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REVIEW

Oligomerization of higher α-olefins to poly(α-olefins)

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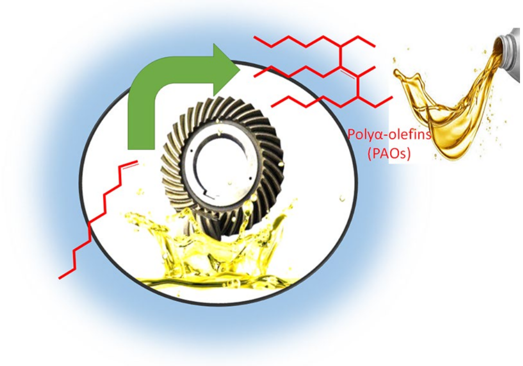
Abstract

Poly(α-olefin) (PAO) type synthetic lubricants have attracted considerable interest in both the academic and industrial sectors in the last two decades. The continuous growth of commercial demand for PAO products has motivated the development of new catalysts for the production of advanced PAOs with high yield and engineered structures. Today, industrial synthesis of PAOs requires precise control of the architecture (including molecular weight and its distribution, branching type and ratio) of oligomers. These microstructural features tune the final end-use properties of this type of lubricants in terms of pour point, kinematic viscosity (KV) and viscosity index (VI). PAO microstructural control, successfully accomplished by conventional Lewis acids such as $AlCl_3/BF_3$ systems, transition metal-based catalysts, and ionic liquids as active precursors are reviewed here. However, researchers are still looking for green catalysts employed at moderate temperatures to produce low-viscosity PAOs, which make up a large market share of PAO products. Structure–properties relationship in PAO-type lubricants as well as the various applications of PAOs such as engine oils, high-viscosity oils, and greases are other topics discussed here. Finally, with emphasis on new developments in PAO as well as weaknesses in the field under study, some new promising areas for future research are introduced.

Graphical abstract



Keywords Poly(α-olefin) · Oligomerization · PAO · Oil · Catalyst · Lubricant

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Introduction to poly(α-olefins)

Poly(α-olefins) (PAO), the hydrogenated oligomers of C_8-C_{12} type α-olefins, are classified as the group IV of American Petroleum Institute (API) category and possess about 42% share of total synthetic oils market around the world [1–3]. In fact, they belong to a class of molecularly engineered oligomers with optimized viscosity index (VI), pour point, volatility, oxidative stability and etc. The PAO fluids are usually produced from 1-dodecene (C_{12}) and 1-decene (C_{10}) as the starting materials [4]. The main growth of PAOs in Western Europe and North America took place in the late 1980s in response to increasing market demand in the automotive lubricant industry [5], and to date, the highest demand for PAO product has been requested by the above industry sector.

In comparison with conventional mineral oils, PAOs exhibit excellent performance [6, 7], i.e., higher viscosity index (VI), lower evaporative loss, lower pour point and higher thermal-oxidative stability [2]. They are widely used as surfactants, fragrances, corrosion protective coatings, adhesives, and synthetic lubricants [8]. PAOs are generally graded and differentiated for different applications by their kinematic viscosities at 100 °C (KV^{100}). The most common grades have a kinematic viscosity between 2 and 100 cSt. PAOs meet a number of characteristics of an ideal hydrocarbon lubricant. In this lubricant family, the chain length has a dramatic effect on the characteristics of the final product, so with increases in straight chain alkanes its viscosity is sharply increased. This trend is also true for the pour point and the viscosity index. The volatility of PAOs is lower than that of petroleum oils of the same viscosity, and these synthetic base oils contain also very small amounts of unsaturated chains. The amount of sulfur and nitrogen impurities in these oils is insignificant. However, in some oxidation experiments, additive-free PAOs have shown lower resistance to oxidation than petroleum oils. This seems to be due to the small amounts of natural antioxidants that have survived various refining processes and remained in petroleum base oils. The response and compatibility of PAOs toward antioxidants is better than that of petroleum products. On the other hand, the low polarity of these compounds makes polar additives less soluble in these products.

The commercial process for the production of PAOs involves several steps, including oligomerization and hydrofinishing followed by distillation to isolate α-olefin oligomers with similar molecular weights, which are subsequently blended in suitable ratios to obtain different grades [8]. A wide range of catalytic routes and reaction conditions are employed to synthesize PAOs. Among them, Lewis acid catalysts such as boron trifluoride and aluminum trichloride are the dominant catalyst categories in PAO production industry. In addition, several other catalytic routes have been reported in patents and published literature, mainly including metallocenes, post-metallocenes, and ionic liquid-based systems.

Given the importance of this class of lubricants, in this review we have focused on the application of catalyst systems for oligomerization of α-olefins to PAOs. Then, structure–properties relationship in these lubricants, and their applications have been discussed. Finally, emerging techniques have been presented as an opportunity to synthesize high quality PAOs.

Cationic systems for oligomerization of higher α-olefins

PAOs, based on their KV^{100} (i.e., kinematic viscosity at 100 °C), are classified into several categories of 2, 4, 6, 8, 10 and 100 cST. Among them, PAO4 and PAO6 are the most popular among them, as they are employed in the automotive industry as engine oils [9]. In fact, the PAO market is steadily growing, which is in line with the advances in the automobile industry that needs PAO-type synthetic lubricants, since they can efficiently improve fuel economy by diminishing wear and tear on engine parts. Cationic oligomerization of higher α-olefins is commercially performed in the presence of a Lewis acid catalyst, such as BF_3 or $AlCl_3$, coupling with high conversion of greater than 90% toward primary monomer reactant [10]. $AlCl_3$ can produce high-viscosity ($KV^{100} > 10$ cSt) and VI ($200 > VI > 130$) base stock, while BF_3 is a preferred choice for the synthesis of low-viscosity PAOs ($KV^{100} < 10$ cSt). The difference is originated from the Lewis acid strength of the above compounds. In the case of strong Lewis acid catalyst, i.e. BF_3, the formation of carbonium ion that initiates the cationic oligomerization, should be faster, leading to low molecular weight products. In the following sections, the reported works accomplished with two mentioned cationic systems are considered in detail and the advantages/disadvantages of each system are discussed.

BF_3-based systems

BF_3 is a widely used catalyst for the oligomerization of α-olefins. In particular, it is commercially employed for the production of low-viscosity oil ($KV^{100} = 2$–10 cSt), suitable for low-temperature applications. In this regard, besides BF_3 catalyst, different active H-containing compounds such as H_2O [11], Nafion [12], butanol [13], alcohol alkoxylates [14], and acid anhydrides [15] as co-initiator have been successfully employed to produce low-viscosity PAO with $VI > 123$. The combination of initiator and co-initiator produces the H^+ intermediate, acting as active catalyst. A considerable enhancement on the molecular weight distribution control was patented by Mobil Oil that BF_3 gas was used as a pre-catalyst and alcohol as a co-initiator [16]. The oligomerization product was mainly C_{30} trimer, when 1-decene was used as feedstock. In fact, due to the skeletal branching, the final PAO oil contained a highly branched structure that was useful at low pour point. This characteristic enhanced excellent lubrication properties to PAOs, especially when starting the engine in cold temperature environments. Notably, Mobil commercialized the process to introduce the 1™ family of PAOs into the US market in 1974.

It was well accepted that in olefins oligomerization using acid catalysts [17], the reaction begins when the olefin monomers are converted to carbonium ions on Brønsted acid sites and are further combined with other olefin monomers in the reaction pool to form long chains [17].

Furthermore, the use of a two-step process in two-step tank reactors has also been reported to achieve high conversions over 95% [18]. It was claimed that by controlling the percentage of oligomerization conversion in each reactor and overall conversion, the relative ratio of multiple oligomers and thus the product viscosity could be suitably controlled [19].

In catalyst systems used, the accurate controlled composition of different olefins can decrease the pour point of the product to the required level. Bagheri and coworkers have reported oligomerization of C_{16} vinylidene monomers and 1-tetradecene using BF_3/butanol/butyl acetate system [20]. The final PAO in a specific monomers composition showed a $KV^{100}$of 3.93 cSt, $KV^{40}$of 17.3 cSt, VI of 124 and pour point of − 63 °C. The features of obtained product were comparable to those of commercially available PAO4 ($KV^{100} = 4.0$ cSt).

The major drawback of the oligomerization process based on a BF_3/donor system is the liberation of fluorine-based by-products, which are converted to highly corrosive HF acid during PAO production. Due to toxicity and difficulties in handling BF_3 gas and dangerous treatment of effluents, operations and maintenance costs increase. To solve this problem, researchers have tried to find a good alternative against dangerous BF_3 system.

$AlCl_3$-based systems

Similar to BF_3, $AlCl_3$ is also a commercial catalyst for α-olefin oligomerizationin combined with a second moiety, consisting of active H-containing molecules such as water and various alcohols. In this regard, the use of Al powder and polyester along with $AlCl_3$ as the catalyst mixture was also reported [21], which produces halogen-free PAOs. The nature of co-initiator can influence the viscosity of PAO product [22]. In the conventional $AlCl_3$/alcohol system, the viscosity of PAO decreases with the molecular weight of alcohol (from methanol to ethanol and butanol) [23]. In these systems, the molar ratio of $AlCl_3$ to co-initiator is usually around 0.5 [24].

As an interesting study, the promotion effects of haloalkane and metal chlorides (VCl_3, $CrCl_3$, and $TiCl_3$) on oligomerization activity and properties of 1-decene oligomers were investigated. The results obtained indicated that a small amount of VCl_3 added to the $EtAlCl_2-CHCl_3$ catalyst can increase the oligomerization yield and VI values [25].

