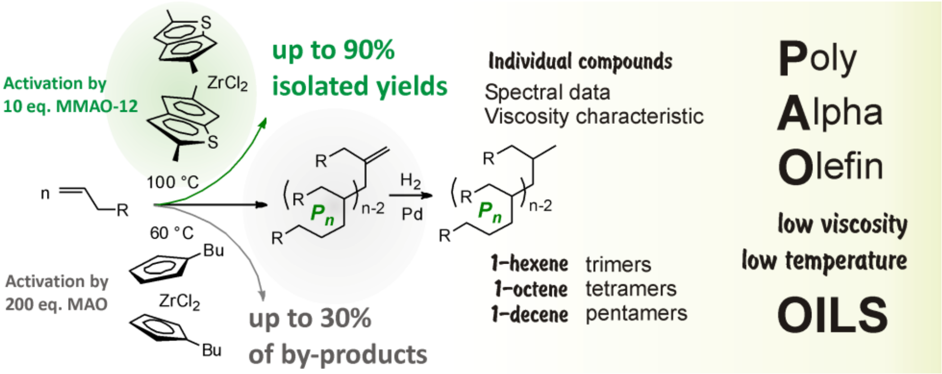
Graphical Abstract



Highlights

- Heterocene activated by 10 eq. of MAO is effective in α-olefin oligomerization
- Up to 90% isolated yields of lightweight α-olefin oligomer fractions were achieved
- Unsaturated and saturated α-olefin oligomers were isolated as individual compounds
- Hydrogenated 1-octene and 1-decene oligomers outperformed conventional PAOs

Abstract

An original approach to α-olefin oligomerization as well as novel thermally stable zirconocene catalysts for use in such reactions has been elaborated. The method reported allows the achievement of fractions of lightweight α-olefin oligomers up to 90% yields without considerable formation of byproducts like internal alkenes, alkanes, and higher oligomers. Trimers, tetramers, and pentamers of 1-hexene, 1-octene, and 1-decene were isolated as individual compounds and were hydrogenated. Viscosity characteristics of the isolated saturated and unsaturated hydrocarbons have been studied at various temperatures. The isolated saturated oligomers of 1-octene and 1-decene outperform the traditional electrophilic oligomerization products in terms of viscosity indexes, pour points, and low-temperature viscosity.

Keywords: α-olefins, oligomerization, zirconocenes, oil base stocks, viscosity

1. Introduction

Saturated high-boiling hydrocarbons are traditionally used as base stocks of engine oils and lubricants. Hydrocarbon-based oils can be divided into four groups of products [1]. Group I represents the dewaxed and deasphalted crude oil fractions, whose catalytic hydrogenation leads to Group II oils. Group III represents *semi-synthetic* oils produced by the catalytic hydrocracking of higher crude oil distillates. This process is accompanied by partial transformation of linear paraffins into branched saturated hydrocarbons. Group IV represents *fully synthetic* oils, which comprise the hydrogenated α-olefin oligomers. Compounds that belong to this group are generally called poly-alpha-olefin (PAO) oils or PAOs. High-quality engine oil should have moderate viscosity at low temperatures, which is necessary for a safe "cold start" of the engine. The reliability of engine oil at low temperatures is characterized in terms of the pour point (PP) and kinematic viscosity at −40 °C (KV^{-40}). At the same time, engine oil should remain viscous at working engine temperatures to minimize friction and engine aging. A commonly accepted quantitative characteristic that describes the dependence of oil viscosity on the temperature is the viscosity index (VI), which is determined by a standard method, ASTM D-2270, in which the values of kinematic viscosity of an oil at 40 °C (KV^{40}) and 100 °C (KV^{100}) are compared against the viscosities of two reference oils.

It was found that the PP and VI values of oils depend strongly on the architecture of the constituent hydrocarbons [2–5]. Long, linear hydrocarbons, petroleum waxes (Fig 1A), present in high quantities in Group I and II oils, are characterized by high PPs. It is for this reason that Group I and II oils cannot be used at low temperatures. Group III oil base hydrocarbons, which contain compounds with short branches (Fig 1B) and cycloalkanes (Fig 1C), also have relatively high PP and KV^{-40} values. On the other hand, long-chain branched hydrocarbons (Fig 1D) are characterized by low PPs and high VIs. Oligomerization of α-olefins followed by hydrogenation is the only way to obtain hydrocarbons with the structure type D [3]. An important aspect of PAO use is their biodegradability, which is also dependent from the hydrocarbon molecular structure. It has been determined [6] that the presence of quaternary carbon atoms blocks the oxidative breakdown of hydrocarbons in surrounding media. It has been reported [7] that PAOs based on 1-decene are characterized by satisfactory biodegradability, surpassing that of Group III oils. Therefore, structural type D offers prospects in minimizing the environmental impact of the use of PAOs.

Compounds of the structural type D are targeted for Group IV base stock synthesis *via* α-olefin oligomerization. However, bulk scale production of low-viscosity PAOs utilizes electrophilic catalysis with significant skeletal isomerization (Scheme 1a). In particular, many methyl groups are generated at random positions along the carbon chain with formation of type B structures [4,5,8]. In some cases, alicyclic type C products are formed [9–11]. These skeletal isomerizations lead to complex hydrocarbon mixtures containing spillover components having lower viscosity indexes than those of targeted type D hydrocarbons. An alternative approach to olefin oligomer synthesis is based on coordination polymerization. Various catalytic systems using this process have been studied. It has been determined that coordination oligomerization in the presence of heterogeneous titanium–aluminum [12,13] and chromium [14] Ziegler–Natta catalysts is also accompanied by skeletal rearrangements. Isomerization of the skeleton has been observed even for oligomerization catalyzed by dimethylzirconocenes, activated by perfluoroborates [15], and post-metallocene catalysts [16–18].

It was found that undesirable side reactions are minimal for oligomerization of α-olefins when the process is catalyzed by zirconocene dichlorides ($LZrCl_2$) activated by methylalumoxane (MAO) [19–22]. In this case, chain growth occurs only by 1,2-insertions and the chain terminates by β-hydride elimination or β-hydride transfer. As a result, the products of this process characterized by Flory-Shultz distribution are vinylidene-type α-olefin oligomers with uniform molecular structures (Scheme 1b). Vinylidene dimers of α-olefins are not suitable for use as oil base stocks because of their low VI and high PP. However, they can be transformed into hydrocarbons structurally similar to type D species by electrophilic dimerization (Scheme 1c) [23].

To date, vinylidene dimers of 1-hexene, 1-octene, and 1-decene have been isolated and characterized [23–26]. Higher α-olefin oligomers prepared by single-site catalysis have been usually isolated in the form of mixtures with a large P_n range [26–32]. Thus, the characteristics of individual oligomers and hydrogenated oligomers of 1-hexene, 1-octene, and 1-decene as a components of PAO base stocks are currently unknown. The determination of these characteristic remains a fundamental issue.

The main practical issue of zirconocene catalysis of α-olefin oligomerization to obtain type D hydrocarbons lies in reaching the maximum isolated yield of dimers and lower oligomers, corresponding to a degree of oligomerization $P_n = 2$ and 3–5, respectively. The problem in the selective synthesis of α-olefin *dimers* ($P_n = 2$) has been successfully solved by using low Al_{MAO}/Zr ratios (1–10 by mol) and zirconocene catalysts of specific structural types. It was reported that zirconocene dichloride $(\eta^5\text{-}C_5H_5)ZrCl_2$ (**1**) [24–27], ring monosubstituted zirconocenes [29], and *ansa*-complexes $Z(C_5H_4)_2ZrCl_2$ [33] selectively dimerize α-olefins in the presence of a minimal excess of MAO activator to produce dimers of the vinylidene structure (Scheme 1). It has been found that an increase in the Al_{MAO}/Zr ratio for reactions of **1**, $(\eta^5\text{-}C_5H_4R)ZrCl_2$, and certain ring disubstituted zirconocenes leads to the growth of the proportion between the contents of lower oligomers and dimers, which can reach ~1:1 [26,29,31,34,35]. Basing on GC data, Kissn and Schwab [23,36] reported that **1** and $(n\text{-}BuC_5H_4)_2ZrCl_2$ (**2**) are very effective in 1-hexene and 1-decene oligomerization at $Al_{MAO}/Zr = 200$.

At first glance, the effectiveness of the α-olefin oligomerization process can be qualified only by the distribution of lightweight α-olefin oligomers, since the mass fraction of higher oligomers usually does not exceed several mass percent. However, real yields of oligomers are also affected by some side processes. One such process is the isomerization of initial α-olefins. In our recent work [37], we showed that internal alkenes can comprise as much as 25% of the yield during zirconocene-catalyzed oligomerization. Another such side reaction is the reduction of starting α-olefins and the formation of *n*-alkanes through hydroalumination. This reaction is stimulated on increasing the Al_{MAO}/Zr ratios and has not been studied yet.

In this paper, we report our study of α-olefin oligomerization catalyzed by a series of catalysts derived from zirconocenes **1–14** (Scheme 2), at medium (200) and low (10) Al_{MAO}/Zr ratios. We found that the catalyst prepared from the heterocyclic zirconocene **14** demonstrated the best performance. As far as α-olefin oligomerization in the presence of zirconocene **14** at low Al_{MAO}/Zr ratios went without any isomerization of the skeleton, we have managed to isolate for the first time and study as individual compounds the trimers, tetramers, and pentamers of 1-hexene, 1-octene, and 1-decene and the products of their hydrogenation. Moreover, we studied the physical properties and viscosity indexes of the newly obtained unsaturated and saturated hydrocarbons and compared the data obtained with known characteristics of conventional oligomers prepared using electrophilic catalysts. The results of this comparison allowed us to draw conclusions regarding the use of zirconocene oligomers as PAO base stocks.

