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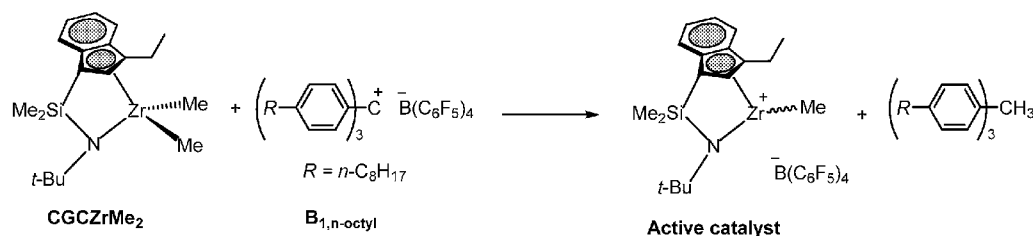
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FIG. 2



(57) **Abstract:** Low molecular weight, highly branched polyolefins are provided. Also provided are catalyst-mediated methods of making the low molecular weight, highly branched polyolefins and a catalyst system for carrying out the methods. The catalyst system is a homogeneous catalytic system that includes a single-site organozirconium complex and hydrocarbon-soluble perfluoroarylborate co-catalyst that is highly active for the oligomerization of olefin monomers in non-polar media.

HIGHLY BRANCHED, LOW MOLECULAR WEIGHT POLYOLEFINS AND METHODS FOR THEIR PRODUCTION

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims priority to U.S. provisional patent application number 62/626,879 that was filed February 6, 2018, the entire contents of which are incorporated herein by reference.

BACKGROUND

[0002] Polyethylenes (PEs) represent one of the most extensively used plastics worldwide. Depending on the molecular mass, molecular mass distribution, branch architecture, and branch density, polyethylenes exhibit a wide range of useful and informative properties, and this importance has stimulated both active fundamental and targeted research for decades. Typically, polyethylene syntheses target high molecular masses (>10 kg/mol), which are desirable for exceptional mechanical and rheological properties. Another potentially useful polyethylene product, low molecular mass (M_n), highly branched polyethylenes (HBPE), which have potential as synthetic lubricant oil alternatives, have been overlooked largely due to the lack of general and economical methods of production. The structures of low M_n HBPE are mainly defined by branch pattern (methyl, ethyl, *n*-propyl, *n*-butyl, *n*-propyl, and long chain branches ($\geq C_6$)) and branch densities.

[0003] In order to produce HBPE from ethylene, homogeneous Ni- or Pd-catalyzed “chain-walking” polymerizations (CWPs) or group 4 transition metal tandem oligomerizations of ethylene were developed. Ni and Pd catalysts are generally limited by low activity and thermal instability at typical polyolefin production temperatures. For the aforementioned group 4 tandem processes, there are limitations of low activity, solid side-products (high M_n PE), and complex process engineering. There is currently no industrial process for the production of low molecular weight HBPE.

[0004] Despite the great success of early transition metal polymerization catalysts, their implementation in the selective synthesis of highly branched polyethylenes, especially those with low molecular mass, has been sparse. For example, constrained geometry precatalyst **CGCZr**, activated with $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ (**B1, H**), catalyzes ethylene polymerization in toluene to yield low M_n polyethylenes with both short (ethyl, *n*-butyl) and some long chain branches

(LCB, $\geq$ C6). However, reported activities are low, as is the total branch density of ca. 10/1000 C. (Li, L. *et al. J. Am. Chem. Soc.* **2002**, 124, 12725-12741)

SUMMARY

[0005] Low molecular weight, highly branched polyolefins (highly branched olefin oligomers) and catalyst-mediated methods of making them are provided.

[0006] Various embodiments of the branched polyolefins have a number average molecular weight of no greater than 2100 g/mol and a branch density of at least 40 branches/1000 C. The branches comprise ethyl branches and butyl branches, and typically less than 30% of the branches are odd-numbered branches and at least 60% of the end groups on the branches are vinylidene groups. Internal double bonds make up no greater than 10% of the total polyolefin unsaturation. The branched polyolefins include ethylene homopolymers and ethylene copolymers.

[0007] One embodiment of a method for making the branched polyolefins includes combining olefin monomers with a single-site organozirconium complex and a perfluoroarylborate compound in a non-polar non-coordinating solvent or a halogenated solvent, whereby the single-site organozirconium complex and perfluoroarylborate compound mediate the oligomerization of the olefin monomers into an olefin oligomer.

[0008] Other principal features and advantages of the invention will become apparent to those skilled in the art upon review of the following drawings, the detailed description, and the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Illustrative embodiments of the invention will hereafter be described with reference to the accompanying drawings, wherein like numerals denote like elements.

[0010] FIG. 1 depicts polyethylene categories and typical branch types.