Unlike prominent benefits, $AlCl_3$ is corrosive in its pure form and has hazardous characteristics. Hence, researchers try to find green processes to overcome these drawbacks [4]. In this regard, supported catalysts present improved catalytic activity in α-olefin oligomerizations, and using these catalysts, the architecture of oligomer, viscosity and PDI will be easily accessible [26]. Moreover, supporting $AlCl_3$ is a very promising approach to minimize the production costs and environmental impacts of the process [27]. Immobilization of $AlCl_3$ on the supports, such as silica and alumina can be successfully accomplished through the reaction of $AlCl_3$ with the support in the gas–solid phase [28] or in the gas–solid phase using CCl_4 or $CHCl_3$ as the solvent [29]. The most studied method to obtain an immobilized $AlCl_3$ catalyst has been based on the chlorinated Al_2O_3 support, which was subsequently employed in the polymerization of 4-methyl-1-pentene [30], the copolymerization of propylene and butane [31], and the polymerization of isobutene [32–34]. Notably, γ-Al_2O_3 is a thermally resistant support with a high amount of Lewis acid sites, which can improve catalytic activity [35, 36]. These catalysts are categorized as heterogeneous acid catalysts. In these systems, the support can act as counter ion and influence dramatically the final PAO characteristics in terms of molecular weight and chain architecture [37].

The utilization of bimetallic catalysts by immobilizing $AlCl_3$ and $TiCl_4$ (together) on different chlorinated supports was also reported in the production of 1-decene-based PAOs using a fixed-bed reactor [38]. In the employed heterogeneous systems, a linear relationship was found between PAO yield and chlorine content of the support. In addition, a study of $AlCl_3$ immobilization on Al_2O_3, SiO_2, as well as $FeCl_3/Al_2O_3$ and $FeCl_3/SiO_2$ mixed carriers approved different efficiency of the utilized support in controlling PAO microstructure [4]. In the gel permeation chromatography (GPC) report, the use of single supports enhanced oligomer molecular weight, while in bi-supported catalysts, this property was reduced.

Besides $AlCl_3$, other Al-alky-halogen compounds, such as $AlEt_2Cl$ and $AlEtCl_2$ [39] were also employed in the preparation of Al/support heterogeneous precursors to catalyze 1-decene oligomerizations [40]. It was established that Al compound is located onto the silica surface through Si–O-$AlCl_2$ bond. By changing halogen nature from Cl to Br, in $EtAlBr_2$, the yield of olefin oligomerization considerably decreased, however, using these heterogeneous systems, a relatively high VI was obtained [41]. The molecular weight of PAOs obtained from the homogenous and heterogeneous catalysts was similar, although, the molecular weight distribution was slightly broader in the heterogeneous systems.

Transition metal-based complexes for oligomerization of higher α-olefins

Higher α-olefins oligomerization using transition metal-based single-site organometallic complexes has attracted considerable attention in the last decade. In fact, significant skeletal isomerization occurs when performing bulk oligomerization of α-olefins to produce low-viscosity PAOs through a cationic system (Fig. 1a). However, undesirable side reactions are considerably decreased by utilizing transition metal-containing complexes, mostly activated by methylaluminoxane (MAO) cocatalyst. These catalysts provide uniform PAO chains (Fig. 1b) through 1,2-insertions of monomers in the metal-C bond, which is subsequently terminated by the β-hydride transfer mechanism [42].

Metallocenes, developed by Kaminsky, in conjunction with MAO cocatalyst have widely been employed as catalyst systems for the synthesis of metallocene-based PAOs (mPAOs) [43]. Almost all reports are based on bridged metallocene catalysts, because they have less steric hindrance as the monomer approaches the metal center. Alongside catalyst architecture, catalyst-to-MAO molar ratio can also affect the polymerization activity and the molecular weight of produced PAOs. Moreover, the mPAOs molecular weight can be altered by polymerization conditions, i.e., temperature, metallocene-to-monomer ratio, and addition of hydrogen [44]. The excellent choice of metallocene catalysts for the production of highly valuable mPAOs makes them a good candidate for the synthesis of these special mPAO products. In fact, mPAOs could find more advanced applications than conventional PAOs owing to their outstanding features like extremely high VI, wider temperature range application coverage, and fluidity at lower temperatures (lower pour points) [45].

It was found that in metallocene catalysts, the symmetry of ligand/catalyst plays an important role in determining PAO tacticity [46], where the amorphous PAO is suitable for lubricant applications [47]. In addition to catalyst symmetry, ligand architecture is another important factor in controlling PAO microstructure. Notably, substituted Cp rings represent high viscosity and VI PAO [48], however, the kinematic viscosity (KV) decreases with the reaction temperature [49].

Nifant'ev and coworkers did a comprehensive study on the ability of some zirconium catalysts (Fig. 2) activated by tri-isobutyl aluminum and MAO activators in the 1-hexene, 1-octene and 1-dodecene oligomerizations [42]. They found that the production of normal alkanes decreases in low Al/Zr ratios. Among the studied complexes, catalyst No. 3 demonstrated the highest efficiency of 98% after 4 h of testing at 60 °C, which yielded oligomers with a degree of polymerization in the range of 2–5.

Alt and coworkers synthesized different bis(arylimino) pyridine complexes of Fe(III) (Fig. 3) with different halide

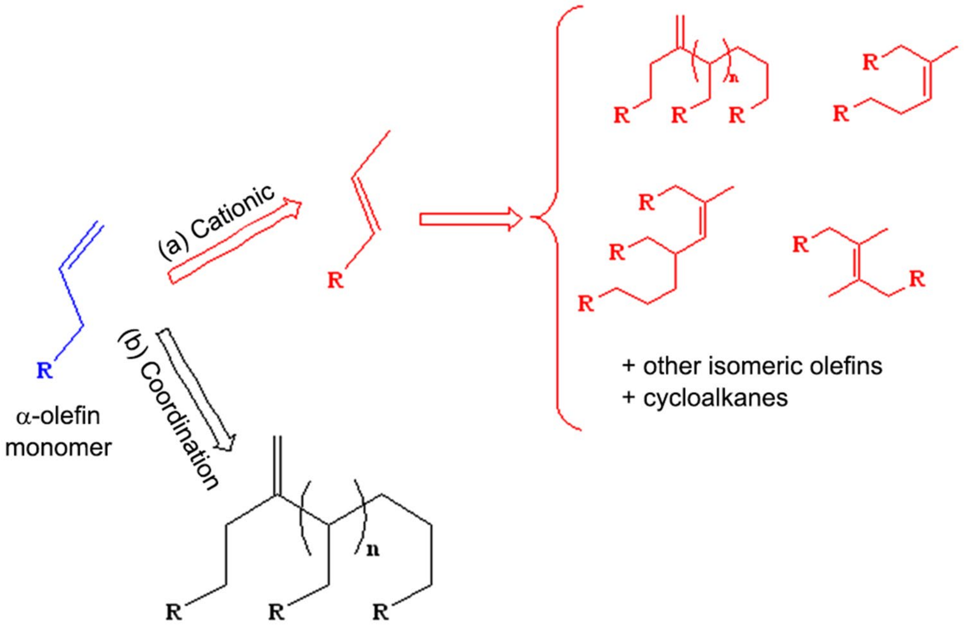


Fig. 1 PAO structures from **a** cationic, and **b** coordination polymerization systems

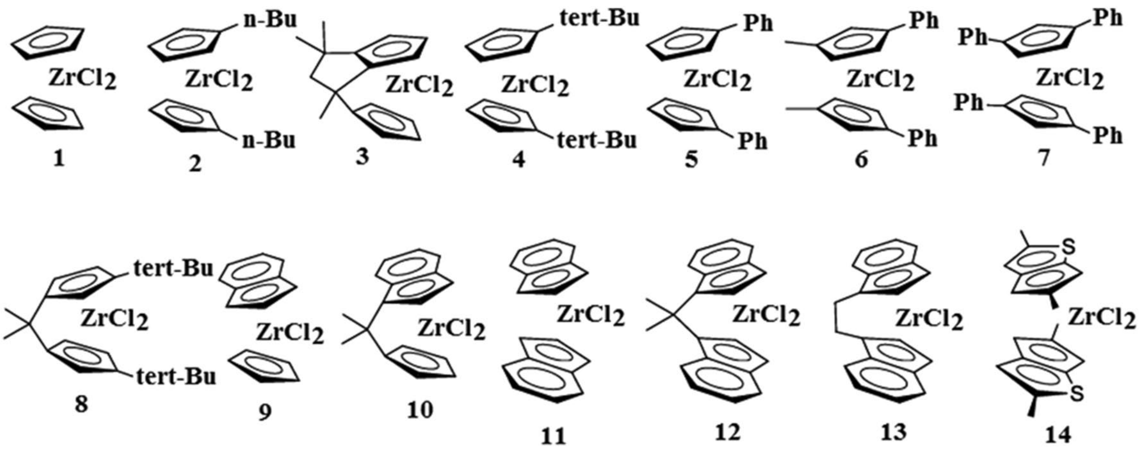


Fig. 2 Metallocene catalysts studied by Nifant'ev and coworkers [42]