2. Experimental section

2.1. Solvents, reagents and catalysts

Benzene, *n*-heptane, 1-hexene, 1-octene and 1-decene (Sigma-Aldrich) were stored over Na wire and distilled under argon. Diethyl ether was refluxed over Na/benzophenone and distilled under argon. CH_2Cl_2 was refluxed over CaH_2 and distilled before use. MAO (1.51M solution in toluene), MMAO-12 (1M solution in toluene), TIBA (1M solution in hexane), 2-methylthiophene, chlorotrimethylsilane (TMSCl), $ZrCl_4$, $SnCl_4$, propionyl chloride, $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ (**1**) and $(\eta^5\text{-}C_5H_4\text{-}n\text{-}Bu)_2ZrCl_2$ (**2**) were used as purchased (Sigma-Aldrich). Zirconocene pre-catalysts **3** [37], **4** [38], **5** [33,39], **6** [40], **7** [41], **8** [42], **9** [43], **10** [44], **11** [45], **12** and **13** [46] (Scheme 2) were synthesized according to previously reported procedures.

2.2. Analysis

$CDCl_3$ (Cambridge Isotope Laboratories, Inc., D 99.8 %) was used as purchased. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (400 MHz) at 20 °C. The chemical shifts are reported in ppm relative to the solvent residual peaks.

The distribution of α-olefin oligomers produced in zirconocene-catalyzed reactions and the conversion of the oligomers in post-oligomerization reactions were measured by gas chromatography (GC) method. GC analysis was carried out with a KRISTALL-2000M gas chromatograph equipped with a SolGel-1ms (60m×0.25mm×0.25μm) column and a flame ionization detector. Helium was used as a carrier gas at a rate of 1.364 cc/min and with a split ratio of 73.3 : 1. The injection temperature was 320 °C, and the column temperature was 200 °C within 5 min and then increased from 200 °C to 300 °C at a rate of 10 °C/min.

Size exclusion chromatography (SEC) of polyhexene samples was performed on an Agilent PL-GPC 220 chromatograph equipped with a PLgel column, and THF was used as the eluent (1 mL/min). The measurements were recorded with universal calibration according to a polystyrene standard at 40 °C. Elemental analysis (C, H) was performed on a Perkin Elmer Series II CHNS/O Analyzer 2400.

2.3. Preparation of zirconocene **14**

All of the synthesis experiments were conducted under an argon atmosphere. Zirconocene **14** was prepared in six stages starting from 2-methylthiophene (Scheme 3) and characterized by ^{1}H, ^{13}C NMR spectroscopy (see Appendix A) and by elemental analysis.

2.3.1. 1-(5-Methyl-2-thienyl)-1-propanone

$SnCl_4$ (117 g, 450 mmol) was added dropwise to a well-stirred solution of propionyl chloride (41.6 g, 450 mmol) and 2-methylthiophene (44.1 g, 450 mmol) in dry benzene (300 mL) at 0 °C. The solution was allowed to warm to room temperature and stirred for additional 16 h. HCl (10% aq., 500 mL) was added dropwise, water phase was extracted by benzene (3×100 mL), combined organic fraction was washed by water, aq. $NaHCO_3$, and dried over $MgSO_4$. Solvent was removed under reduced pressure, and the residue was distilled *in vacuo*. B.p. 100–106 °C/10 Torr. The yield was 50.0 g (72%) as a pale-yellow liquid. ^{1}H NMR ($CDCl_3$, 20 °C) δ: 7.54 (d, 1H); 6.80 (d, 1H) {-CH=}; 2.89 (q, 2H, $-CH_2-$); 2.54 (s, 3H, $-CH_3$); 1.23 (t, 3H, $-CH_3$).

2.3.2. 2-Methyl-1-(5-methyl-2-thienyl)-2-propen-1-one

1-(5-Methyl-2-thienyl)-1-propanone (50 g, 324 mmol), hexamethylenetetramine (63.6 g, 454 mmol) and Ac_2O (56 mL, 583 mmole) were mixed in a 250 mL flask, sparged with argon, and stirred for 48 h at 100 °C. The mixture was cooled to 60 °C and poured into 1 L of 2M aq. NaOH. The resulting mixture was extracted by CH_2Cl_2 (5×250 mL), combined organic fraction was washed by 1M HCl, aq. $NaHCO_3$, and dried over $MgSO_4$. Evaporation of solvents gave crude product (~55 g, 80% of desired compound by NMR) used without further purification. ^{1}H NMR ($CDCl_3$, 20 °C) δ: 7.50 (d, 1H); 6.80 (d, 1H) {-CH=}; 5.76 (bs, 1H); 5.73 (bs, 1H) {$=CH_2$}; 2.54 (s, 3H, $-CH_3$); 2.05 (s, 3H, $-CH_3$).

2.3.3. ***2****,5-Dimethyl-4,5-dihydro-6H-cyclopenta[b]thiophen-6-one*

Crude 2-methyl-1-(5-methyl-2-thienyl)-2-propen-1-one in CH_2Cl_2 (50 mL) was added to heated to 50 °C MSA (260 mL). The resulting mixture was stirred for 2 h, poured into ice/water (500 mL) and extracted by CH_2Cl_2 (5×200 mL). Combined organic phase was washed by aq. $KHCO_3$, water, and dried over $MgSO_4$. The resulting dark brown solution was evaporated and distilled in vacuo (b.p. 105-120 °C/1 torr) yielding 17.74 g of the product as colourless liquid. The yield based on 1-(5-methyl-2-thienyl)-1-propanone was 32.9%. ^{1}H NMR ($CDCl_3$, 20 °C) δ: 6.66 (s, 1H, -CH=); 3.12 (dd, ^2J = 16.5 Hz, ^3J = 7.0 Hz, 1H); 2.85 (ddt, ^3J = 7.0 Hz, 7.0 Hz, 2.8 Hz, 1H); 2.41 (dd, ^2J = 16.5 Hz, ^3J = 2.8 Hz, 1H) {ABC of C_5 ring}; 2.49 (s, 3H, $-CH_3$); 1.23 (d, ^3J = 7.0 Hz, 3H, $-CH_3$). ^{13}C NMR ($CDCl_3$, 20 °C) δ: 199.4 (>C=O); 167.3; 157.0; 137.5 (>C=); 122.4 (-CH=); 46.1; 16.4 ($-CH_3$); 32.7 ($-CH_2-$).

2.3.4. 2,5-Dimethyl-4H-cyclopenta[b]thiophene

2,5-Dimethyl-4,5-dihydro-6*H*-cyclopenta[*b*]thiophen-6-one (8.31 g, 50 mmol) in Et_2O (30 mL) was added dropwise to cooled (–40 °C) suspension of $LiAlH_4$ (0.52 g, 13.8 mmole) in Et_2O (100 mL). The resulting mixture was allowed to warm to room temperature and stirred for additional 1 h. Then H_2O (10 mL) was added, the resulting suspension was poured into CH_2Cl_2 (200 mL) and filtered. Organic phase was washed by water and evaporated. The flask was sparged with argon; benzene (150 mL) and p-TsOH (0.3 g) were added, and the resulting solution was refluxed with Dine-Stark head (control by TLC, benzene/EtOAc 4:1) within ~40 min. Then the resulting yellow solution was washed by water, aq. $KHCO_3$, dried over $MgSO_4$, passed through silica gel (benzene), evaporated and dried *in vacuo* yielding 6.5 g (86.5%) of yellow oil. ^1H NMR ($CDCl_3$, 20 °C) δ: 6.72 (bs,1H) {thiophene ring}; 6.42 (m); 6.38 (m) {Σ=1H; -CH= of cyclopentadienyl ring}; 3.22 (bs, 1H); 3.12 (bs, 1H) {Σ=2H, -CH_2-}; 2.55 (s, 3H, -CH_3 of thiophene ring); 2.51 (bs); 2.17 (bs) {3H, -CH_3 of cyclopentadiene ring).

2.3.5. Bis(η^5-2,5-dimethyl-4H-cyclopenta[b]thienyl)dichlorozirconium (IV) ***14***

n-BuLi (17 mL, 2.5 M in hexane, 42.5 mmol) was added at –60 °C to a solution of 2,5-dimethyl-4*H*-cyclopenta[*b*]thiophene (6.0 g, 40 mmol) in Et_2O (50 mL). The resulting mixture was allowed to warm to room temperature, stirred for 1 h, and cooled to –40 °C. TMSCl (5.6 mL, 44 mmol), was added, the mixture was stirred for 12 h at room temperature, and filtered. Solvents were removed under reduced pressure, toluene (10 mL) was added, and removed in vacuo to eliminate the traces of the ether. The residue was dissolved in CH_2Cl_2 (80 mL), the mixture was cooled to –40 °C, and $ZrCl_4$ (4.6 g, 19.7 mmol) was added. The mixture was allowed to warm to room temperature, stirred for 12 h, volatiles were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (20 mL), *n*-hexane was added dropwise at room temperature until the beginning of the crystallization. The resulting mixture was stored overnight at –20 °C. Light green crystalline product was filtered off, the residue was evaporated to one half of the initial volume and stored for 3 days at –20 °C. The crystalline product was filtered off and combined with the first portion of the product. The yield was 6.2 g, 68%. ^1H NMR ($CDCl_3$, 20 °C) δ: 6.69 (m); 6.67 (m) {1H, thiophene ring}; 5.93 (bs); 5.80 (bs) {1H}; 5.74 (bs); 5.46 (bs) {1H}; 2.52 (s, 3H); 2.17 (s, 3H). ^{13}C NMR (CD_2Cl_2, 20 °C) δ: 147.58; 147.46; 137.92; 136.82; 136.00; 135.41; 129.41; 128.04; 116.94; 116.90; 105.27; 104.53; 104.09; 103.64; 17.29; 16.69. Elemental Analysis: Calc. C, 46.94%; H, 3.94%. Found: C, 47.03%; H, 3.90%.