[0011] FIG. 2. Precatalyst CGCZrMe₂ + cocatalyst/activator B_{1, n-octyl} activation process to yield the active ion-paired active olefin polymerization catalyst.

[0012] FIG. 3A – FIG. 3D depict trends in CGCZr + B_{1, n-octyl} catalyzed ethylene polymerizations. FIG. 3A shows solvent effects on oligomer branch densities in CGCZr + B_{1, n-octyl} catalyzed ethylene polymerizations. FIG. 3B shows solvent effects on oligomer end

group densities in **CGCZr** + **B₁**, *n*-octyl catalyzed ethylene polymerizations. FIG. 3C shows the relationship between polyolefin M_n , polyolefin yield, and reaction time in MeCy. FIG. 3D shows the relationship between oligomer M_n , oligomer yield, and reaction time in **CGCZr** + **B₁**, *n*-octyl catalyzed ethylene polymerizations.

[0013] FIG. 4A – FIG. 4C. Tribological evaluations of the **CGCZrMe₂** + **B₁**, *n*-octyl catalyzed ethylene homo-polymerization product HBPE vs. commercial poly- α -olefin (PAO4) base oil lubricant. FIG. 4A. Viscosity and viscosity index (VI) of saturated HBPE and PAO4 oils. VI measures the viscosity stability with temperature change, a higher VI indicating a smaller change in viscosity with increasing temperature and greater thermal stability. Dynamic viscosities (DV) of the samples at 40°C and 100°C were determined by the density and kinematic viscosity data as per ASTM. FIG. 4B. Elastohydrodynamic lubrication (EHL) evaluations of film thickness vs. entrainment speed. The EHL tests were performed using a steel ball in contact with a glass disc under a 20 N load. Tests were performed under pure rolling conditions in which the ball and disc rotated at the same speed. The entrainment speed is the average speed of the ball and disc, and is the rate at which lubricant enters the contact area. FIG. 4C. Friction as a function of speed and time. A speed-ramp test was conducted at 1, 10, and 100 mm/s, represented by letters 'i', 'ii', and 'iii', respectively, to evaluate the oils in different regimes of lubrication for time intervals of 15 minutes each, for a total test time of 45 minutes.

[0014] FIG. 5. Table 1 showing the ethylene polymerization data from the Example.

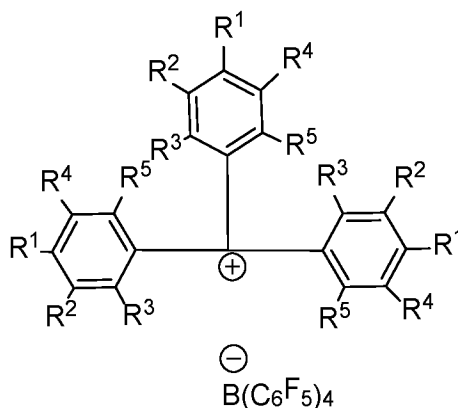
[0015] FIG. 6. Table 6 showing GC-MS analysis of ethylene homopolymerization reaction mixtures from the Example.

DETAILED DESCRIPTION

[0016] Low molecular weight, highly branched polyolefins, including low molecular weight, highly branched homo- and copolymers of polyethylene (HBPE), are provided. Also provided are catalyst-mediated methods of making the low molecular weight, highly branched polyolefins and a catalyst system for carrying out the methods.

[0017] An illustrative comparison of the microstructure, including typical branch types, of low molecular weight HBPEs with high-density polyethylene (HDPE), linear low-density polyethylene (LLDP), and low-density polyethylene (LDPE) is provided in FIG. 1.

[0018] The catalyst system, which is a homogeneous catalytic system that includes a single-site organozirconium complex and the hydrocarbon-soluble perfluoroarylborate co-catalyst, is highly active for the oligomerization of olefin monomers in non-polar media. The perfluoroarylborate compound has the structure:



where: each R^1 , R^2 , R^3 , R^4 , and R^5 is independently chosen from $-H$, F , Cl , substituted or unsubstituted (C_4-C_{40}) alkyl, substituted or unsubstituted (C_4-C_{40}) alkenyl and substituted or unsubstituted (C_4-C_{40}) cycloalkyl, wherein the substituted (C_4-C_{40}) alkyl and substituted (C_4-C_{40}) cycloalkyl are substituted with one or more R^S , where each R^S is chosen from (C_1-C_{20}) alkyl and halogen; provided that at least one of R^1 , R^2 , R^3 , R^4 , or R^5 is chosen from substituted or unsubstituted (C_4-C_{30}) alkyl and substituted or unsubstituted (C_4-C_{40}) cycloalkyl. One embodiment of the perfluoroarylborate compound, has an $n-C_8H_{17}$ group at the para positions of the benzene rings. The structure of this compound, which is referred to as $B_{1, n-octyl}$, along with the structure of the single-site organozirconium complex referred to as CGCZr are shown in the left panel of FIG. 2.