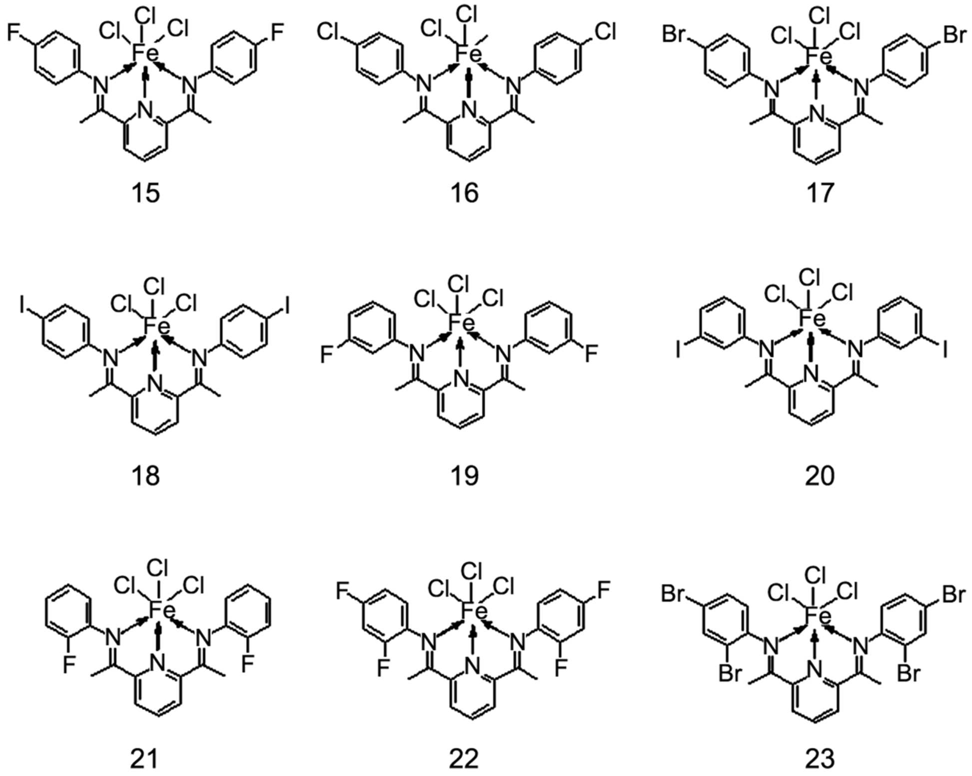


Fig. 3 Structure of bis(arylimino)pyridine ligands with different substituents employed by Alt and coworkers [50]

substituents (F, Cl, Br, I) at different positions of the iminophenyl group of the ligand and applied them for homogeneous 1-pentene and 1-hexene oligomerization and co-oligomerization reactions. Notably, catalyst activities decreased in the order of I > F > Br > Cl from 152 to 43, 24 and 23 kg/mol.h for the catalysts containing halogen atom in the *para* position (i.e., catalysts 15 to 18 in Fig. 3) due to the electronic effects. Furthermore, according to the authors, the fluorine substituent in the meta-position of the iminophenyl ring has made (1 kg/mol.h) homo oligomerization reactions unpleasant but necessitates co-oligomerization reactions of 1-pentene and 1 hexene. Evidently, small steric or electronic differences at the catalyst active sites are responsible for this result [50, 51].

Group IV metal complexes-containing aryloxide ligands provided with heteroatom donors (generally ONNO-type bis(*o*-aminophenolato)s are an important class of organometallic catalysts. In fact, the steric as well as electronic character of the final complexes can be tuned easily by employing the above mentioned ligands [52, 53]. It was demonstrated that in zirconium catalysts bearing phenolate rings, the catalyst activity and the architecture of synthesized polymer are affected by alteration of steric and electronic features by the substituents on the phenolate rings [54, 55]. Actually, bulky substituents in the *ortho* position caused isotactic polymerization, while electron-withdrawing groups provided highly active catalysts, which yield polymers with low tacticity and low molecular weight. According to the reported theoretical [56, 57] and experimental [58–60] results conducted on different group IV complexes-containing chelating alkoxide ligands, high electron density on the metal center reduces barrier energy for monomer insertion between the metal center and growing polymer chain. On the other hand, there is a report that electron-donating moieties increase catalytic activity in a class of titanium bis(phenolate) complexes [61].

Among different ONNO-based ligands, salan type ones are significantly important in the α-olefin polymerization and oligomerization reactions. They principally possess identical phenolate rings [62], in which bulky substituents diminish catalytic activity, however, improve polymer isotacticity; and electron-withdrawing groups enhance their activity [63–65]. Liu and coworkers reported the oligomerization of 1-hexene at 20 °C with bimetallic catalysts obtained by the reaction of titanium and zirconium (IV) with organometallic compounds [66]. Then, they investigated the effect of the central metal, the substations attached to them, and the effect of the auxiliary catalyst on oligomerization. Ayoub and coworkers synthesized zirconium catalysts based on imidazole, whose oligomerization behavior for 1-hexene was changed by adding trimethyl phosphine ligand to the polymerization behavior [67]. The ability to force a catalytic converter to change from oligomerization to polymerization behavior or vice versa can help finding the potential missing links in the mechanism of action of these catalysts and can also lead to the discovery of new applications for these materials. Wu and coworkers examined the isomerization and oligomerization of 1-hexene with nickel-based ketoimine complexes [68]. The results of GC and GC-Mass showed that hexene isomers and isomers from dimerization accounted for a large percentage of the products.

Abu Omar and coworkers studied the kinetics of 1-hexene oligomerization using four zirconium-based bis-phenolate amine catalysts to study the effect of the electronic nature of pyridine ligand on their kinetics [69]. The studied kinetic parameters included molecular weight, monomer consumption and end group analysis. The results showed that the electronic nature of pyridine ligand affects the placement of the monomer in the growth, misplacement and recovery steps. The structures of the catalysts and ligands studied are shown in Fig. 4. In the next study, they studied the kinetics of 1-hexene oligomerization using a self-synthesized zirconium-based amino bis-phenylate catalyst [70]. This time, they investigated the effect of the amount of co-catalyst on the loss of the benzyl group and the subsequent kinetic consequences [71]. They showed by kinetic studies that reducing the amount of co-catalyst (B $(C_6F_5)_3$) reduces the consumption rate of the monomer and also narrows the

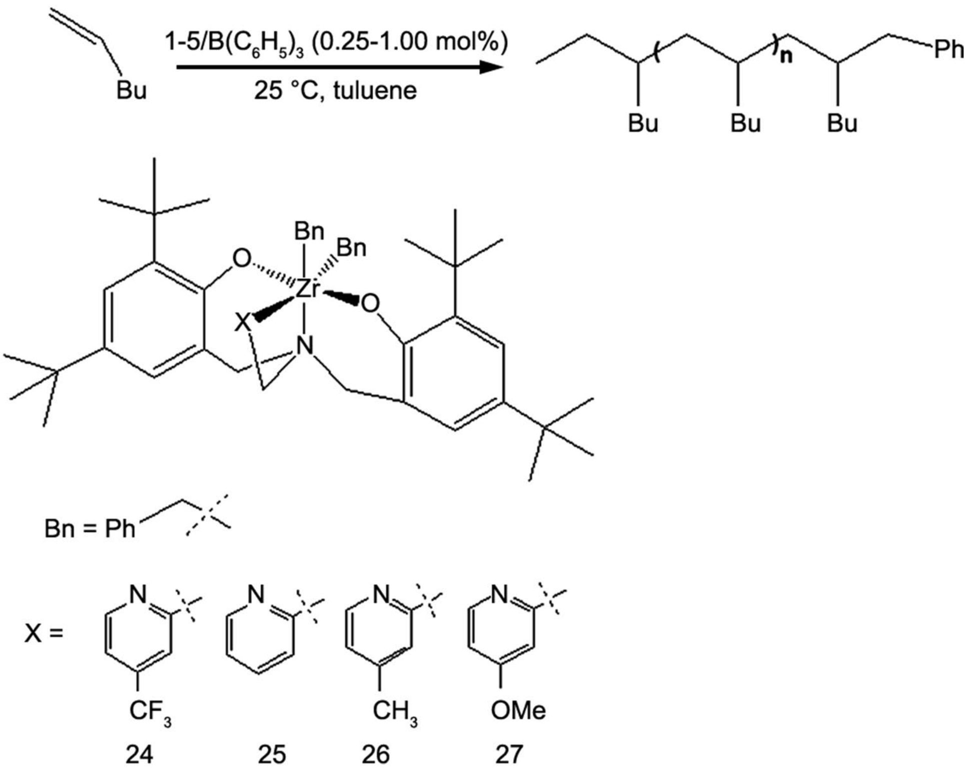


Fig. 4 Structure of the catalysts studied in the work of Abu Omar and coworkers [69]

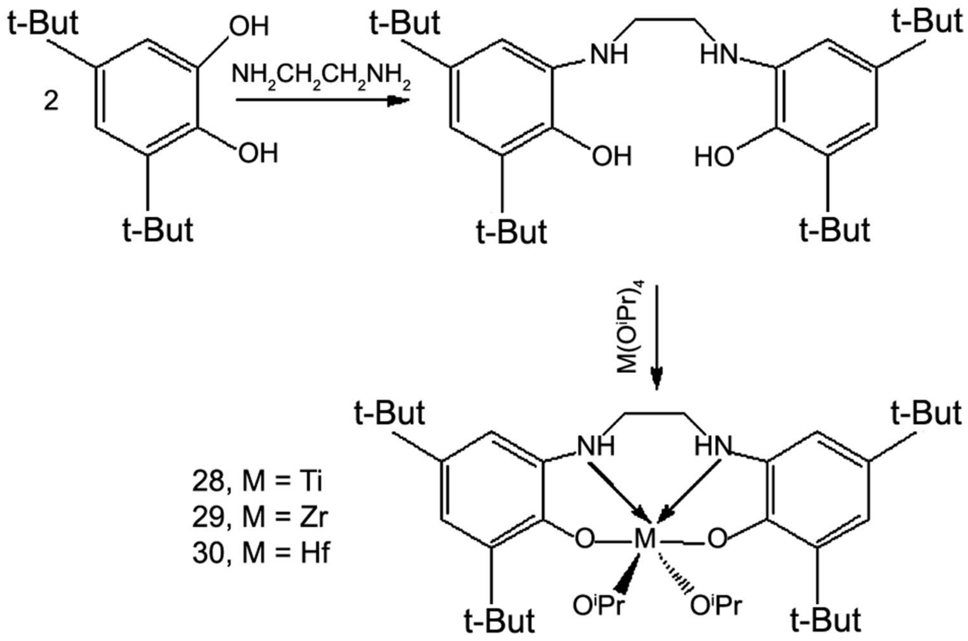


Fig. 5 The procedure used for the synthesis of ONNO-based catalysts [8]