2.4. Oligomer preparation and characteristics

All of the synthetic experiments were conducted under an argon atmosphere.

Oligomerization of 1-hexene, 1-octene and 1-decene to prepare individual oligomers was carried out in bulk or in *n*-heptane solution using 2 mol of α-olefin, 10 mmol of zirconocene dichloride catalyst activated subsequently by 200 mmol of TIBA and 100 mmol of MMAO-12 as reported ealier [33]. After treatment with a minimal quantity of ethanol and water, the reaction mixtures were rectified *in vacuo.* The basic characteristics of the products (boiling points, GC retention times) are provided in Appendix A. The isomeric purity of the products is confirmed by GC, and by the absence of 4.9-6 ppm peaks in ^{1}H NMR spectra. ^{1}H and ^{13}C NMR spectra of all obtained oligomers are provided in Appendix A.

Dimerization of α-olefin dimers **H2** (1-hexene dimer), **O2** (1-octene dimer) and **D2** (1-decene dimer) was conducted in the presence of *tert*-BuCl and $EtAlCl_2$ (1% mol) at –30 °C. 98% dimer conversion was achieved after two hours. After treatment with a minimal quantity of methanol and aqueous $KHCO_3$ the reaction mixtures were rectified *in vacuo.* Results: 1-hexene dimer of dimer **H22** (yield 92%, B.p. 140-142 °C/ 0.1-0.2 Torr), 1-octene dimer of dimer **O22** (yield 89%, B.p. 196-200 °C/ 0.1-0.2 Torr) and 1-decene dimer of dimer **D22** (yield 84%, B.p. 230-235 °C/ 0.1-0.2 Torr). For spectral data, see Appendix A.

2.5. Hydrogenation of oligomers

Hydrogenation was performed in a stainless steel apparatus with mechanical stirrer, equipped with temperature and pressure sensors. Oligomer mixture and Pd/Al_2O_3 catalyst (0.1% Pd) in molar ratio 3000:1 were loaded, apparatus was filled with hydrogen *via* a three-fold increase of pressure to 3-5 bar with subsequent decrease to 0.1 bar. The process was conducted at 88–90 °C and hydrogen pressure of 10-11 bar; the magnetic stirrer was set to 500-550 rpm. The hydrogenation was finished after the hydrogen absorption rate was reduced 100-fold, after which the reaction mixture was separated from the catalyst and analyzed by GC and ^{1}H NMR spectroscopy. For spectral data, see Appendix A.

2.6. Viscosity and Pour point determination

The kinematic viscosity of the oligomers at 40, 100 and –40°C was determined in accordance with ASTM D445-17 after a certain volume of liquid passed under gravitational pull through a calibrated capillary flow meter. VI values were calculated according to the ASTM D2270-10 (2016). Pour points were determined in accordance with ASTM D97 method.

Oil density at 20 °C was determined with a pycnometer in accordance with ASTM D1480. Oil density at -40°C was calculated with the formula:

$d^t = d^{20} - \Delta t(t - 20)$,

where Δt is the temperature differential to density per 1 degree, calculated by:

$\Delta t = (18.319 - 13.233 \cdot d^{20}) \cdot 10^{-4}$

3. Results and discussions

3.1. Zirconocene-catalyzed α-olefin oligomerization at the ratio MAO/Zr = 200

We began our work with the investigation of 1-hexene, 1-octene, and 1-decene oligomerization with catalysts prepared from the zirconocenes **1** and **2** by activating them with significant excesses of MAO up to Al_{MAO}/Zr ratios ≈ 200. These catalysts were first studied by Kissin and Schwab [23] and have been reported as effective in olefin oligomerization. In our experiments, we used a MMAO-12 dissolved in heptane along with standard MAO. The results are summarized in Table 1.

We found that zirconocene dichloride **1** activated by 200 eq. of MMAO-12 at 60 °C demonstrated high activity in the oligomerization of 1-hexene, 1-octene, and 1-decene. 99% monomer conversion was achieved after 4 h (Table 1, runs 1–3). Investigation of the product yields demonstrated fractions with $P_n = 2–5$ (dimer and lightweight α-olefin oligomers) comprising 65.5% (1-hexene) to 73.4% (1-decene) of the products. In most cases, α-olefin oligomer distribution could be described by Flory-Schulz equation and a parameter α which correlates with relative rates or propagation *vs* termination (Table 1, column 6) [47]. For runs 1–3, α are 0.25 (1-hexene), 0.30 (1-octene) and 0.33 (1-decene).

The fraction of higher-weight α-olefin oligomers was inversely proportional to the starting hydrocarbon length, ranging from 21% for 1-hexene to 11.7% for 1-decene. We also observed formation of ~1% internal alkenes (mainly, 2-alkenes) and 12–14% *n*-alkanes (*n*-hexane, *n*-octane and *n*-decane). *n*-Alkanes formation under high Al/MAO ratio can be attributed to alklyl transfer to aluminium processes. Therefore, with **1**, primarily α-olefin dimers are formed and yields of lower oligomers do not exceed 30%. Assuming high loss of the initial olefin due to formation of alkanes and internal alkenes, zirconocene dichloride **1** at Al_{MAO}/Zr ≈ 200 cannot be considered an effective oligomerization catalyst.

The data we obtained for complex **2** (Table 1, run 5) were considerably different from those published in [23] (Table 1, run 4).[1] In our experiments at 70 °C using **2** activated by 200 eq. of MAO, conversion of 1-hexene after 4 h was 91%, and the resulting reaction mixture contained only 19.9 wt% of vinylidene dimer. Approximate yield of the fraction, corresponding to $P_n = 2–5$ (dimer and lightweight oligomers), was 53.6%. Replacing MAO with MMAO-12 (Table 1, run 6) led to an

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[1] The closest result to these data is the spread of oligomers obtained during catalysis of **1** (run 1).

insignificant increase in the conversion and an increased dimer fraction in the products without change of α value (0.49 and 0.48, respectively); the fraction of higher-weight oligomers ($P_n > 5$) decreased from 32.8 to 22.6%. In both cases, we observed a formation of ~1.5% of internal hexenes and significant quantities (about 12 wt%) of hexane.[2] We also studied the oligomerization of 1-hexene in the presence of **2** in a hydrogen atmosphere (Table 1, run 7). The hydrogen pressure was 1 bar and did not practically affect the yield of the targeted fraction (61.5%) with the dimer/lightweight oligomer ratio at 0.87. However, the quantity of internal hexenes in the products decreased to 0.3%, but the quantity of *n*-hexane increased to 14%. We also investigated the oligomerization of 1-hexene in bulk (Table 1, run 9). An insignificant increase in the conversion was accompanied by increase of the higher-weight oligomer fraction in the reaction products to 41%; yield of the targeted fraction (dimer and lightweight oligomers) constituted only 45.1%. Oligomerization experiments for 1-octene and 1-decene in the presence of **2** allowed us to achieve 71–72% yield of the target fraction with a dimer/lightweight oligomer ratio of 0.73 and 0.81, respectively. Therefore, use of the zirconocene **2** activated by 200 eq. of MAO allowed us to achieve satisfactory dimer/lightweight oligomer ratios (up to ~1:1). However, the isolated yield of the target compounds, vinylidene dimers and lightweight oligomers, amounted to about 70%. A significant part of the initial olefin, up to 15%, was wasted because of the formation of isomerization products, internal alkenes and α-olefin reduction products.

Therefore, considering the losses of α-olefins due to the formation of *n*-alkanes and the high cost of MAO, as well as the obvious preparatory difficulties at the step of hydrolyzing the reaction mixtures with a high concentration of aluminum–organic compounds, the use of high ratios of Al_{MAO}/Zr in zirconocene-catalyzed α-olefin catalysis is ineffective.

3.2. Zirconocene-catalyzed α-olefin oligomerization at MAO/Zr ratio = 10

In order to increase the target product yield and reduce the loss of α-olefins arising after the *n*-alkane formation *via* alkyl transfer to aluminium side reaction, we turned to low Al_{MAO}/Zr ratios in oligomerization experiments. Since zirconocene dichlorides do not effectively transform into an active, soluble form after treatment with a few eq. of MAO, in our catalytic experiments we used a recently developed method [33] based on the subsequent interaction of zirconocene dichloride with 20 eq. of TIBA and 10 eq. of MMAO-12. At the first stage of this study, we examined the catalytic properties of a range of described zirconocene dichlorides **1**–**13** (Scheme 2) during oligomerization of 1-hexene in bulk at 60 °C (monomer/Zr ratio = 2000:1). In all experiments (Table 2, runs 1-6, 9, 10) relative low *n*-alkane formation was detected, due to use of relative low Al/Zr ratios.