[0019] Polyolefins that can be formed using the methods described herein include, but are not limited to, homopolymers and copolymers of ethylene, propylene, 1-hexene, and/or 1-octene. The polyolefins are characterized by a high degree of branching and low molecular weights. By way of illustration, various embodiments of the low molecular weight polyolefins, including various embodiments of the low molecular weight ethylene homopolymers and copolymers, have a branch density of at least 40 branches/1000 C. This includes embodiments of the low molecular weight polyolefins having a branch density of at least 50 branches/1000 C, at least 60 branches/1000 C, at least 70 branches/1000 C, at least 80 branches/1000 C, and at least 90 branches/1000 C. For example, the polyolefins may have a branch density in the range from 50 to 100 branches/1000 C. The branch density for the

polyolefins can be measured from the ^1H NMR intensity ratio of methyl groups versus the overall integral, as illustrated in the Example.

[0020] The branches of the polyolefins can include short chain branches (SCBs), long chain branches (LCBs), or a combination thereof. For the purposes of this disclosure, an SCB refers to an alkyl chain having five or fewer carbon atoms. Ethyl and butyl groups are examples of SCBs. An LCB refers to an alkyl chain having six or more carbon atoms. Generally, the polyolefins will include ethyl branches and butyl branches, but few, if any odd-numbered branches. As used herein, the term “odd-numbered branches” refers to alkyl group branches where the alkyl group has an odd number of carbon atoms in the chain. Thus, methyl group branches (one carbon atom) and propyl group branches (3 carbon atoms) are odd-numbered branches. Some embodiments of the polyolefins have no more than 30% odd-numbered branches. This includes embodiments having no more than 15% odd-numbered branches, embodiments having no more than 5% odd-numbered branches, embodiments having no more than 1% odd-numbered branches, and embodiments that have no odd-numbered branches.

[0021] As illustrated in the Example, the relative number of LCBs and SCBs on a given branched polyolefin can be tailored by adjusting the polymerization conditions (e.g., temperature and time), the comonomers, and/or the polymerization solvent. By way of illustration, in various embodiments of the low molecular weight polyolefins, including various embodiments of the low molecular weight ethylene homopolymers and copolymers, LCBs account for at least 20% of the branches and SCBs, such as ethyl branches and butyl branches, account for no more than 80% of the branches. This includes embodiments of the polyolefins in which LCBs account for at least 30% of the branches and SCBs account for no more than 70% of the branches. For example, the polyolefins include those in which LCBs account for 30% to 50% of the branches and SCBs account for 50% to 70% of the branches.

[0022] The terminal groups on the polyolefin branches, which include carbon-carbon double bonds, may be vinyl groups ($\text{H}_2\text{C}=\text{C}(\text{H})-\text{R}$), vinylidene groups ($\text{H}_2\text{C}=\text{CRR}'$), or a combination thereof, where R and R' represent alkyl/polymeryl moieties). In some embodiments of the polyolefins, vinylidene groups dominate the terminal groups on the branches. By way of illustration, in various embodiments of the low molecular polyolefins, including various embodiments of the low molecular weight ethylene homopolymers and copolymers, at least 60% of the terminal groups of the branches are vinylidene groups. This

includes embodiments of the polyolefins in which at least 70% of the terminal groups of the branches are vinylidene groups, and further includes embodiments of the polyolefins in which at least 80% of the terminal groups of the branches are vinylidene groups. The polyolefins may also be characterized by a very low number of internal double bonds (e.g., $R'HC=CHR''$ and $R''HC=CRR'$ double bonds, where R, R', and R'' represent alkyl/polymeryl moieties). By way of illustration, in various embodiments of the low molecular polyolefins, including various embodiments of the low molecular weight ethylene homopolymers and copolymers, internal double bonds make up no more than 5% of the total polyolefin saturation. This includes embodiments of the polyolefins in which internal double bonds make up no more than 2% or no more than 1% of the total polyolefin saturation.

[0023] The polyolefins can be made with low molecular weights and, therefore, can be referred to as oligomers. By way of illustration, various embodiments of the low molecular polyolefins, including various embodiments of the low molecular weight ethylene homopolymers and copolymers, have a number average molecular weight (M_n) of no greater than 10000 g/mol. This includes embodiments of the polyolefins having a M_n of no greater than 5000 g/mol, no greater than 3000 g/mol, no greater than 2100 g/mol, or no greater than 1200 g/mol. For example, some embodiments of the polyolefins have a M_n in the range from 400 to 2100 g/mol. The M_n of the polyolefins can be determined from the ^1H NMR intensity ratio of the unsaturated terminal groups versus the overall integral, as illustrated in the Example and explained below.