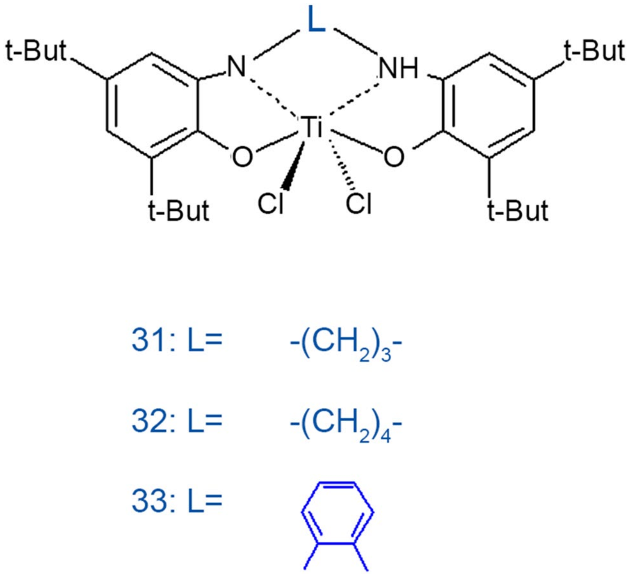


Fig. 6 Molecular formula of ONNO-based complexes [72]

molecular weight distribution index and shifts it to lower values.

Recently, we employed a family of group IV diamine bis(phenolate) catalysts for the oligomerization of 1-decene (Fig. 5). According to the obtained results, catalyst **29** had the highest activity of 479.21 followed with **30** (475.68) and **28** (472.86 g (oligomer)/mmol cat.h). Observed tacticity values for the synthesized catalysts were according to the following order: **28** (88.5%) > **29** (87.3%) > **30** (86.8%). Notably, there was found a close relationship between the type of metal and oligomers molecular weight, and, as expected, increasing oligomerization temperature widened PDI (M_w/M_n) values [8]. Then, to unravel the effects of ligand structure on the catalytic oligomerization of 1-decene monomer, a series of new titanium (IV) complexes bearing tetradentate [ONNO] salan type ligands: $Ti[2,2'-(OC_6H_2-4,6-{}^tBu_2)_2NHC_3H_6NH]\ (Cl)_2$ (**31**), $Ti[2,2'-(OC_6H_2-4,6{}^tBu_2)_2NHC_4H_8NH]\ (Cl)_2$ (**32**), and $Ti[2,2'-(OC_6H_2-4,6-{}^tBu_2)_2NHC_6H_4NH](Cl)_2$ (**33**) (Fig. 6) were synthesized by our research group using a simple two-step procedure. Under the same reaction conditions, **33** oligomerized 1-decene with a high activity of 718.81 g (oligomer)/mmol cat.h. According to the GPC data, the molecular weight of the obtained oligomers had a close relationship with the ligand architecture used i.e., PDI shifted to the higher values as the length of the aliphatic linkage between nitrogen donor atoms increased. The 1-decene oligomers obtained by **33** exhibited the highest isotactic value, whereas the oligomers obtained from **31** and **32** demonstrated the lower tacticities of 74% and 71%, respectively [72].

Ionic liquid-based systems for oligomerization of higher α-olefins

Ionic liquids (ILs) are regarded as low melting point organic salts (below 100 °C) that have high electric conductivity and mostly demonstrate environmental-friendly feature. The cations in the structure of ILs are generally formed from quaternary ammonium or heterocycles, while various organic or inorganic compounds can be useful as anions. Indeed, the versatility of the cation and anion in the IL backbone makes them prominent with specific properties and utility

[73–75]. In the recent years, there have been several reports on the oligomerization of α-olefins using ILs in solid or liquid form, together with $AlCl_3/BF_3$ catalyst [76] or alone. In combination with Lewis acids, a catalyst to IL molar ratio of 2:1 is preferred [77], where both decrease and increase in the molecular weight of PAO were reported in the so called systems [78, 79].

In this subject, it was reported that, the combination of the haloaluminate ionic liquid and halide component can be considered as a catalyst system for the oligomerization of higher olefins [80]. For example, Hogg and coworkers synthesized some new IL catalysts consisting of picoline or pyridine and BCl_3 moieties that were employed as suitable alternatives to corrosive neat BF_3. It was shown that catalytic activity was widely affected by the nature of the anion, substituents on the cation, and oligomerization temperature [81]. Ding and coworkers have reported an IL system originated from $AlCl_3$ and 1-butyl-3-methyl imidazolium which showed high performance in 1-decene oligomerization with 74% yield [82]. According to the published results, it was found that ILs have significant impact on the final PAO properties produced by IL/cationic catalyst systems.

As mentioned before, a very carefully balanced level of branching is needed in commercial PAOs to attain sufficiently low pour point without sacrificing the temperature-dependent viscosity properties in terms of VI. This is mostly depended on the catalyst system and polymerization condition used in the PAO production. PAO4 and PAO6 that have the largest market share along the series, are mainly composed of 1-decene trimer (C30), tetramer (C40), and pentamers (C50). These oligomers are commercially synthesized by a BF_3/nBuOH cationic system, which offers high yield process with extremely low dimer content and no heavy byproducts in the crude PAO product. The essential problem is BF3 toxicity and release of HF after its hydrolysis by minor amount of humidity. It has safety and hazardous concerns in the industrial plants. Chlorogallate-based ionic liquids could achieve the desired products distribution with more than 90% yield, but they are much too expensive for commercial use [83].

Lewis super acidic borenium ionic liquids with the $[BCl_2(L)][M_nCl_{3n+1}]$ (L = pyridine or picoline, $n = 1$ or 2) formula have been employed to successfully synthesize PAO4 and PAO6 with good yield of > 90%. By changing the ligand (L) structure on the borenium cation, the oligomerization reaction condition, the amount of the chlorometallate anion and the catalytic activity and molecular weight of the PAO chains could be tuned [9].

Recently, our group has focused on the utility of $IL/AlCl_3$ catalytic systems for the oligomerization of 1-decene. In this regard, the nature of cation and anion moiety in the IL structure, in simple compound or polymeric form, was studied in detail.

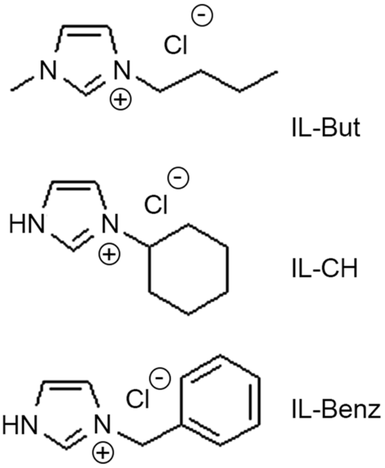


Fig. 7 Structure of ILs used in 1-decene oligomerization in combination with $AlCl_3$ catalyst [75]

In the first study, the effect of alkyl chloride type as 1-butyl chloride, cyclohexyl chloride and benzyl chloride in the 1-methylimidazole-based ILs structure on the performance of $IL/AlCl_3$ catalyst was investigated. The structure of studied ILs is illustrated in Fig. 7 [75]. It was demonstrated that the catalytic efficiency of the final catalysts can be controlled by the change of alkyl chloride nature, where the catalysts containing butyl chloride and benzyl chloride-based ILs yielded more uniform PAO chains with low molecular weight, KV, and branching ratio, and high VI values. However, the PAO form third IL had a basic characteristic similar to the one from neat $AlCl_3$.

Those outstanding achievements motivated us to pursue our studies on this subject. Then, the efficiency of IL system as simple component or in polymeric form together with $AlCl_3$ catalyst was targeted in the oligomerization of various olefin monomers, from C6 to C10. The structure of IL, synthesized from the combination of benzyl chloride,1-vinyl imidazole and PIL, and obtained by polymerization of the as-synthesized IL using AIBN initiator is displayed in Fig. 8. It was realized that molecular weight decreases by employing lighter α-olefin monomers. Furthermore, while the PAOs synthesized in the presence of $IL/AlCl_3$ catalyst contained almost heavier fractions, the chains from neat $AlCl_3$ and $PIL/AlCl_3$ represented similar molecular weight and KV^{100} values, and more uniform architecture with low short-chain branching which is beneficial to higher VIs [84].