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[2] The exact calculation of hexane levels in reaction products by GC was difficult due to the use of TIBA solution in hexane.

We determined that the zirconocenes **1–13** demonstrate markedly different reactivities depending on their structure (Table 2, runs 1–13). Zirconocene dichloride **1** (Table 2, run 1) primarily catalyzed the formation of 1-hexene dimers; α was only 0.11. The yields of lightweight oligomers and internal hexenes were only 12.2% and 3.4%, respectively. The fraction of the monomer reduction product (*n*-hexane) did not exceed 2%. We found that if ring monosubstituted *bis*-cyclopentadienyl complexes **2**, **4**, and **5** are used, significant quantities of oligomer products are formed along with the 1-hexene dimer (α = 0.55, 0.44 and 0.38, correspondingly). The catalyst productivity depends on the type of substituents in cyclopentadienyl rings. Zirconocenes **2** and **5** are comparable to **1** with respect to activity, while complex **4** is not very active. Lightweight oligomers fraction yield with catalysis by **2** was 70.8% (dimer/lightweight oligomers ratio of 0.98) with 20% yield of high-weight oligomers, with over 7% internal hexenes and ~2% of *n*-hexane. Complex **3**, which we studied earlier [37], demonstrated properties similar to those of **2** and **5** (α = 0.41). However, the dimer/lightweight oligomers ratio for this complex was 1.33. We found that catalysis with disubstituted (such as **6**, α = 0.81) or mixed-ligand indenyl-cyclopentadienyl complexes **9** and **10** (α = 0.50 and 0.52) leads to a higher concentration of oligomers relative to dimers; however, these zirconocenes are not very promising for lightweight oligomers preparation due to high concentrations of higher oligomers in the reaction mixtures. Bis-indenyl complexes **11–13** as well as ring-substituted *ansa*-zirconocene **8** catalyzed the polymerization reactions. Based on the experiments we performed, one can conclude that the use of low Al_{MAO}/Zr ratios in olefin oligomerization is reasonable. For example, for zirconocene **2** activated by 10 eq. of MMAO-12 (Table 2, run 2), the target fraction yield was more than 1.5 times greater than the yields in the presence of 200 eq. of MAO (Table 1, run 9). Complex **2** as well as *ansa*-zirconocene **3** had the best characteristics among the examined zirconocenes **1–13**. Target fraction yields (P_n = 2–5) for these complexes were similar and amounted to ~70%. On catalyzing with complex **2** (Table 2, run 2), the yield of the lightweight oligomer fraction (P_n = 3–5) was significantly higher (35.7% *vs* 29.3% for **3**). On the other hand, reaction with **2** showed higher losses for isomerization into internal hexenes.

Complexes **2** and **3** were used in studying the oligomerization of 1-hexene, 1-octene, and 1-decene with the purpose to optimize the yields of lower α-olefin oligomers. The results of the conducted experiments are summarized in Table 3 (runs 1–13). For zirconocene **2**, we studied the influence of hydrogen, the monomer type, and the temperature on the product distribution. We determined that, at 1 bar of hydrogen during oligomerization of 1-hexene (Table 3, run 2), the dimer/lower oligomer ratio increased from 0.98 to 1.65, and the yield of the fraction corresponding to P_n 3–5 decreased from 35.7% to 30.7%. The introduction of 1-octene (Table 3, run 3) and 1-decene (Table 3, run 4) into the reaction led to decrease in the catalytic productivity and had very little influence on the dimer/lower oligomer ratio. When the temperature was raised 100 °C (1-decene), the catalyst partially lost activity and the quantity of the byproducts, internal decenes, increased to 11.2% (Figure 2).

Similar results were obtained for zirconocene **3**. With this catalyst, we were able to synthesize oligomers of 1-hexene characterized by a dimer/lightweight oligomer ratio of ~1 (Table 3, run 8) with an isolated yield of 68.4%. Similar yields were achieved with oligomers of 1-octene (Table 3, run 9). Oligomerization of 1-decene at 100 °C (Table 3, run 10) catalyzed by complex **3** progressed with a higher productivity than that by **2** (Figure 2), with the fraction of internal decenes in reaction products comprising 5.6%.

Therefore, “classic” zirconocenes demonstrated a limited applicability in the synthesis of lower oligomers even at low Al/Zr ratio. The main problems with their use arise from the formation of significant quantities of internal alkenes (complex **2**) or high-weight oligomers (complex **3**). The use of molecular hydrogen or increasing the temperature with the aim to lower the high-weight oligomer fraction was not effective for **2** due to side reactions, such as the formation of *n*-alkanes in the presence of molecular hydrogen and internal alkenes at high temperatures. At $Al_{MAO}/Zr = 200$, the oligomerization catalyzed by zirconocene **2** was not influenced by hydrogen. One can suppose that the mechanism of chain release in primary alkyl complex A during oligomerization at $Al_{MAO}/Zr \sim 10$ (Scheme 3) “switches” from traditional β-hydride transfer [36] to β-hydride elimination. This mechanism was proposed earlier by Bergman [24,25] for selective dimerization of α-olefins. After β-hydride elimination, the zirconocene-hydride complex **B** is formed [24]. This complex, compared to primary alkyl complex **A** (Scheme 3), is less sterically hindered and more susceptible to monomer 2,1-insertion. Products of monomer 2,1-insertion, such as secondary alkyl complexes **C**, represent the "resting states" in zirconocene-catalyzed polymerization. Their reactivation can run *via* isomerization into primary alkyl complexes as well as *via* β-hydride elimination with internal alkene formation [48] (Scheme 3).

The high concentration of internal alkenes in oligomerization products can be considered as an experimental criterion of β-hydride elimination and low regioselectivity of α-olefin coordination/insertion in hydride complex **B**. Besides generally slowing down the reaction and formation of 2-alkenes, 2,1-insertion hinders the use of molecular hydrogen. In the presence of hydrogen, the main reaction pathway becomes hydrogenation of the Zr-C bond and the formation of *n*-alkanes, which leads to decreased target oligomer product yields. Both side reactions were observed for zirconocene complexes **2** and **3**, with **3** only moderately surpassing **2** in terms of regioselectivity.

The results of the performed experiments allowed us to formulate the criteria for a promising oligomerization catalyst. This catalyst should be very regioselective that can be demonstrated by the formation of low amounts of internal alkenes, and should be characterized by relatively high α level. Besides, it should be very stable, retaining high productivity at high temperatures and low ratios of Al_{MAO}/Zr.

3.3. Novel zirconocene catalyst for α-olefin oligomerization

It is known that zirconocenes derived from cyclopentadienes with condensed donor heterocyclic fragments (heterocenes) demonstrate high thermal stability and productivity even at low ratios of Al_{MAO}/Zr [49–56]. We proposed that α-olefin oligomerization can be effectively performed with a heteroanalogue of *bis*-indenyl complex **11**, which catalyzed the formation of low-molecular-weight polyhexene at 60 °C (Table 2, run 11). We elaborated the synthesis of a new zirconocene **14** (Scheme 4) starting from the commercially available 2-methyl-thiophene and using an effective Si-Zr transmetallation reaction [46] on the final stage.

We carried out the oligomerization of 1-hexene in bulk catalyzed by **14** (Table 3, run 12) in the same conditions as those for complexes **1**–**13** (Table 2, runs 1–13). In contrast to complexes **1**–**13,** zirconocene **14** demonstrated higher productivity. However, the target product yield (oligomer fraction with P_n = 2–5) amounted to only 26.2%. At the same time, catalysis with **14** led to the formation of minimal quantities of internal hexenes (0.8%) with a 0.55 dimer/lightweight oligomer ratio, and α = 0.63. This experiment demonstrated the high potential of the precursor **14**. The low concentration of internal hexenes in oligomerization products allows us to assume that the main mechanism of chain release at low MAO/Zr ratios is β-hydride transfer to the monomer. Both temperature and molecular hydrogen can be used to regulate the P_n during oligomerization with **14**.

We conducted the oligomerization of 1-octene at 60 °C in bulk, and the target fraction yield (P_n = 2–5) was 52.9%. Increasing the temperature to 100 °C resulted in an increased yield of 60.7%. On lowering the monomer concentration by adding heptane (1/2 by volume) at 100 °C (Table 3, run 16), we achieved 86.7% of the target fraction yield (dimer/lightweight oligomers ratio = 1.18, α = 0.43). As a result of the oligomerization of 1-decene at 100 °C (Table 3, run 18), the yield of the dimer/trimer/tetramer mixture amounted to 89.1% (dimer/lightweight oligomers ratio = 0.96, α = 0.51). Moreover, we found that oligomerization in a hydrogen atmosphere at an elevated temperature in the presence of **14** (Table 3, runs 19–25) allowed 77% *isolated* yields of octene and decene oligomers with ~5% loss due to monomer reduction and ~15% loss due to higher oligomer formation ($\alpha = 0.3$-0.6). The resulting oligomers were partially hydrogenated.

Therefore, increasing the temperature and using molecular hydrogen in the case of **14** turned out to be effective instruments for increasing the yield of lower α-olefin oligomers. By using **14**, we undertook preparatory synthesis of 1-octene and 1-decene oligomers (Table 3, runs 22 and 25). Our method of carrying out oligomerization experiments under ambient pressure did not allow us to effectively use **14** in the oligomerization of 1-hexene. 1-Hexene oligomers were obtained by catalysis by **3** (Table 3, run 8).