[0024] The branched polyolefins are formed by combining the olefin monomers with the single-site organozirconium complex and the perfluoroarylborate compound co-catalyst in a non-polar organic solvent for a time sufficient to polymerize the monomers. Polymerization can be carried out at room temperature (~ 23 °C). However, because the catalyst system is thermally stable, the polymerization can also be conducted at elevated temperatures of, for example, up to 60 °C or higher. The polyolefins can be formed in a relatively short reaction time, including reaction times of 60 minutes or less. For example, reaction times in the range from 2 minutes to 40 minutes can be used.

[0025] The use of a highly non-polar non-coordinating solvent is desirable because such solvents can increase the polymerization activity and/or increase the polyolefin branch density relative to that of polyolefins that are formed in aromatic hydrocarbons, such as toluene, or a more polar halogenated solvent, such as chlorobenzene (PhCl). A non-polar

non-coordinating solvent is differentiated from toluene in that it is a saturated hydrocarbon compound that does not include any double bonds or aromatic unsaturation. Suitable non-polar non-coordinating solvents include, but are not limited to, pentane, hexane, heptane, octane, methylcyclohexane (MeCy), cyclohexane, and Isopar-E. As illustrated in the Example, using the polymerization methods described herein, ethylene homopolymerization can be carried out with an activity of $2000 \text{ kg (mol of metal)}^{-1} \text{ h}^{-1} \text{ atm}^{-1}$ or higher (for example, in the range from 2000 to $3000 \text{ kg (mol of metal)}^{-1} \text{ h}^{-1} \text{ atm}^{-1}$) and ethylene1-hexene copolymerization can be carried out with an activity of $3400 \text{ kg (mol of metal)}^{-1} \text{ h}^{-1} \text{ atm}^{-1}$ or greater (for example, in the range from 3400 to $5000 \text{ kg (mol of metal)}^{-1} \text{ h}^{-1} \text{ atm}^{-1}$).

[0026] MeCy is particularly useful due to its highly non-polar non-coordinating character. As illustrated in the Example, the CGCZr + B_{1, n-octyl} co-catalyst system shows remarkable aliphatic solvent effects on catalytic activity and branch density in the product polyolefins, with a very high activity, when the polyolefins are formed in a MeCy solution. Optionally, the polyolefins can be post-functionalized by reacting the terminal double bonds on the branches with various reactive molecules to form branch end-functionalized polyolefins with novel branched structures and/or block copolymers with unique physical properties. The C=C bonds of the unsaturated polyolefins can also be hydrogenated to form fully or partially saturated polyolefins.

[0027] Once formed, the low molecular weight, highly branched polyolefins can be used in a variety of applications, including as synthetic lubricant base oils and as feedstocks or building blocks for the production of other chemicals, or as fuels, plasticizers, or polymer processing additives.

EXAMPLE

[0028] This example demonstrates a borate co-catalyst B_{1, n-octyl} (FIG. 2) with long alkyl chains introduced on the *para* positions of the Ph₃C⁺ phenyl groups. B_{1, n-octyl} has excellent solubility in industrially preferred aliphatic solvents such as MeCy. Dramatic solvent effects were observed for CGCZr + B_{1, n-octyl} -catalyzed olefin polymerization. Solvent polarity increased in the order of MeCy < toluene < PhCl with dielectric constants of 2.02, 2.38 and 5.62, respectively. The activity, however, was much higher in more polar PhCl and less polar MeCy than in toluene. Unprecedented low M_n, highly branched, olefin-terminated polyolefins were produced with very high activity. CGCZr+B_{1, n-octyl} -catalyzed ethylene polymerization occurred with activities of 3393 and $2516 \text{ kg} \cdot (\text{mol of metal})^{-1} \cdot \text{h}^{-1} \cdot \text{atm}^{-1}$ in

PhCl and MeCy respectively, which were $4.3\times$ and $3.2\times$ higher than that in toluene (Table 1, entries 1, 4 vs. 2). In comparison, no activity was observed when **B**_{1, H} was used as the co-catalyst in MeCy, likely reflecting the insolubility of **B**_{1, H} in MeCy (Table 1, entry 3).