Synthesis of PAOs using heterogeneous ionic liquid-based catalysts allows performing the cationic oligomerization in more controlled manner and greener and safer conditions, and so, this subject is quite attractive for researchers. However, only a few reports regarding to the PAOs production by supported ILs are available in the literature. In the same subject, the utilization of supported ILs on halloysite

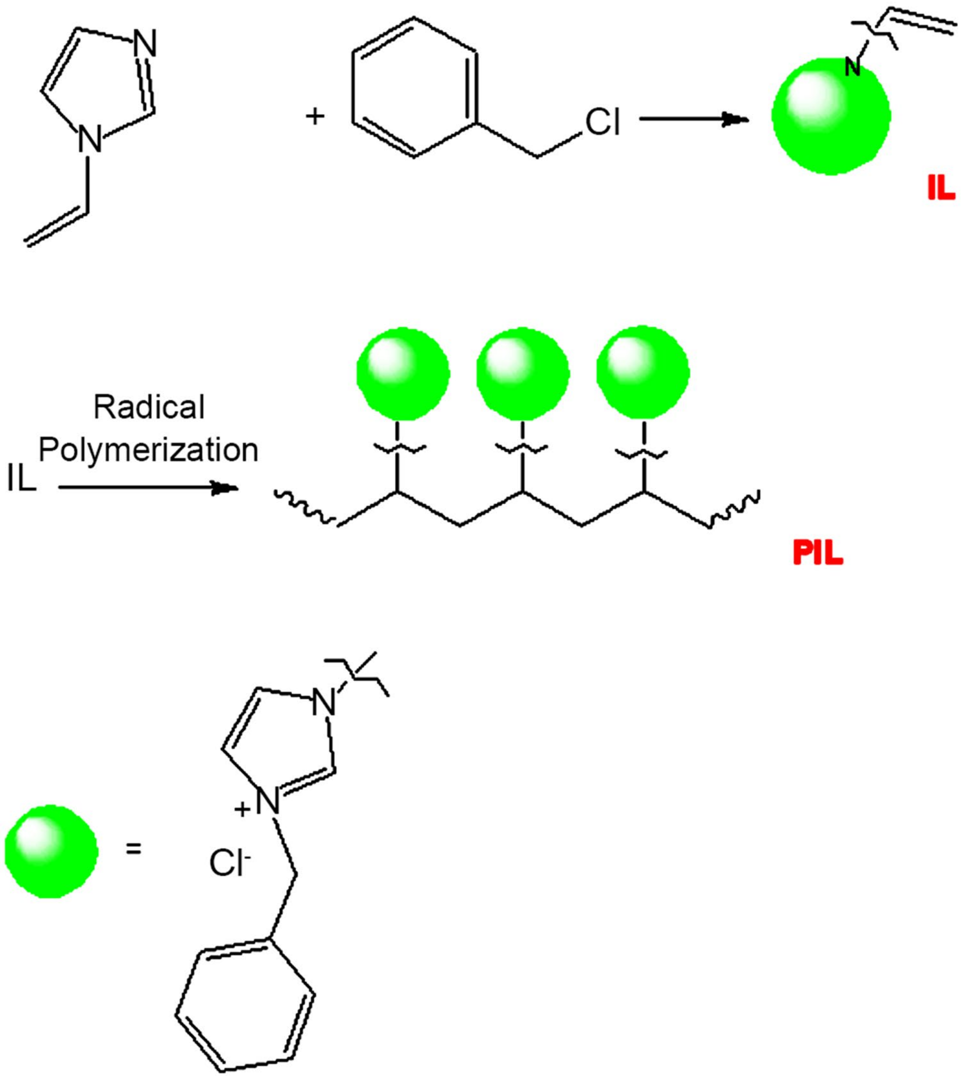


Fig. 8 Synthetic route for the production of IL and PIL [84]

nano clay was rationalized together with $AlCl_3$ catalyst in the oligomerization of 1-decene monomer [84, 85]. It was found that using supported ILs (Fig. 9b) in the composition of the catalyst, PAOs with nearly identical characteristics to the one from neat $AlCl_3$ can be obtained; as related simulated distribution (Sim Dis) curves in Fig. 9a.

With extremely low vapor pressure, non-toxic nature and low T_m (melting point, in case of neat ILs without support), ionic liquids have attracted immense attention from academic and industrial fields. Various technologies were proposed to separate and recycle the ionic liquids from different solutions after their function in order to minimize the cost and environmental effects. These methods mostly rely on adsorption, aqueous two-phase extraction, membrane separation, extraction, distillation, crystallization and force field separation methods [86].

In the commercial oligomerization of α-olefin monomers to yield PAO using BF_3 and $AlCl_3$ catalysts, there is a recycling section in industry where a continuous process is used. This is successfully achieved by simply distillation of the PAO products, just after the reactor outlet, to separate unreacted monomers. In this section, unreacted BF_3 is also recovered, together with monomer, and re-entered to the oligomerization reactors since it is gaseous in the PAO medium. However, recycling of $AlCl_3$ and ionic liquids cannot be achieved easily at the PAO plant, since they do not evaporate by simple distillation at the temperature used. In the case of supported ionic liquids, the separation can be easily performed by solid–liquid extraction. After separation from the solution, its recycling and purification can be successfully achieved by repeated washing using proper solvents and distillation process. The state of the art procedures in ionic liquids recycling has been discussed briefly in reference [86].

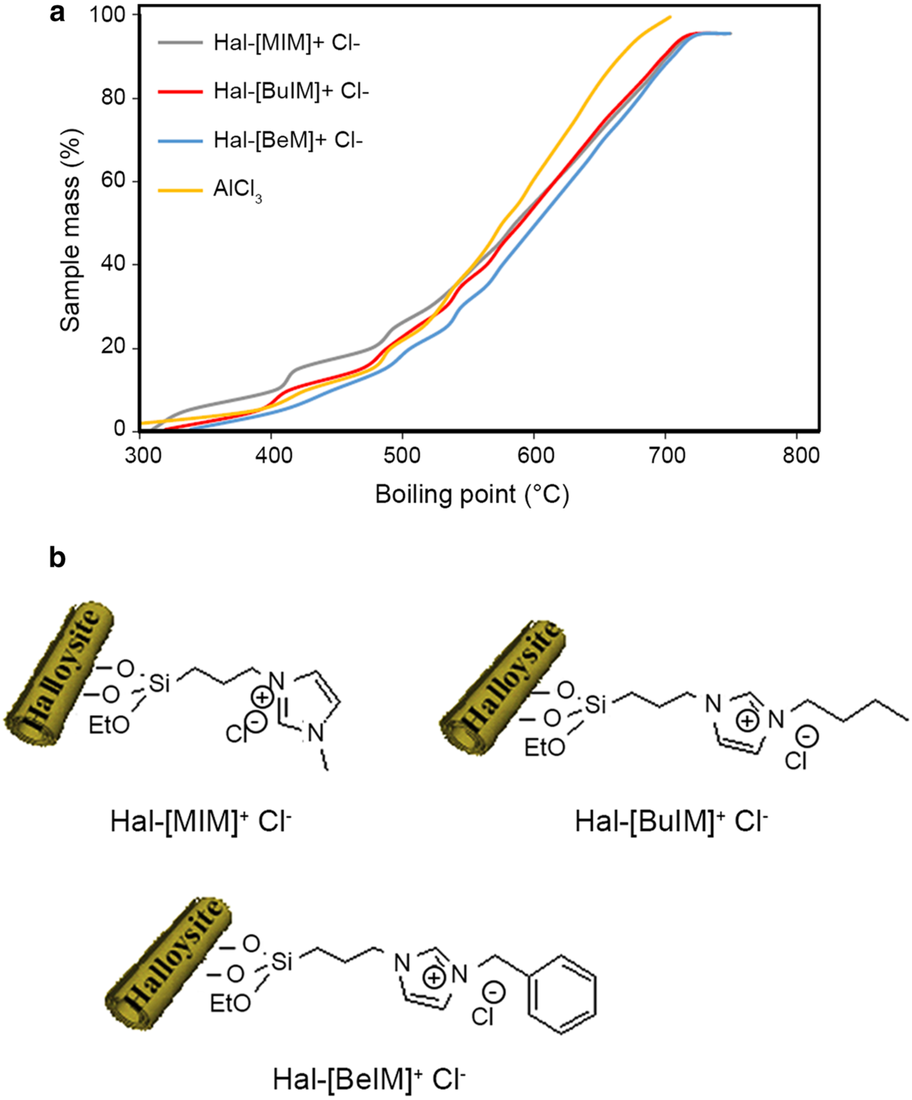


Fig. 9 **a** Simulated distribution curves of the as-prepared PAOs from supported IL/AlCl$_3$ catalysts, and **b** Structure of related ILs [85]

PAOs from mixed monomers

1-Decene and 1-dodecene monomers yield high VI and low pour point PAOs which are necessary in engine oil applications. Demand for PAO lubricants is growing rapidly, often leading to a shortage of 1-decene feedstock, which raises the price of the final product. On the other hand, the price of high olefins (> 10) is relatively high compared to low carbon olefins (< 10). Therefore, co-oligomerization procedure using relatively inexpensive α-olefins has been extensively performed to achieve properties similar those of 1-decene-based PAOs, however, at lower production cost [4, 87, 88].