The high efficiency of **14** in comparison with that of **2** and **3** in the oligomerization of 1-decene is illustrated in Fig. 2, which shows the fragments of ^{1}H NMR spectra corresponding to vinyl proton peaks for reaction mixtures of oligomerizations in bulk at 100 °C after 4 h. At this temperature, the sandwich complex **2** demonstrated the lowest activity. In the presence of both **2** and **3**, significant quantities of internal decenes formed. Conversely, in the presence of **14**, almost full monomer conversion was observed and the formation of 1-decene isomerization products was not significant.

3.4. Characterization of α-olefin oligomers

The obtained oligomers were colorless liquids. According to ^{1}H and ^{13}C NMR spectra, all oligomers contained only vinylidene unsaturation, $>C=CH_2$, and appeared as individual type D (Fig. 1) compounds from the point of view of structural isomerism. Spectra of all newly obtained compounds are given in Appendix A; the data for 1-hexene trimer coincided with what has been published earlier [33,57].

The boiling points of α-olefin oligomers, on the whole, correlated with the GC retention times (see Appendix A). At equal molar weights, the more branched oligomer was characterized by a slightly lower boiling point, as well as a significantly lower retention time, that that of the less branched oligomer. For example, C_{24} hydrocarbons **H4** and **O3** were characterized by relatively close boiling points of 392 and 396 °C at 760 Torr, respectively. The retention time of **H4** was 13.18 min and 14.79 min for **O3**. This observation should be considered when separating and analyzing the hydrocarbon mixtures by GC.

3.5. Dimerization of α-olefin dimers

An alternative way to prepare hydrocarbons of definite structure that can be applied to the production of PAOs consists of dimerization of vinylidene dimers in the presence of acids (Scheme 1c) to get “dimers of dimers.” These hydrocarbons can also be categorized as long-chain branched (Fig.

1D) hydrocarbons, which makes them promising PAO base stocks. It was shown by Kissin and Schwab that the dimer of 1-decene, in the presence of $EtAlCl_2$/silica, forms C_{40}-hydrocarbons with a yield of ~80% at room temperature [23]. We have also studied the acid-catalyzed dimerization of α-olefin dimers and found that $EtAlCl_2$ in the presence of ternary chloride, *tert*-BuCl, is a much more effective catalyst than $EtAlCl_2$/silica. This catalyst provided more than 95% substrate conversion after 2 h of reaction even at –30 °C. The main reaction products were "dimers of dimers" of **H22**, **O22**, and **D22**, which were separated by rectification *in vacuo* with respective yields of 92, 89, and 84%. We determined that besides the target "dimers of dimers," isomers of the initial dimers were formed as reaction byproducts, as well as insignificant (5–7%) quantities of higher oligomers. ^{1}H and ^{13}C NMR spectra of α-olefin "dimers of dimers" **H22**, **O22**, and **D22** are given in the Appendix A. These substances represent mixtures of isomers that differed by the position of double bonds.

3.6. Hydrogenation

In the industrial production of PAOs, a nickel catalyst is usually used for α-olefin oligomer hydrogenation. The nickel catalyst is characterized by moderate activity, and the process is carried out at high temperature and pressure [15,29]. Since the aim of the current study was the synthesis of individual compounds with defined molecular structures, we preferred not to carry out the hydrogenation in rigorous conditions. By using a more active catalyst, palladium on aluminum oxide (0.1% Pd), we performed comprehensive hydrogenation at 90 °C and 10 bar of pressure at a molar olefin/catalyst ratio of 3000:1. The typical experiment was completed in 3–5 h. According to GC and NMR spectroscopy (see Appendix A) data, no isomerization of initial oligomers was observed during the hydrogenation.

3.7. Viscosity characteristics

The kinematic viscosity (KV) of the obtained α-olefin oligomers was determined at temperatures of –40, 40, and 100 °C. The values KV^{40} and KV^{100} as well as the viscosity indexes (VI) are given in Table 4. Known characteristics of α-olefin oligomers, produced by acid catalysis, are given in the same table for comparison.

Analysis of the obtained data allowed us to make several important conclusions (Table 4).

1-Hexene oligomers. Tetramer **H4H** and pentameter **H5H** as well as the dimer of dimer of hexene **H22H** represented low-viscosity oils (KV^{100} 2.1, 3.8, and 2.72 cSt, respectively). However, these oligomers were characterized by low viscosity indexes.

1-Octene oligomers. The oligomers of 1-octene prepared by zirconocene-catalyzed processes had medium viscosity and outperformed octene oligomers obtained in the presence of BF_3–ROH in terms of viscosity indexes, while possessing the same low-temperature kinematic viscosity.

1-Decene oligomers. The decene oligomers synthesized by us, as expected, significantly outperformed electrophilic oligomers obtained in the presence of BF_3–ROH in terms of viscosity ratings and can be considered as base stocks for modern PAOs.

Dimers of α-olefin dimers. Given equal molecular mass, dimers of α-olefin dimers had slightly lower viscosity than coordination α-olefin oligomers. The tentative application of these compounds as low-temperature single-component oil base stocks [23] is limited by their high KV^{-40} values.

4. Conclusions

We have studied the catalytic activity of zirconocenes activated by minimal excesses of TIBA and MMAO-12, in oligomerization of 1-hexene (**H**), 1-octene (**O**), and 1-decene (**D**). Using of low Al/Zr ratios leads to reduction of *n*-alkane formation caused by hydroalumination processes. As a result, we found effective catalysts to produce the oligomer mixtures with oligomerization grades P_n = 2–5 with yields of up to 90% with a lightweight oligomer fraction (P_n 3–5) of up to 50%.

Conducting oligomerization experiments in the 2–5 mol scale, we obtained and separated as individual compounds the oligomers, corresponding to P_n = 2–5. α-Olefin trimers (**H3**, **O3**, and **D3**), tetramers (**H4**, **O4**, and **D4**), and pentamers (**H5** and **O5**) have been characterized as individual compounds for the first time. “Dimers of dimers” of α-olefins **H22**, **O22**, and **D22** were synthesized by cationic dimerization of vinylidene dimers **H2**, **O2**, and **D2**, and characterized as structurally homogeneous compounds. All newly obtained α-olefin oligomers were hydrogenated under mild conditions with the hydrogenation products characterized as individual compounds.

In order to match the viscosity ratings of hydrogenated α-olefin oligomers with the ratings of oligomeric mixtures obtained by conventional electrophilic catalysis we determined the pour points and kinematic viscosities at –40, 40, and 100 °C and also calculated the viscosity indexes for all the oligomers obtained (Table 4, Fig. 3). We determined that the hydrogenated coordination oligomers of 1-hexene are characterized by quite low VI values, significantly lower than those of the hexene products obtained under conditions of “soft” electrophilic catalysis (BF_3/ROH), and as a result cannot be used as oil base stocks. On the contrary, hydrogenated coordination oligomers of 1-decene significantly outperform the products of 1-decene cationic oligomerization which are base stocks of high-quality PAOs.

Despite the favorable properties of 1-decene-based PAOs, however, their production cost is high and the search continues for cheaper raw materials that can provide oil base stocks with similar properties to those of base stocks made from 1-decene. It is important that the octene-based PAOs obtained by coordination oligomerization show only slightly inferior main characteristics than those of the commercial 1-decene-derived products synthesized by electrophilic catalysis (Fig. 3). Recent progress in the development of selective methods of ethylene tetramerization [58–63] can make 1-octene more readily available than 1-decene as the raw material in the near future. This allows us to view 1-octene-based products as available alternatives to conventional decene PAOs.

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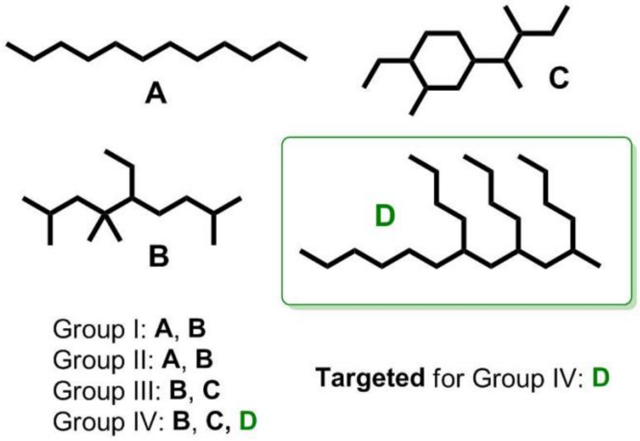