[0029] In addition to modifying polymerization activity, the reaction solvent had a dramatic influence on the product branch identities/densities, product molecular weight, and product end group ratio. Switching from PhCl to MeCy resulted in a dramatic change from linear to highly branched oligomers (FIG. 3A). The product obtained in MeCy had 61 branches/1000 C, which was higher than the products obtained in PhCl and toluene (36 and 25 branches/1000 C, respectively, Table 1, Entries 4 vs. 1 and 2). The high *n*-butyl and LCB branch densities were unprecedented, considering that ethylene was the only monomer and that the reaction took place in a single batch reactor with a single catalyst system. Note that LCB content was remarkably high in comparison to Ni/Pd catalyzed CWP. The latter produces polyolefins with predominantly short chain methyl, ethyl, and *n*-propyl branches. (See, Wiedemann, T., *et al.*, *J. Am. Chem. Soc.* 2014, 136, 2078-2085.) Interestingly, negligible branches with odd numbers of carbons were present in the present products, indicating that a coordination-insertion mechanism, rather than a CWP mechanism, predominated. Solvent effects on molecular weight were also observed. The low molecular weight was well beyond the detection limit of GPC; thus, polyolefin M_n was calculated based on ¹H NMR. Polyolefin molecular weight increased in the order of toluene < MeCy < PhCl, which were 430, 700, and 2080 g/mol, respectively. Thus, this catalyst + co-catalyst system allows for the synthesis of polyolefins with a wide range of molecular weights.

[0030] Another major difference resulting from solvent choice was the product end group ratio (Table 4, FIG. 3B). In all the solvents studied here, polyolefins obtained from **CGCZr** + **B**_{1, n-octyl} contained predominantly terminal double bonds (vinyl and vinylidene); internal double bonds represented less than 4% of the total unsaturation present. While the polyolefin obtained in toluene had predominantly vinyl end groups (80%), the polyolefin obtained in MeCy contained predominantly vinylidene end groups (81%) together with vinyl end groups (18%). This sharply contrasts with late transition metal catalysis (Pd/Ni), which yield polyolefins with predominantly internal double bonds. Terminal double bond functionality is often more desirable than internal double bonds for post-reaction functionalization. Thus, the oligomer product in this example may undergo direct post-functionalization in comparison to products from other processes.

[0031] When the reaction time for CGCZr + B_{1, n-octyl} –mediated ethylene oligomerization was increased from 10 to 30 min in MeCy at 25 °C, the oligomer yield increased in approximate proportion to the reaction time, accompanied by a slight decrease in activity (Table 1, shown in FIG. 5, entries 4-6). Remarkably, branch density and M_n were virtually time-independent (FIG. 3C and FIG. 3D).

[0032] Thermal stability of the active catalyst is also a critical parameter in evaluating a catalyst system's potential applications. CGCZr + B_{1, n-octyl} in MeCy showed a steady 30-min activity up to polymerization temperatures of at least 60 °C. At a polymerization temperature of 80 °C, the activity dropped by 55%, and the product polyolefin had a lower branch density (38 vs. 61 branches/1000 C at 80 °C vs. 25 °C, Table 1, entries 9 vs. 4). The decreased solubility of ethylene with increasing temperature likely contributed, in part, to the fall in activity. Polyolefin M_n increased 1.5× with increasing temperature, indicating suppressed chain termination relative to the chain propagation process. Interestingly, internal double bond ratios for the present systems were consistently lower than 2%, suggesting that little double bond isomerization occurs even at 80 °C.

[0033] Next, 1-hexene comonomer was introduced in ethylene polymerizations to determine the effect on product branch pattern and density and the flexibility in tuning product compositions (Table 1, entries 10-13). Ethylene/1-hexene copolymerization activity increased 4.7× by switching the solvent from toluene to MeCy (entries 9 vs. 10). Solvent effects were analyzed at similar polyolefin-yield levels to minimize the influence of comonomer concentration changes throughout the polymerization. On changing the solvent from toluene to MeCy, ethyl and *n*-butyl branch densities increased 2.6× and 2.4×, respectively, concurrent with essentially unchanged LCB density (entries 9 vs. 10). In ethylene homopolymerizations, however, LCB density increased by about twice when the solvent was changed from toluene to MeCy (entries 3 vs. 1). This indicates that enhancement of 1-hexene incorporation competes with LCB incorporation, providing a facile means to adjust highly branched polyethylene microstructures by introducing inexpensive α -olefin monomers.

[0034] Small amounts of 1,2-difluorobenzene (DFB, 60 equiv. per metal) were added to the polymerization solution to promote solubility of co-catalyst B_{1, H} in preparing active catalyst solutions. This represented about 1.2% v/v of DFB in the polymerization solution. The ethylene polymerization results showed minimal change after adding small amounts of

this relatively high polarity halogen-containing solvent in terms of activity, polyolefin molecular weight, and product branch densities (Table 2).

Table 1. Ethylene Polymerizations with and without 60 equiv. of DFB per Metal Catalyst.