1-Butene, as one of the side-products in petroleum refining by catalytic cracking process, is considered as a potential raw material in the PAO production, although its oligomers generally represent high branching degrees, resulting in high pour points and KVs [10]. Many efforts were conducted on the oligomerization of 1-butene with C8-C12 olefins, mostly employing zeolites or Ni-based catalysts [89–91]. Jiang and coworkers showed that 1-butene oligomerizations with higher α-olefins (from 1-hexene to 1-tetradecene) using $(Me_4Cp)_2ZrCl_2$/MAO catalyst system produce low molecular weight oily oligomers [92]. In fact, addition of the α-olefin to 1-butene decreased oligomerization activity, oligomer molecular weight and KV, but enhanced oligomer VI. Alt and coworkers synthesized 1-pentene and 1-hexene-based (co) oligomers using different bis(arylimino)pyridine complexes of Fe(III) containing different halide substituents (F, Cl, Br, I) at different locations in the iminophenyl ring of the ligand [50]. Figure 10 shows the distribution of co-oligomers with various catalysts. It can be realized that the catalysts used mostly yield dimer products. In another work, Alt and coworkers reported 1-pentene and 1-hexene co-oligomerization with 13 homogeneous metallocene catalysts. The co-dimerization reactions of 1-pentene with

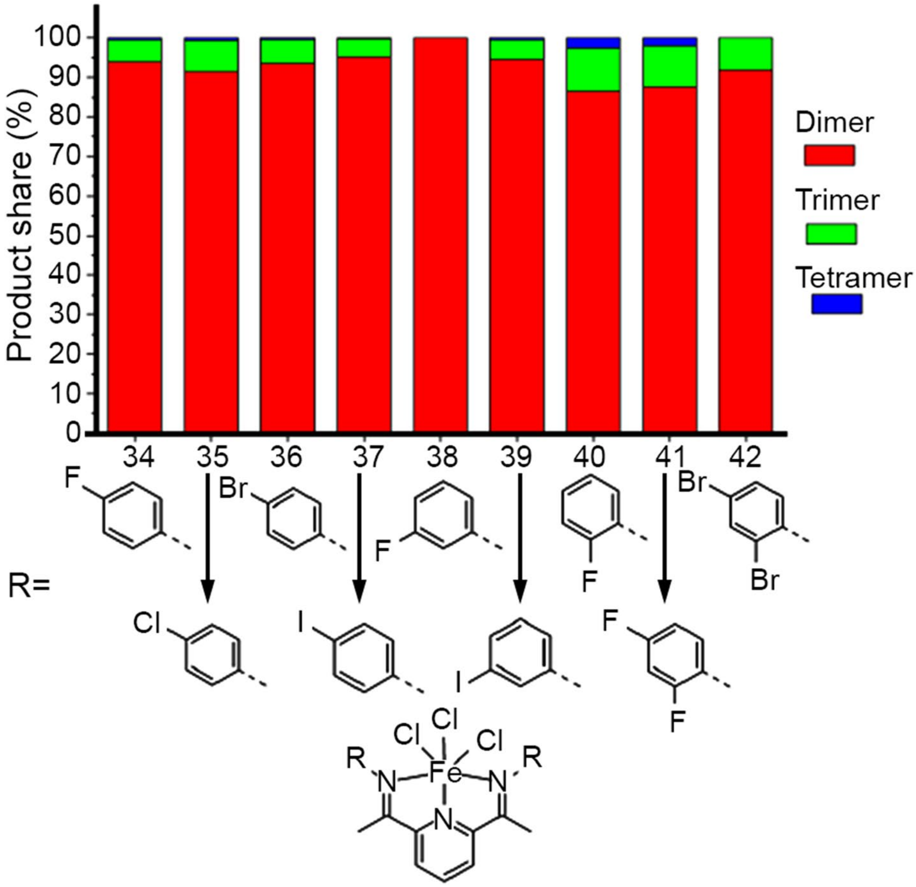


Fig. 10 Product distribution of 1-pentene/1-hexene co-oligomerization with different catalysts [50]

1-hexene yielded chains with binomial character in which the ratio of C10:C11:C12 was 1:2:1. In the same time, a ratio of 1:3:3:1 was found for C15 up to C18 type trimers. By changing the 1-pentene/1-hexene ratio in the feed, the binomial distribution progressed to products that were mainly composed of monomers with higher concentration in the feed. Notably, binomial product distribution was even recognized using the methyl branched olefinic feeds. Also, internal olefins could not be oligomerized using these conditions [51].

Structure–properties relationship in the PAO-type lubricants

High quality oils should have moderate viscosity at low temperatures because this property is essential for cold engine start. The quality of a motor oil is tested at low temperatures with its pour point and kinematic viscosity at – 40 °C (KV^{-40}). Engine oils must be viscous at operating engine temperatures to reduce engine friction and aging. The pour point and viscosity of oils are strongly related to the microstructure of hydrocarbons [8, 72, 93]. Linear and long chain oligomers (Fig. 11), which are classified in groups I and II

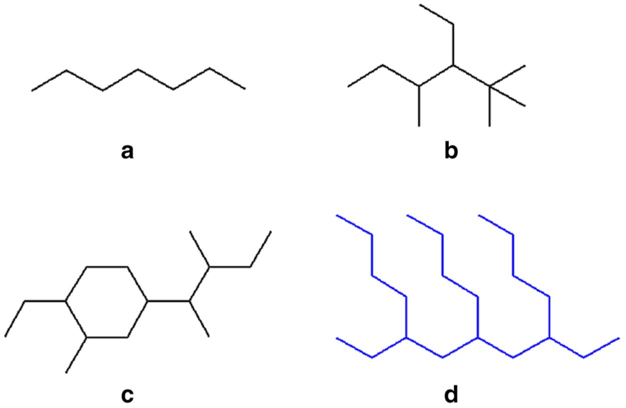


Fig. 11 Types of main structures of hydrocarbons [94]

of oils (according to the API classifications), have a very high pour point. Therefore, the oils of these groups (I and II) cannot be employed at low-temperature applications. Group III oils include hydrocarbons with short, cyclic branches (Fig. 10b, c). The oils in this group have a high pour point and KV^{-40}. Oppositely, long branched chain hydrocarbons (Fig. 10d) have a low pour point and a high-viscosity index. Sequential oligomerization and hydrogenation are the only available method to obtain oils with structure (d) [94]. These oils are classified as category IV.

In fact, the chain microstructure in terms of side chain length and degree of polymerization plays a major role in the final characteristic of PAO. As a general rule, the presence of a long linear chain as a branch or main chain enhances PAO VI, however, it is detrimental to low pour point. In other words, highly branched structures improve low-temperature characteristics (lower pour point), but, excessive short-chain branching diminishes the VI value. Therefore, the combinational effect of side chain and main chain lengths should be considered [25].

In cationic polymerizations, a complex mixture of polymeric chains is achieved owing to extreme skeletal isomerizations during polymerization reaction and various chain transfer mechanisms. In fact, polymerization due to less than 10% of the polymer chains in a reaction pool is initiated by the cationic initiator used, the rest being produced through the initial carbenium sites resulting from the chain transfer reactions [95]. Given the different isomerization mechanisms and the complex architecture of oligomer chains, it is clearly important to realize the possible relationship between the PAO skeleton and its viscosity-temperature properties. In this line, Sarpal and coworkers investigated the microstructure of three different hydrogenated base oils by ^{13}CNMR and tried to correlate VI and pour point to the structural parameters [96]. It was found that long chain branches, CH_3 branching in the PAO chain center, low aromatic ring, less ethyl branches and less tertiary carbons are favorable to high VI [97]. Scheuermann and coworkers studied the molecular structure of α-olefin dimers and its effect on temperature-VI relationship. According to their findings, when the amount of linear isomers increases, the dependence of PAO viscosity on temperature decreases [98]. Furthermore, long aliphatic side chains have a positive effect on lowering pour point values [99].

Distortionless enhancement by polarization transfer (DEPT) technique is commonly used to elucidate the oligomer chain microstructure, and to achieve an accurate view of the molecular skeleton. It relies on ^{13}CNMR technique and determines methyl (CH_3), methylene (CH_2), methine (CH), and quaternary carbons in a spectrum. Worth mentioning, in the DEPT spectra, the peaks under the base line stand for CH_2 moieties. Indeed, DEPT is an essential technique in the analysis of chain branching in PAO hydrocarbons. It was employed by our group to acquire information about the effect of solvent nature on the microstructure of final PAO, prepared from 1-decene oligomerization by $AlCl_3$ in the xylene and heptane media [100]. According to the obtained data, the PAO oligomers from the $AlCl_3$/heptane system demonstrated lower short-chain branching, higher long chain branching, and so higher VI values. In the above study, different branch types were explored from the ^{13}CNMR and DEPT spectra, including the structures depicted in Table 1, in which the moieties depicted in entries 3 and 5 are considered as long chain branching degree.