Fig 1 Main structural types of hydrocarbons – components of oils

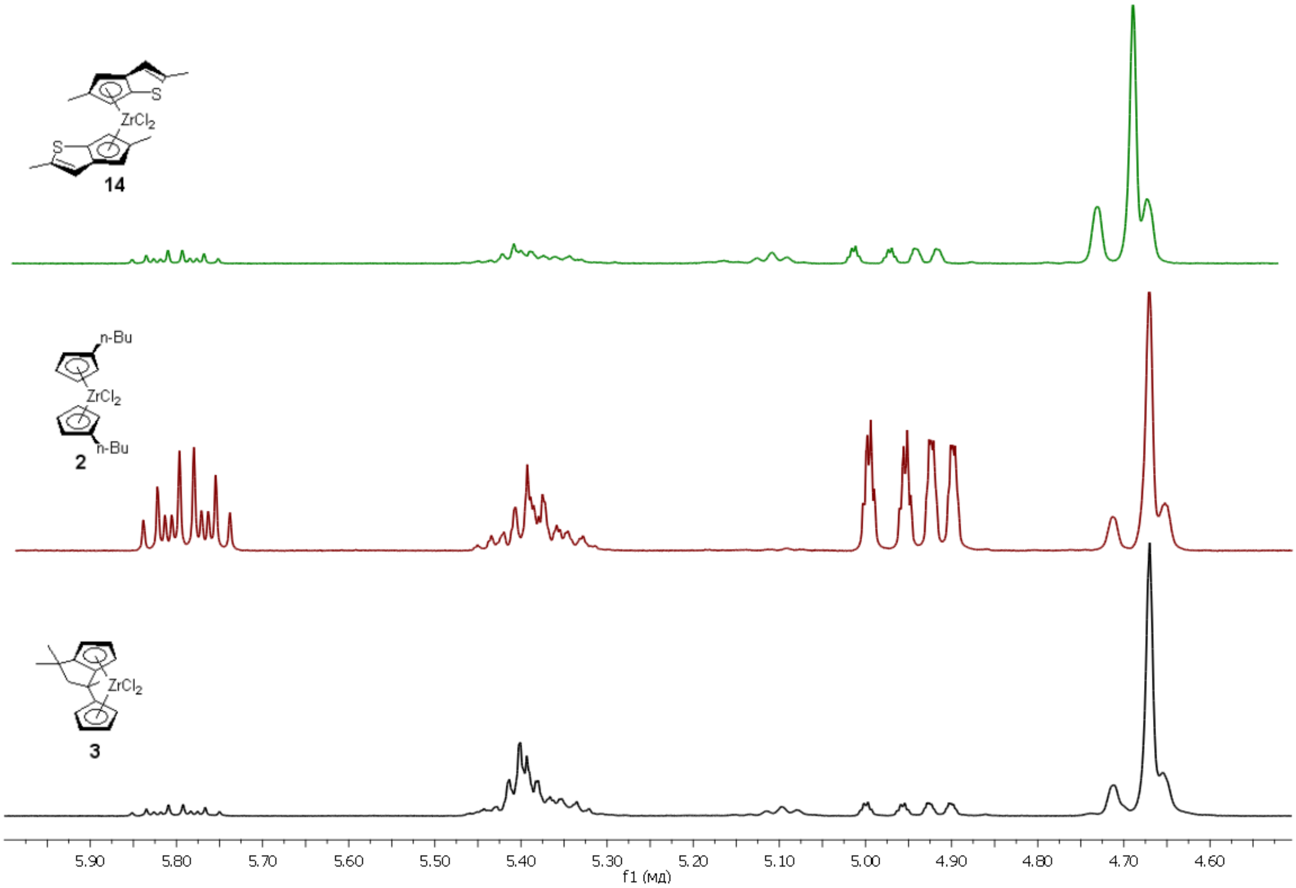


Fig 2 Vinyl proton peaks in reaction mixtures of 1-decene oligomerization in the presence of zirconocenes **2**, **3**, and **14** (4 h, 100 °C).

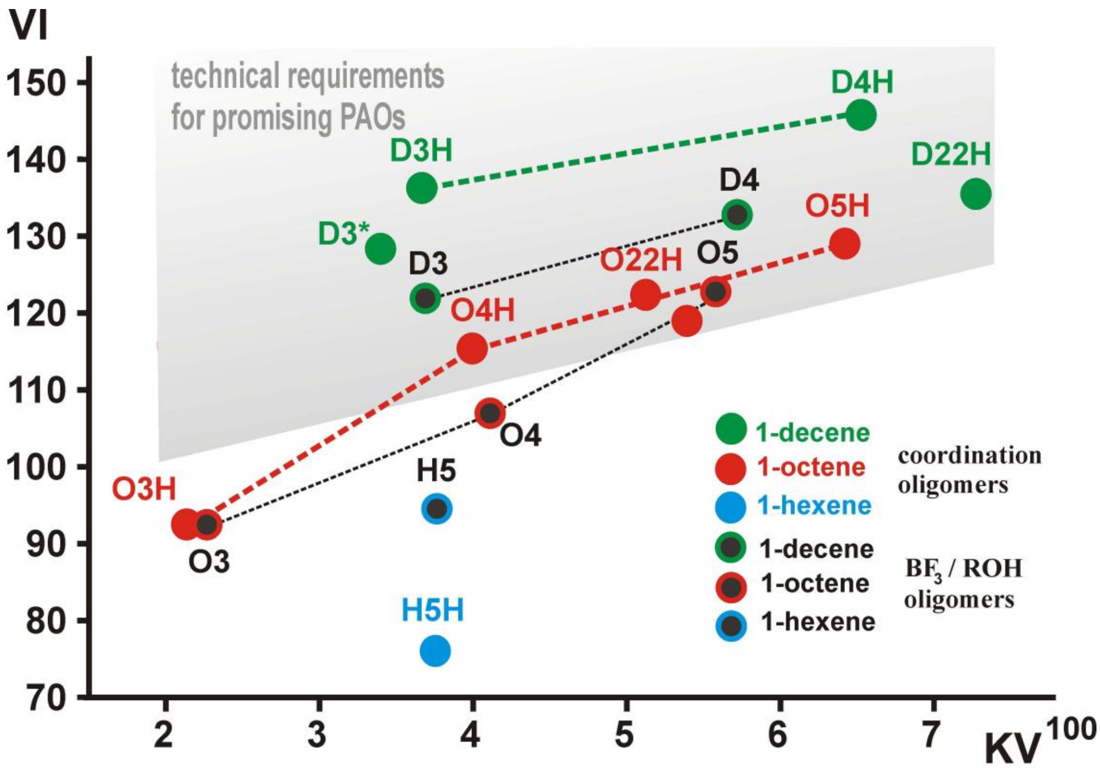
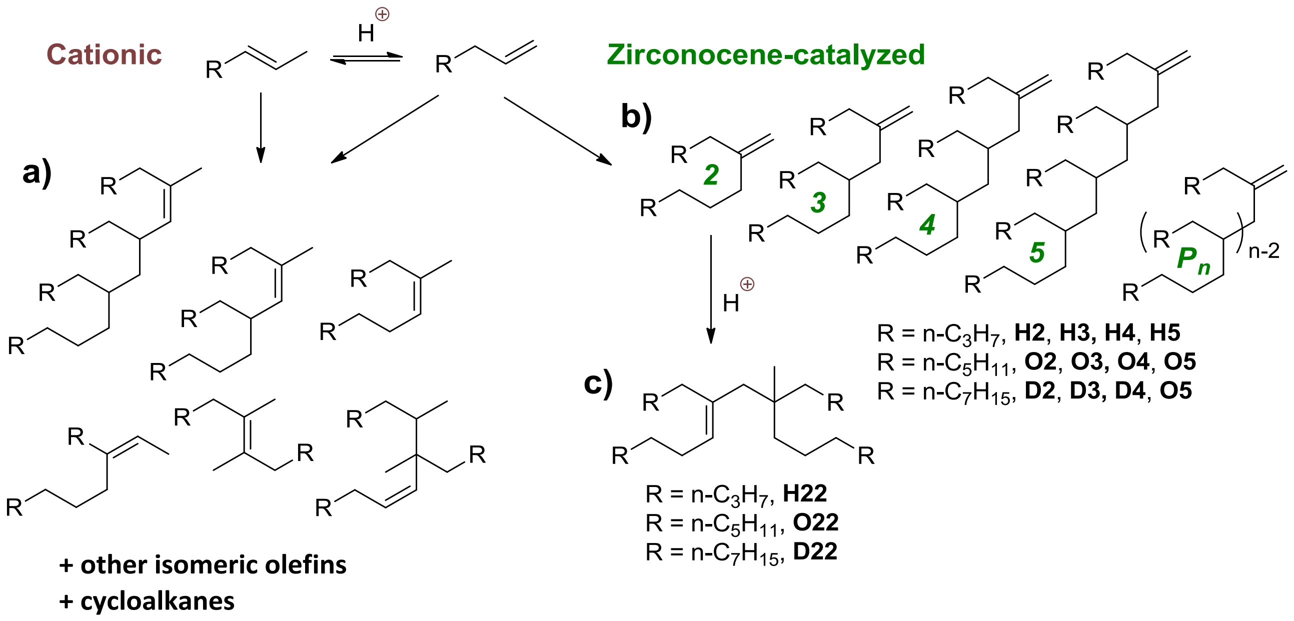
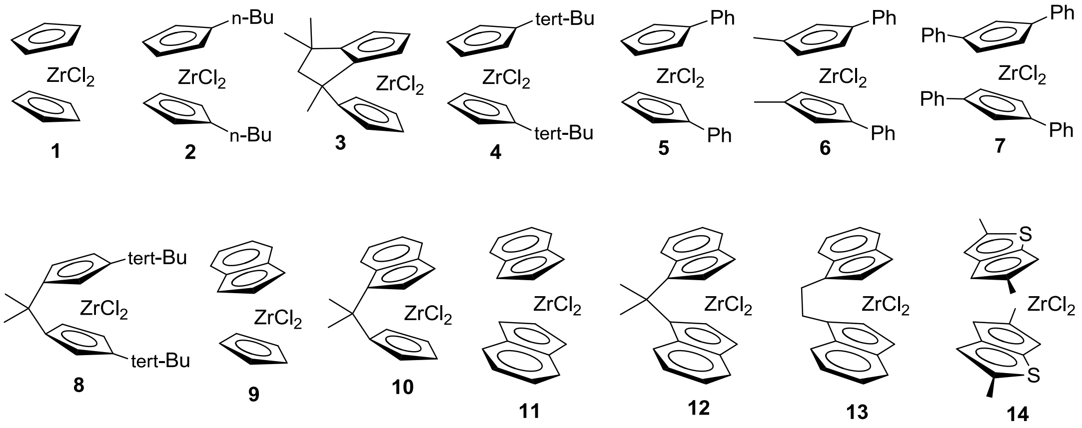