Entry	Solvent	Additive	Cocat.	Polymer (g)	act ^b	M _n (g/mol) ^c	Branches/1000 C ^d
1	Tol	none	B_{1, n}	3.96	790	430	25
2	Tol	DFB	B_{1, n}	2.53	506	419	18
3	MeCy	none	B_{1, n}	12.57	2516	700	61
4	MeCy	DFB	B_{1, n}	13.36	2672	687	55
5	MeCy	DFB	B_{1, H} ^e	8.45	1689	652	58

Conditions: catalyst, **CGCZr**, 10 μmol; cocatalyst, 10 μmol; ethylene, 1 atm; water bath, 25 °C; solvent: toluene or MeCy, 50 mL; **1.2 % v/v of DFB used (60 equiv./metal)** for entries 2, 4 and 5. ^b Unit is kg·(mol of metal)⁻¹·h⁻¹·atm⁻¹. ^c M_n calculated from ¹H NMR intensity ratio of unsaturated end groups vs. overall integral. ^d Branches/1000 C calculated from ¹H NMR intensity ratio of methyl groups vs. overall integral. ^e likely due to precipitation of active catalyst when MeCy is introduced.

[0035] Note that the products obtained in this study structurally resembled poly(α-olefin)s (PAOs). PAOs, oligomers of 1-decene and 1-dodecene, are important commercial synthetic lubricant base oils that provide better performance than petroleum-based lubricant base oils. The superior performance of PAOs derives from their unique branched microstructure, i.e., multiple long chain branches on a short backbone core. The oligomers produced in the present example had high branch densities, with particularly high LCB densities, and topologically resembled PAOs. Product oligomer M_ns were in the range 500-2100 g/mol, close to those of commercial PAOs. To evaluate the oligomers for lubricant oil performance, the viscosity and viscosity index were measured and compared to that of commercial lubricants. Kinematic viscosity (40 °C and 100 °C) and viscosity index of the sample in entry 13, Table 1, were similar to those of a commercial lubricant 5W30 blend (Table 5), demonstrating the usefulness of the oligomers produced here as a PAO alternative. One significant advantage of these oligomers over conventional PAOs is their low cost, since they are obtained directly from inexpensive ethylene, and in some cases, with less expensive α-olefins, such as 1-hexene. In contrast, PAOs are currently produced from 1-decene/1-dodecene oligomerization processes, and the high cost of 1-decene/1-dodecene produced from statistical ethylene oligomerization/separation significantly increases the cost of PAO.

In addition, the HBPE samples in the current example contained predominantly terminal double bonds, which are ideal starting materials for further functionalizations to important intermediates with novel branched structures, such as surfactants. Terminal double bond functionality is more desirable than internal double bonds for direct post-functionalization since it doesn't require a second catalyst to convert/isomerize internal double bonds to terminal double bonds. For the same reasons, the subject invented materials could also be used as building blocks for the preparation of block copolymers that have unique physical properties/applications.

Tribology. HBPE vs. PAO4 and potential applications.

[0036] The HBPE products not only had high branch densities but had particularly high LCB densities. Furthermore, their M_n s of 500-1200 g/mol are within the range of commercial high-performance PAO lubricants. To rigorously evaluate the tribological performances of the HBPEs, such as viscosity characteristics, film stability, and friction reduction ability vs. commercial PAO4, the HBPE C=C bonds were hydrogenated to afford a fully saturated HBPE. Viscosities were then measured, and viscosity indices calculated, while a PCS elastohydrodynamic lubrication (EHL) system (PCS Instruments) was used for both film thickness and traction analyses at identical viscosities by adjusting the measurement temperature: 62°C for saturated HBPE, 35°C for PAO4. FIG. 4A shows the viscosities of the saturated HBPE and PAO4 oils vs. temperature and the corresponding viscosity index numbers, indicating that the viscosity index for the saturated HBPE is significantly greater than that for PAO4, and that the viscosity of the former is more stable over a wide temperature range. FIG. 4B compares the lubrication film thicknesses for saturated HBPE and PAO4 at a constant viscosity, showing comparable film thickness, and thus a comparable lubricity over the entire speed range evaluated. Two sets of speed-ramp pin-on-disk friction tests were next conducted for the two lubricants in different regimes of lubrication at 62°C and 35°C, which are again at the equalized viscosities to ensure a fair comparison. FIG. 4C shows that saturated HBPE consistently delivers lower friction than PAO4. Taken together, these results demonstrate that saturated HBPE offers superior tribological performance, and also indicates that saturated HBPEs of optimized molecular masses would have still higher viscosity indices, greater lubrication capacity, and lower friction than corresponding commercial PAOs.