Notably, short-chain branching and branching ratio amounts were quantified using Eqs. 1 and 2 as follows [101]:

$$\text{Branching ratio} = \left[15 \times \sum \left(^{13}\text{C integral } 11\text{–}17\text{ppm}\right) \middle/ \right. \\ \left[15 \times \sum \left(^{13}\text{C integral } 11\text{–}17\text{ppm}\right) \right. \\ \left. + 14 \times \sum \left(^{13}\text{C integral } 18\text{–}44\text{ppm}\right)\right] \quad (1)$$

Table 1 CH_3 types in the commercial PAOs structure

	Methyl type-branching amount	Branching type	Chemical shift	PAO6	PAO4
1	CCH_2CH_3	SCB[1]	10.8	0	0.67
2	$(CH_3)CHCH_2CH_3$	SCB	11.3	0	0.39
3	$CHCH_2CH_2CH_3$	LCB[2]	14.5	4.59	4.15
4	$CH(CH_3)CH_2CH_2CH_3$	SCB	14.3	1.51	0.84
5	$(CH_2)_nCH_2CH_2CH_3$ $n > 1$	LCB	14.0	78.7	82.8
6	$CH_2CH(CH_3)CH$	SCB	15–17	15.14	9.9
7	$CH_2CH(CH_3)CH_2$	SCB	19.6	0	1.16
8	$CH_3CH(CH_3)CH_2$	SCB	22.6	0	0
9	Short chain branching (%)		–	22	21
10	Branching ratio		–	0.179	0.128
11	Viscosity index			130	133

[1] Short chain branching

[2] Long chain branching

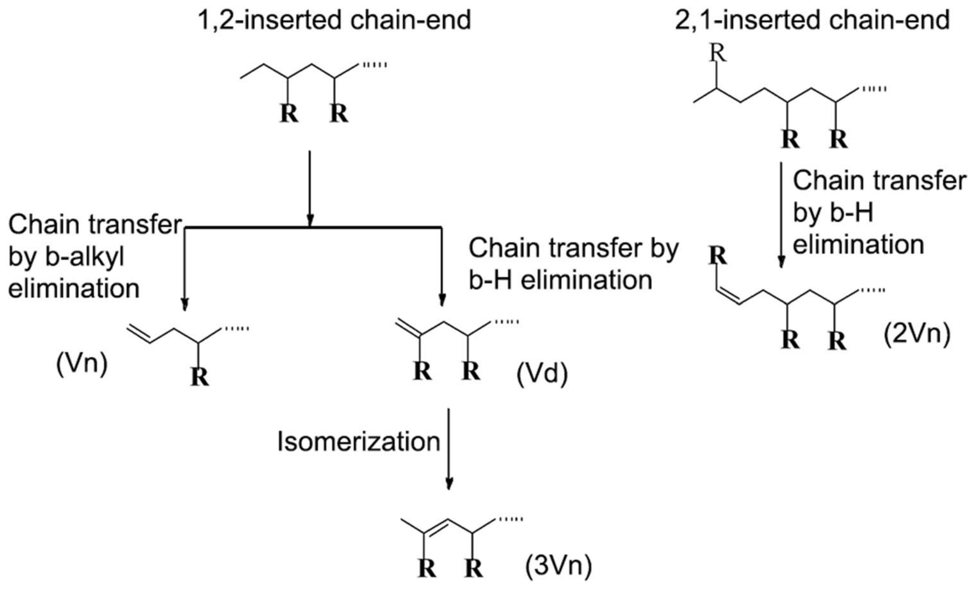


Fig. 12 Molecular structure of unsaturated C=C bonds in the PAO chains [75]

$$\text{Short} - \text{chain branching percentage} = \left[\sum \left({}^{13}\text{C integral short chain} - \text{methyl} \right) / \sum \left({}^{13}\text{C integral all methyl} \right) \right] \times 100 \tag{2}$$

These values are derived from CNMR information. As an example, the share of each CH_3 type, branching ratio and short-chain branching of commercial PAO4 and PAO6 are listed in Table 1. It can be realized that high-viscosity PAO and PAO6 have a higher amount of long chain branching [97], which reveals its effect on higher VI.

In PAO synthesis, chain propagation is stopped when chain transfer or termination occurs, which limits the molecular weight of the final product [102]. Due to chain transfer mechanisms, different C=C double bounds are found in the molecular structure of PAO chains associated to termination after monomer insertion through either 1,2- or 2,1-mechanism. They include vinylidene (V_d), vinyl (V_n), tri-substituted vinylene ($3V_n$), and di-substituted vinylene ($2V_n$, Fig. 12) moieties. The peaks at vinylic region in the CNMR spectra, i.e. $\delta = 4.80–5.40$ ppm, are usually analyzed to identify the type of the unsaturated C=C bonds. It is worth to mention that, 3Vn, 2Vn and V_d are converted to branched structures after PAO hydro-finishing. This is beneficial from tribology point of view since it lowers lubricant pour point. The type and amount of each unsaturated structure is principally dependent on the catalyst nature and polymerization temperature [102]. The design of catalyst systems that yield PAOs with V_d, $3V_n$ and $2V_n$ chain ends enhances the PAO fluidity at low temperatures and should be considered as well.

Applications of poly(α-olefins)

PAO is considered as the workhorse base stock for the most synthetic oils. High viscosity PAOs are commonly employed as industrial oils and greases, where low-viscosity PAOs are utilized in synthetic automotive crank case and gear lubricants, industrial oils and greases. To this day, automobile engine oil is the main application of these products. However, PAOs have been widely used in engine oils, two-stroke oils, bitumen, and greases applications. The industrial applications of POAs include hydraulic oils, compressor oils, as heat transfer fluids, and edible grade oils [5]. The reactivation reaction through unsaturated bonds at the ends of oligomers (usually vinylidine, Fig. 13) provides functional products that have tremendous potential to become adhesives [103], adapters [104], perfumes, lubricants synthetic ions and can even be used in the paper and leather industries [105].

Chemtura (Canada), Chevron Phillips (USA), Exxon Mobil (USA), INEOS (USA), Lanzhou Petrochemical (China), Shanghai Fox (China), and Naco Synthetics (China) are among leading manufacturer which produce either conventional or metallocene-based PAOs.

As mentioned before, automotive engine oils industry has the largest market for PAO lubricants, which is due to the much superior properties of PAOs in comparison with oil-based engine oils (mineral oils) [106–108]. These superior properties are extended lubricant drain interval, advanced engine wear protection, outstanding cold starting efficiency, low oil consumption, high fluidity and pump ability at low temperatures, high temperature stability, and improved fuel economy. These features are originated from PAO's high VI, low pour point, low-temperature viscosity, high oxidative stability, low volatility, etc. The blends of

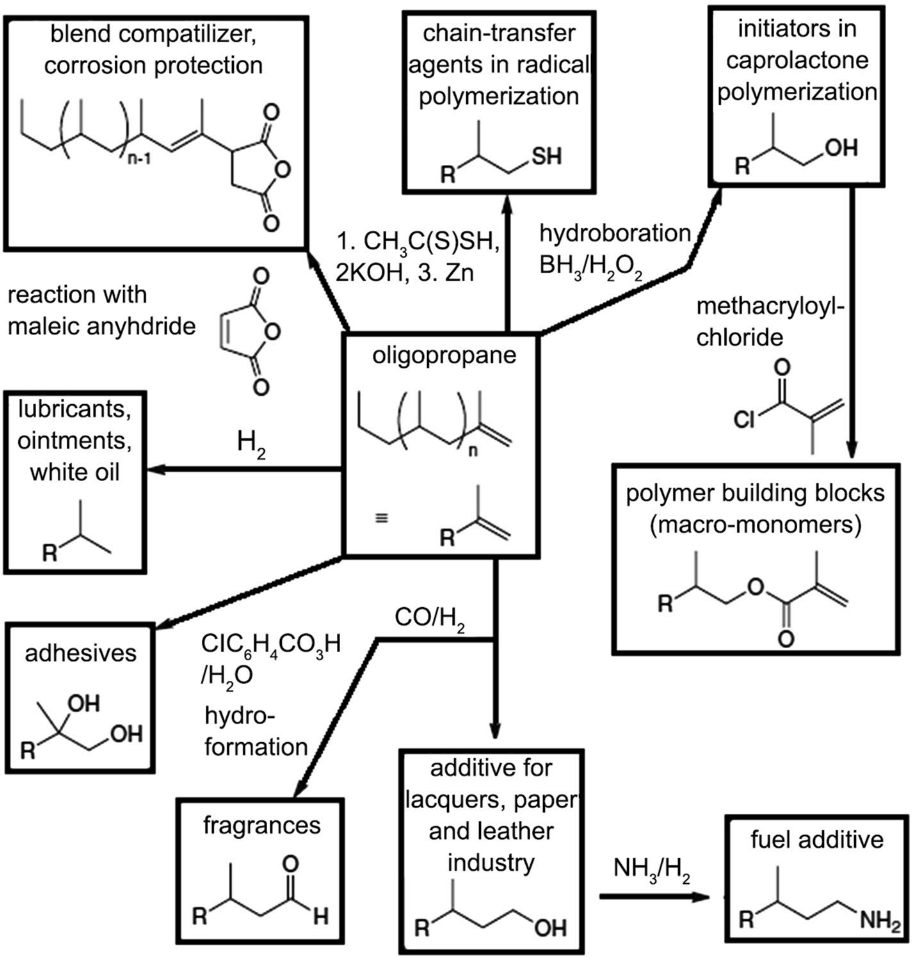


Fig. 13 Different applications of olefin oligomers [103]

mineral oil with PAO are also employed to prepare partial synthetic lubricant formulations. In such compositions, PAO improves oxidative stability, high- or low-temperature viscosity, and volatility of the mineral oil.

Furthermore, PAO-based industrial oils and greases have economic advantages as well as advanced performances over conventional lubricants [106], such as wider application temperature range, improved thermal-oxidative stability, lower equipment down-time and maintenance requirements, longer fatigue life (oil life), etc.

PAO has recently been used in personal care products such as shampoos, conditioners and skin lotions. In fact, in addition to feeling good on the skin, PAO provides emolliency due to its non-greasy and non-comedogenic nature. Owing to the good lubricity POA, off-shore drilling fluid formulation has been also suggested. New applications for PAO products are steadily and continuously emerging [109].

New progress in poly(α-olefins) subject

Generally, PAO-based engine oils are produced by a two-step process, i.e., oligomerization of higher α-olefins and afterwards hydrogenation of end-unsaturated oligomeric chains [110]. Therefore, a one-step production of end-saturated PAO-based engine oils would be a significant achievement which authorize us to be free of further hydrogenation processes which requires harsh reaction conditions [4, 111]. One-step synthesis of end-saturated PAOs can be achieved through living cationic oligomerization of higher α-olefins which requires very low oligomerization temperatures [112–114]. On the other hand, development of hydrogenation catalyst systems which require low-temperature/pressure for hydrogenation reaction of end-unsaturated bonds can be considered as an outstanding achievement to reduce used process costs and risks for production of PAOs.