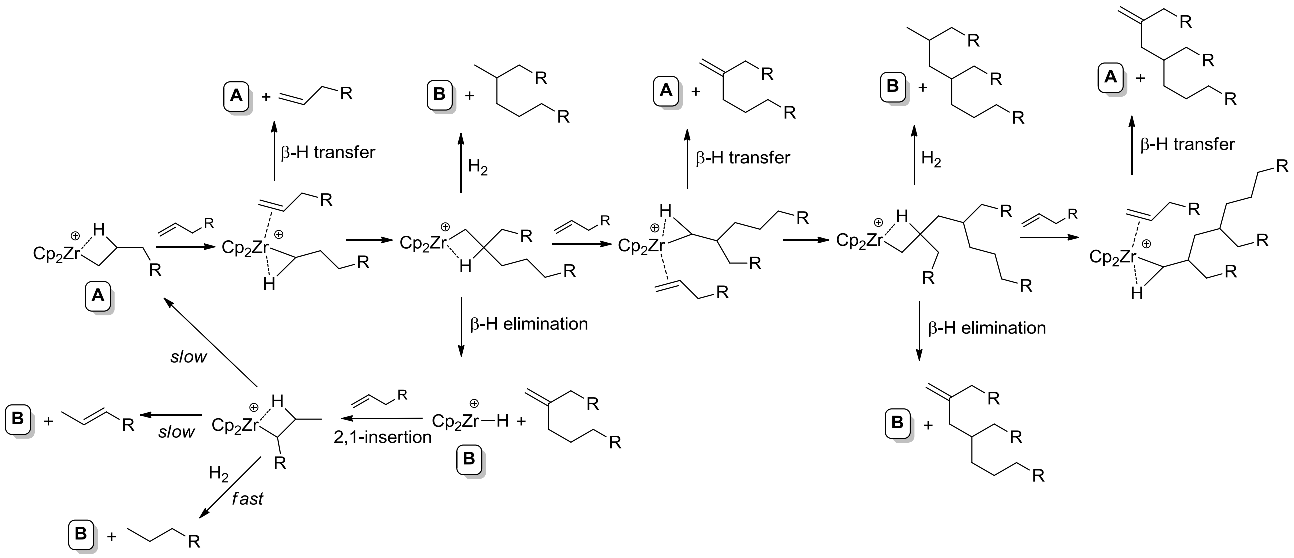
Fig 3 Viscosity characteristics of 1-decene (green), 1-octene (red), and 1-hexene (blue) oligomers obtained by coordination polymerization (this work) and in the presence of BF_3–ROH [3]. **D3***: decene trimer obtained using [EBTHI]$ZrCl_2$–TIBA–perfluoroborate [15]. The range of technical requirements for promising PAOs was limited to the segment corresponding to VI = 100 for KV^{100} = 2 and VI = 120 for KV^{100} = 6.



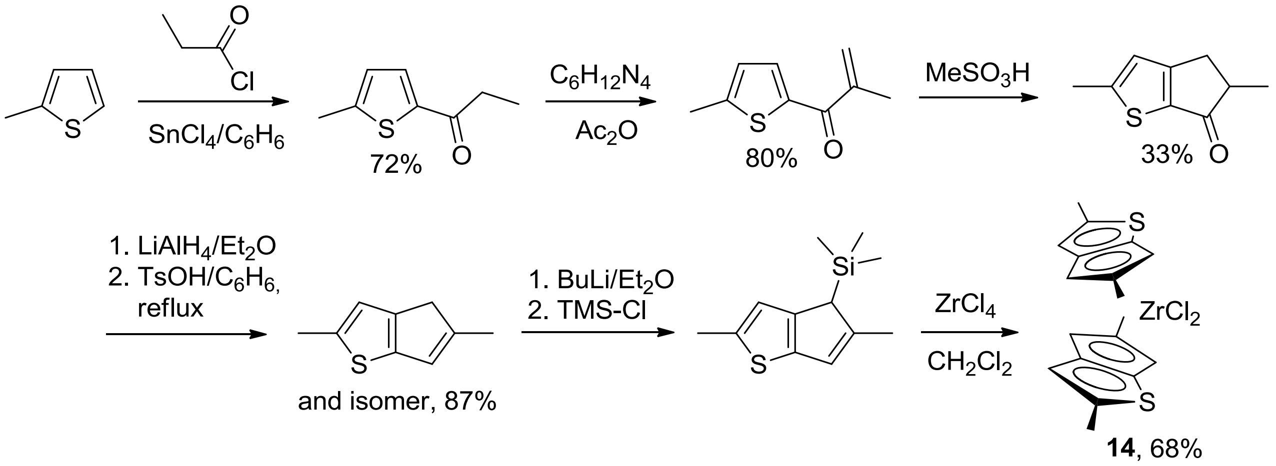
Scheme 1 Cationic (a) and coordination (b) α-olefin oligomerization. Dimerization of α-olefin vinylidene dimers (c)



Scheme 2 Zirconocenes studied in oligomerization of α-olefins



Scheme 3 Alternative pathways of chain release in α-olefin oligomerization



Scheme 4. Preparation of zirconocene **14**.

Table 1 Oligomerization of α-olefins during catalysis with **1** and **2** at $Al_{MAO}/Zr = 200$, $Al_{TIBA}/Zr = 100$. Reaction time: 4 h. Activator: MMAO-12

Run	Cat	α-olefin, solv.	T, °C	α value [1]	Conv. after 4 h, %	GC Data, % wt. of oligomers in the reaction mixture after 4 h, for P_n:				% wt. of components, approximated for 100% conversion					Dimer/ lower olig.
						2	3	4	5	% P_n 2-5 oligomers	% dimer	% P_n 3-5 (lower) oligomers	% 2-alkenes/ alkanes	% residue	
1	**1**	H	60	0.25	99	44.8	13.0	4.4	2.7	65.5	45.2	20.2	1.2/~12[2]	~21	2.24
2		O	60	0.30	99	45.2	15.0	6.0	4.4	71.3	44.8	25.6	1.2/12.8	14.7	1.78
3		D	60	0.33	99	42.3	21.2	9.2	n.d.	73.4[2]	42.7	30.7[3]	0.8/14.1	11.7[4]	1.39
4[5]	**2**	H+C7	70	0.39	72.9	44.9	15.4	8.1	3.3	100	61.6	38.4	n.d.	n.d.	1.60
5[5]		H+C7	70	0.49	91	19.9	11.6	7.6	9.6	53.6	21.9	31.7	1.6/~12[2]	32.8	0.69
6		H+C7	70	0.48	96	25.0	14.8	9.4	11.4	63.2	26.0	37.1	1.2/~13[2]	22.6	0.70
7[6]		H+C7	70	0.46	99	28.3	15.4	9.4	7.8	61.5	28.6	32.9	0.3/~14[2]	24.2	0.87
8		H+C7	60	0.63	97	25.6	12.7	10.7	10.6	64.5	26.4	38.1	1.2/~12[2]	22.3	0.69
9		H	60	0.62	98	14.5	11.0	9.1	9.5	45.1	14.8	30.0	1.9/~12[2]	41	0.49
10		O+C7	60	0.54	98	30.1	16.6	12.0	12.0	72.2	30.7	41.4	1.8/10.4	15.6	0.74
11		D+C7	60	0.49	98	31.3	23.3	15.2	n.d.	71.3[3]	32.0	39.3[2]	0.8/8.2	19.8[4]	0.81
12		D+C7	70	0.60	94	28.2	21.6	17.2	n.d.	71.4[3]	30.0	41.3[2]	1.4/6.6	20.6[4]	0.73

[1] α = tetramer/trimer molar ratio, characteristics of Flory-Schulz distribution shape

[2] Determining the exact concentration of *n*-hexane in reaction mixture was difficult due to the use of TIBA solution in hexane.

[3] Not counting decene pentameter due to low resolution of $C_{50}H_{100}$ by GC.

[4] Including decene pentamer

[5] MAO used instead of MMAO-12

[6] 1 bar of hydrogen

Table 2 Zirconocene-catalyzed oligomerization of 1-hexene at $Al_{MMAO\text{-}12}/Zr = 10$. Reaction time: 4 h, 60 °C, bulk.