Materials and Methods

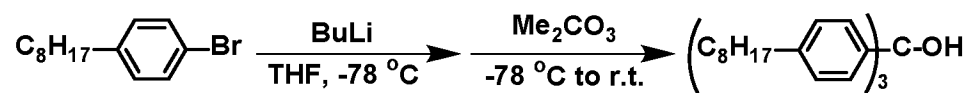
[0037] All manipulations of air-sensitive materials were performed with rigorous exclusion of O₂ and moisture in oven-dried Schlenk-type glassware on a dual manifold Schlenk line, interfaced to a high-vacuum line (10⁻⁶ Torr), or in a N₂-filled MBraun glove box with a high-capacity recirculator (<1 ppm O₂). Argon (Airgas, pre-purified grade) was purified by passage through a supported MnO oxygen-removal column and an activated Davison 4Å molecular sieve column. Ethylene (Airgas) was purified by passage through an oxygen/moisture trap (Matheson, model MTRP-0042-XX). Hydrocarbon solvents (*n*-pentane, *n*-hexane, 1-hexene, methylcyclohexane, and toluene) were dried using activated alumina columns according to the method described by Grubbs and were then vacuum-transferred from an Na/K alloy. (Pangborn, A. B., *et al.*, *Organometallics* **1996**, *15*, 1518-1520.) Benzene-*d*₆ and toluene-*d*₈ (Cambridge Isotope Laboratories, 99+ atom %D) were stored over the Na/K alloy in vacuum and vacuum-transferred immediately prior to use. 1,2-Difluorobenzene and chlorobenzene-*d*₅ were dried with CaH₂ and distilled under vacuum. Chloroform-*d*₃ and 1,1,2,2-tetrachloroethane-*d*₂ were used as received (Cambridge Isotope Laboratories, 99+ atom %D).

Physical and Analytical Measurements

[0038] NMR spectra were recorded on Varian UNITY Inova-500 (FT, 500 MHz, ¹H; 125 MHz, ¹³C), UNITY Inova-400 (FT, 400 MHz, ¹H; 100 MHz, ¹³C), Agilent DD2-HCN600 (FT, 600 MHz, ¹H; 150 MHz, ¹³C) or Bruker ASCEND-400 (FT, 400.13 MHz, ¹H; 100.60 MHz, ¹³C). Chemical shifts for ¹H and ¹³C spectra were referenced using internal solvent resonances and were reported relative to tetramethylsilane (TMS). NMR experiments on air-sensitive samples were conducted in Teflon valve-sealed sample tubes (J-Young). Elemental analyses (CHN) were performed by Midwest Microlab, Indianapolis, Indiana. ¹³C NMR analysis of the polymer microstructure was conducted in 1,1,2,2-tetrachloroethane-*d*₂ at 120 °C with delay time (d₁) = 10 sec. To avoid any detectable double bond isomerization, ¹H NMR spectra were generally recorded first (within ~2 min) followed by ¹³C NMR (~30 min). When a subsequent ¹H NMR spectrum was recorded after ¹³C NMR, the spectrum was still the same as previously recorded, which suggests negligible isomerization during high-temperature polymer analysis.

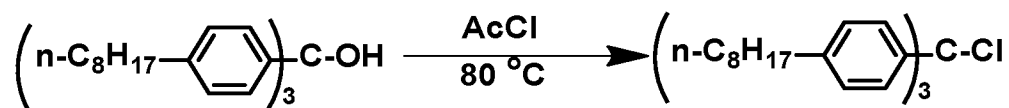
Synthesis of Compounds

Synthesis of the Trityl Alcohol Tr^{n-octyl}-OH



[0039] Tr^{n-octyl}-OH was synthesized following a literature procedure. (Thibeault, D., *et al. Eur. J. Org. Chem.* **2010**, 3049-3067) N-BuLi (11.5 mmol, 4.6 mL, 2.5 M in hexanes) was added slowly via syringe to a THF (50 mL) solution of *p*-octylbromobenzene (3.10 g, 11.5 mmol) at -78 °C. The reaction was kept at -78 °C for 0.5 h. Next, Me₂CO₃ (0.33 g, 3.64 mmol, 0.31 mL) was added to the solution via syringe, and the solution was warmed up to room temperature. After stirring overnight, water was added to quench the reaction. The mixture was extracted 3 times with Et₂O, and the organic extracts were combined and washed twice with brine, dried (Na₂SO₄), filtered, and concentrated to dryness. The resulting crude product was purified by flash column chromatography using basic aluminum oxide (activated, basic, Brockmann I, from Aldrich). Gradient elution (Hexanes, Hexanes/EtOAc = 50/1, EtOAc) gave the pure product as colorless oil, 1.33 g, 58.1% yield. ¹H NMR (400 MHz, C₂D₂Cl₄) δ 7.36 – 7.10 (m, 12H), 2.71 – 2.57 (m, 6H), 1.67 (m, 6H), 1.44 – 1.25 (m, 30H), 1.02 – 0.85 (m, 9H). ¹³C NMR (151 MHz, C₂D₂Cl₄) δ 144.16, 141.63, 127.68, 127.63, 81.85 (Ar₃C, weak signal, confirmed by HMBC experiment), 35.42, 31.77, 31.28, 29.37, 29.32, 29.15, 22.60, 14.14. HR-MS (ESI) Calcd for C₄₃H₆₃ (M-OH)⁺: 579.4930, Found: 579.4946