Tribology problems including wear, friction and lubrication are major challenges for industry, particularly in some fields that need further optimization for practical applications such as electronics, aerospace, and computers. To diminish friction and wear through lubrication, the use of specific additives in the PAO formulation is suggested. In this regard, graphite-based materials [115], CuO nanoparticles [116], some metal oxide nanoparticles [117, 118], and different ionic liquids [118] have been extensively employed as additives to enhance PAOs tribological properties. Incidentally, PAOs are usually mixed with neopentyl polyol ester to improve seal swell and enhance their additives compatibility, since PAOs alone are not promptly miscible with conventional lubricating oil additives.

An approach which can enable us to produce PAOs in a one-step process is coordinative chain transfer polymerization (CCTP) technique [119–121]. In CCTP, the polymer chain is propagating onto a transition metal-based catalyst, and is able to be transferred into a chain transfer agent (CTA), usually a main group metal alkyl [122, 123], like ZnR_2. Therefore, at the end of reaction, instead of producing end-unsaturated oligomer chains, metal-end capped chains will be obtained which can be subsequently hydrolyzed to saturated oligomer chains. In recent years, CCTP has attracted much attentions, mostly due to its ability toward molecular weight controlling, and producing functionalized polymer chains through generating transition metal-end capped chains [124]. As depicted in Fig. 14, the technique includes utilizing of catalyst, co-catalyst, and a chain transfer agent (CTA). In this way, it was reported that, the Ti-based diamine bis(phenolate) catalysts (Fig. 15) have ability to perform CCTP reaction [93] in α-olefin oligomerizations. Indeed, the reversible chain transfer between

Fig. 14 Mechanism of CCTP technique

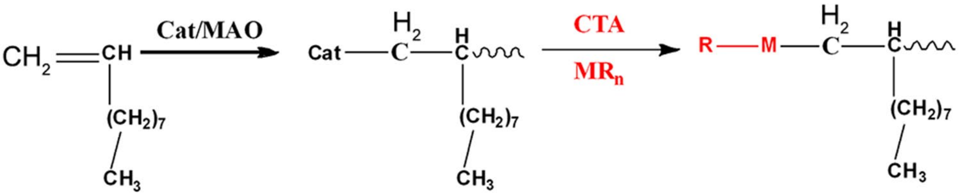
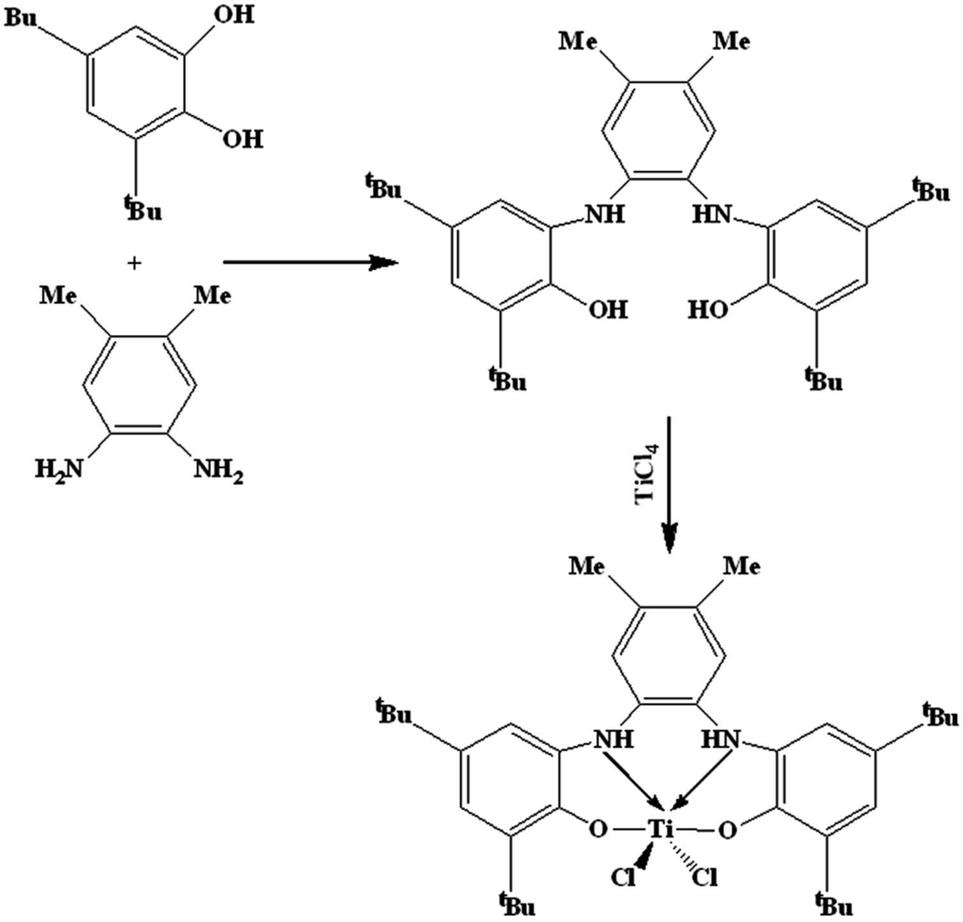


Fig. 15 The procedure used for the synthesis of Ti-based diamine bis(phenolate) catalyst used in CCTP reaction [93]



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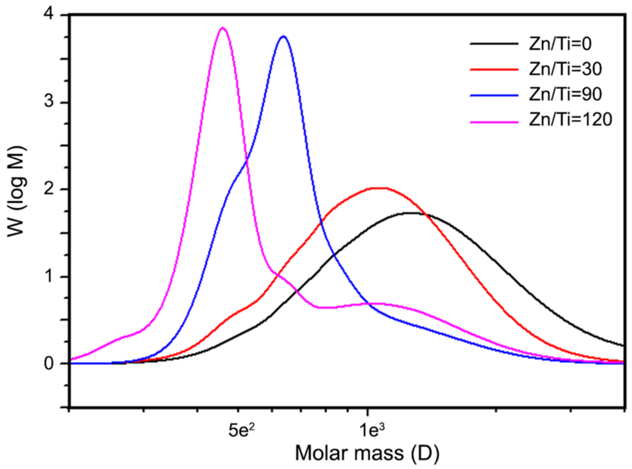

Fig. 16 GPC curves of 1-decene oligomers obtained by CCTP technique [93]

propagating center and CTA (here, $ZnEt_2$) has been recognized in the coordinative chain transfer polymerization of 1-decene. It has reduced the molecular weight of the polymeric chains. Interestingly, due to the fast and reversible chain transfer sequence, the amount of β-H termination reactions decreased dramatically, which was favorable due to the absence of unsaturated bonds in the chain backbone. It was a significant achievement since it eliminates the need for the subsequent oil hydrofinishing step. In fact, using the catalyst structure shown in Fig. 15, living oligomerization of 1-decene was successfully performed through the CCTP technique, in which oligomer chains with the Zn-end capped structure were obtained. Furthermore, the obtained results showed that with increasing the mole fraction of $ZnEt_2$ as the chain transfer agent, the molecular weight of oligomer chains was dramatically decreased, and interestingly the PDI values were narrowed and reduced to lower values (Fig. 16) [93]. This behavior confirmed the living nature of the CCTP technique.

Another innovative approach to produce PAOs can be MAO-free systems in the case of metallocene catalysts [125]. Unlike most other commercial metallocene systems, the Chevron Phillips Chemical (CPC) platform does not use MAO or fluoroorganic boranes. In their suggested system, the support itself can activate (ionize) the metallocenes, and prepare it for olefin insertion at high activity [126–128]. This method can significantly reduce the cost of produced PAO as a final product. In this way, usually polymerization-grade oxide supports such as silica, alumina, and silica-alumina are employed. The given supports were treated with suitable compounds to make the related solid acid with proper acidity value. In this regard, some Cl and F donating compounds, such as carbon tetrachloride and perfluorohexane, were employed during the calcining step to achieve Cl and F functionalized supports [129]. These amazing solid acid supports can be a good alternative to expensive MAO, which significantly decreases the cost of metallocene technology. Studies in this area are continued.

Conclusion

In this review, we have discussed advances in the catalytic oligomerization of higher α-olefins to produce poly(α-olefins) (PAO) lubricants. According to the literature, PAOs can be produced by both cationic and coordination catalyst systems. In comparison to conventional cationic systems, single-site transition metal-based catalysts result in oligomers with narrow PDI values originated from their precision engineered structures that improve the viscosity index (VI) and decrease the pour point of the resulting oils. Besides conventional methods, coordination chain transfer polymerization (CCTP) of α-olefin monomers, which have been introduced in recent years, will be a great feature for the formation of functionalized PAOs with low viscosity in the near future. In fact, this new system, in conjunction with aminobisphenolate type catalysts and chain transfer agents, is a suitable alternative to the traditional BF_3 and metallocene catalyzed process. Therefore, advanced industrial developments are expected based on this outstanding new strategy. However, privileged achievement can be accessed when methylaluminoxane (MAO) co-catalyst is replaced with cheaper solid acid supports; to further develop the PAO product portfolio needs more attention from academia and industry. We are confident that the evolution of PAOs will help advance the understanding of this amazing class of lubricants.

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