Run	Cat.	Conv. after 4 h, %	α value [1]	GC Data, % wt. of oligomers in the reaction mixture after 4 h, for P_n:				% wt. of components, approximated for 100% conversion					Dimer/ lower olig.
				2	3	4	5	% P_n 2-5 oligomers	% dimer	% P_n 3-5 (lower) oligomers	% 2-alkenes/ alkanes	% residue	
1	**1**	97	0.11	79.7	10.1	1.5	0.3	94.0	81.8	12.2	3.4/~2[2]	~1[2]	6.70
2	**2**	85	0.55	29.8	12.7	9.3	8.3	70.8	35.1	35.7	7.2/~2[2]	~20[2]	0.98
3	**3**	98	0.41	40.3	14.2	7.7	6.9	70.4	41.1	29.3	2.4/~3[2]	~24[2]	1.40
4	**4**	16	0.44	6.4	2.4	1.4	1.0	70.0	40.0	30.1	8.8/~2[2]	~19[2]	1.33
5	**5**	92	0.38	32.4	16.0	8.1	4.2	66.0	35.2	30.8	1.2/~2[2]	~31[2]	1.14
6	**6**	72	0.81	5.4	7.1	7.7	9.8	41.7	7.5	34.2	1.4/~2[2]	~55[2]	0.22
7	**7**	<2	-	-	-	-	-	-	-	-	-	-	-
8	**8**	89	Polymer (isotactic); M_n = 3 730, Đ = 3.76										
9	**9**	95	0.50	21.3	13.7	9.2	7.8	54.7	22.4	32.3	4.6/~2[2]	~39[2]	0.69
10	**10**	94	0.52	19.2	12.6	8.8	7.6	51.3	20.4	30.9	6.4/~2[2]	~40[2]	0.66
11	**11**	88	Polymer (atactic); M_n = 2 140, Đ$_M$ = 1.82										
12	**12**	94	Polymer (isotactic); M_n = 9 120, Đ$_M$ = 1.79										
13	**13**	92	Polymer (isotactic); M_n = 3 110, Đ$_M$ = 2.73										

[1] α = tetramer/trimer molar ratio, characteristics of Flory-Schulz distribution shape

[2] Determining exact *n*-hexane concentration in reaction mixture was difficult due to the use of TIBA solution in hexane as a scavenger.

Table 3. α-olefin oligomerization optimization experiments with zirconocenes **2**, **3** and **14**.

Run	Cat.	α-olefin, solv.	T, °C	H_2	Conv. after 4 h, %	α value[1]	GC Data, % wt. of oligomers in the reaction mixture after 4 h, for P_n:				% P_n 2-5 oligomers, *approx*	% dimer, *approx*.	% P_n 3-5 (lower) oligomers, *approx*.	% 2-alkenes/ alkanes	% residue *approx*.	Dimer/ lower olig.
							2	3	4	5						
1	**2**	H	60	-	85	0.55	29.8	12.7	9.3	8.3	70.8	35.1	35.7	7.2/~2[2]	20.0[2]	0.98
2		H	60	1 bar	99	0.39	50.1	16.3	8.5	5.5	81.2	50.6	30.7	0.3/~8[2]	10.5[2]	1.65
3		O	60	-	83	0.52	33.0	13.1	9.0	10.9	76.6	39.8	39.8	7.0/2.6	10.8	1.00
4		D	60	-	72	0.58	27.5	14.3	11.0	n.d.	73.3[3]	38.2	35.0[3]	7.2/2.4	17.1[4]	1.09
5		D	100	-	69	0.40	27.9	16.2	8.7	n.d.	76.4[3]	40.4	36.1[3]	11.2/3.1	9.7[4]	1.12
6	**3**	H	60	-	98	0.41	40.3	14.2	7.7	6.9	70.4	41.1	29.3	2.4/~3[1]	24.2[1]	1.40
7		H+C7	60	-	96	0.42	40.3	14.2	8.0	7.8	73.2	42.0	31.2	2.7/~3[1]	21.1[1]	1.35
8[5]		H+C7	60	-	98	0.53	33.7	14.2	10.1	9.8	68.4	34.0	34.4	2.4/~2[1]	27.5[1]	0.99
9		O	60	-	97	0.47	35.2	14.6	9.2	7.4	68.5	36.3	32.2	2.0/0.6	28.9	1.13
10[6]		D	60	-	96	0.62	29.0	17.4	14.3	n.d.	63.3[3]	30.2	33.1[3]	1.4/0.6	34.7[4]	0.91
11		D	100	-	86	0.22	35.6	19.5	5.6	n.d.	75.2[3]	41.4	33.8[3]	5.6/0.4	18.8[4]	1.22
12	**14**	H	60	-	100	0.63	9.3	6.4	5.4	5.1	26.2	9.3	16.9	0.8/~1[2]	72.1	0.55
13		O	60	-	100	0.47	23.3	12.8	8.0	8.9	52.9	23.3	29.6	0.9/1.1	45.1	0.79
14		O	80	-	100	0.36	27.5	14.3	6.8	5.2	53.8	27.5	26.3	0.9/1.1	44.3	1.05
15		O	100	-	100	0.49	37.0	16.2	8.9	8.6	60.7	37.0	33.6	1.1/1.2	27.0	1.10
16		O+C7	100	-	97	0.43	45.5	19.4	11.0	8.2	86.7	47.0	39.8	2.2/1.8	9.3	1.18
17		O	120	-	100	0.32	44.0	19.0	8.0	4.9	76.0	44.0	32.0	1.4/1.6	21.0	1.38
18		D	100	-	93	0.51	40.5	25.1	17.2	n.d.	89.1[3]	43.5	45.5[3]	2.1/1.4	7.4	0.96
19		H	60	1 bar	100	0.66	13.4	8.6	7.6	7.4	36.9	13.4	23.5	0.4/~6[2]	56.7	0.57
20		O	100	1 bar	100	0.32	47.4	22.9	9.9	6.9	87.1	47.4	39.7	0.8/4.1	8.0	1.20
21		O	120	1 bar	100	0.30	51.0	21.7	8.6	5.0	86.4	51.0	35.4	1.6/2.5	9.5	1.44
22[5]		O	100	1 bar	100	0.38	41.0	19.1	9.6	7.2	76.9	41.0	35.9	0.3/5.1	17.7	1.14
23		D	100	1 bar	99	0.28	44.8	29.4	11.0	n.d.	85.2	44.8[3]	40.5[3]	0.3/8.2	6.3[4]	1.11
24		D	120	1 bar	99	0.28	50.0	23.9	9.0	n.d.	83.8	50.5[3]	33.3[3]	0.3/6.2	9.8[4]	1.52
25[5]		D	100	1 bar	86	0.33	35.6	21.5	9.5	n.d.	77.4	41.4[3]	36.0[3]	0.3/6.1	16.2[4]	1.15

[1] α = tetramer/trimer molar ratio, characteristics of Flory-Schulz distribution shape

[2] Determining the concentration of *n*-hexane in reaction mixture is made difficult due to use of TIBA solution in hexane.

[3] Not counting decene pentameter (low resolution of $C_{50}H_{100}$ by GC)

[4] Including decene pentamer

[5] Preparatory experiment, 5 mol. of monomer, 1 mmol (0.02%) of zirconocene.

[6] Preparatory experiment, 5 mol of monomer, 1 mmol (0.02%) of zirconocene, 8 h.

For [5] and [6] the yield was determined by weighing and GC analysis of fractions rectified *in vacuo* (dimer, oligomers, remainder)

Table 4 Viscosity characteristics of α-olefin oligomers.

No. of C atoms	Oligomer	KV^{-40}, sSt	KV^{40}, sSt	KV^{100}, sSt	VI	PP, °C	d at −40 °C, g/mL	d at 20 °C, g/mL
12	**H2H**	9.00	1.28	–	–	−73	0.7920	0.7412
16	**O2**	–	2.6	–	–		–	–
16	**O2H**	53.1	2.82	–	–	−43	0.8190	0.7699
18	**H3**		3.12				0.8355	0.7878
18	**H3H**	167.2	3.57	–	–	−94	0.8355	0.7878
18	H3H (BF$_3$ catalyst) [3]	165	3.8	1.4	–	< −55		
20	**D2**		4.55	1.7	14			
20	**D2H**		5.30	–	14	−7		0.7829
24	**H4**		7.55	2.10	62			
24	**H4H**	1335	8.93	2.28	46	−79	0.8425	0.7957
24	H4H (BF$_3$ catalyst) [3]	1780	9.8	2.6	94			
24	**H22H**	3030	12.4	2.72	27	−71	0.8475	0.8016
24	**O3**		6.5	2.06	114			
24	**O3H**	552.1	7.56	2.20	92	−86	0.8420	0.7955
24	O3H (BF$_3$ catalyst) [3]	580	8.0	2.3	92	< −55		
30	**H5**		17.55	3.6	76			
30	**H5H**	6798	19.2	3.8	76	−67	0.8465	0.8007
30	H5H (BF$_3$ catalyst) [3]	7850	18.1	3.8	96			
30	**D3**		14.61	3.65	140			
30	**D3H**	1897	15.05	3.70	137	−75	0.8515	0.8058
30	D3H [EBTHI]Zr - borate [15]		13.5	3.39	128			
30	D3H (BF$_3$ catalyst) [3]	2070	15.6	3.7	122	< −55		
32	**O4**		13.94	3.44	125			
32	**O4H**	3135	18.4	4.0	115	−74	0.8655	0.8211
32	O4H (BF$_3$ catalyst) [3]	4750	20.0	4.1	106	< −55		
32	**O22**		28.1	5.4	130			
32	**O22H**	6374	29.4	5.4	119	−68	0.8755	0.8320
40	**O5**		32.9	6.05	132			
40	**O5H**	11651	36.2	6.4	129	−68	0.8750	0.8317
40	O5H (BF$_3$ catalyst) [3]	10225	30.9	5.6	124			
40	**D4**		31.3	6.03	142			
40	**D4H**	8631	34.5	6.52	145	−66	0.8755	0.8322
30	D4H (BF$_3$ catalyst) [3]	7475	29.0	5.7	141			
40	**D22**		29.43	5.90	150		0.8780	0.8346
40	**D22H**	15615	42.0	7.25	136	−52	0.8346	0.7920