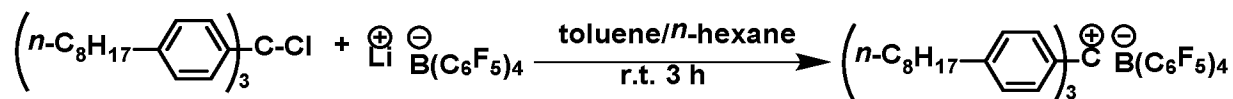
Synthesis of the Trityl Chloride Tr^{n-octyl}-Cl



[0040] Tr^{n-octyl}-Cl was synthesized based on a modified literature procedure. (Bosset, C., *et al. Angew. Chem., Int. Ed.* **2014**, 53, 9860-9864.) AcCl (0.265 g, 3.37 mmol, 0.24 mL) was added via syringe to a stirred solution of Tr^{n-octyl}-OH (0.67 g, 1.12 mmol) in toluene (20 mL) at 80 °C. The reaction was kept at 80 °C for 1 h. All volatiles were then removed, and the resulting oily product was further dried under high vacuum. The product, a light-yellow oil, was pure enough to use without further purification. Yield: 0.69 g, quantitative yield. ¹H NMR (499 MHz, CDCl₃) δ 7.13 (m, 6H), 7.09 (m, 6H), 2.59 (m, 6H), 1.61 (m, 6H), 1.41 – 1.16 (m, 30H), 0.88 (m, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 142.88, 142.41, 129.56, 127.58, 81.82 (Ar₃C, weak signal, confirmed by HMBC experiment), 35.52, 31.89, 31.26, 29.47,

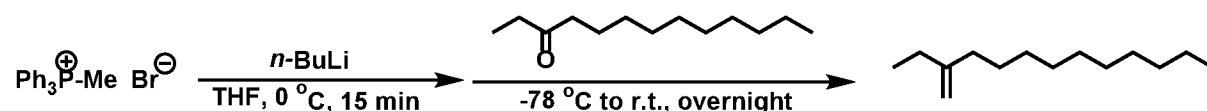
29.40, 29.25, 22.67, 14.10. HR-MS (ESI) Calcd for $C_{43}H_{63} (M-Cl)^+$: 579.4930, Found: 579.4936.

Synthesis of the New Soluble Co-catalyst **B**_{1, n-octyl}



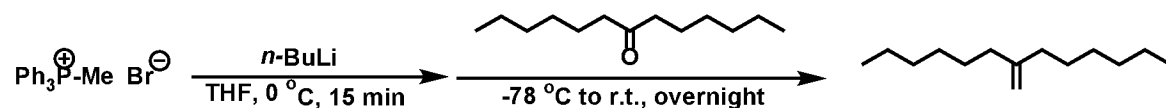
[0041] $\text{LiB}(\text{C}_6\text{F}_5)_4$ was synthesized according to the literature procedure. (Kuprat, M., *et al. Organometallics* **2010**, 29, 1421-1427) $\text{LiB}(\text{C}_6\text{F}_5)_4$ (0.13 g, 0.21 mmol) and $\text{Tr}^{n\text{-octyl}}\text{-Cl}$ (0.21 g, 0.25 mmol) were mixed in toluene (15 mL)/n-hexane (5 mL) in an Mbraun glovebox. After 3 hours, the solution was filtered through Celite. Toluene and hexane were removed under vacuum, and the resulting oil was washed with pentane (10 mL) twice. After drying under high vacuum, the product was collected as red oil. 0.15 g, 58% yield. ^1H NMR (499 MHz, CD_2Cl_2) δ 7.67 (d, $J = 8.0$ Hz, 6H), 7.55 (d, $J = 7.9$ Hz, 6H), 2.94 (m, 6H), 1.79 (m, 6H), 1.49–1.27 (m, 30H), 0.91 (m, 9H). ^{19}F NMR (470 MHz, CD_2Cl_2) δ -133.14 (m, *m*-F, 8F), -163.85 (t, *p*-F, 4F), -167.66 (m, *o*-F, 8F). Elem. Anal. Calcd for $\text{C}_{67}\text{H}_{63}\text{BF}_{20}$: C 63.92, H 5.04; Found: C 64.13, H 10.69, N 5.42

Synthesis of 2-Ethyl-1-dodecene



[0042] To a suspension of 2.14 g (6.0 mmol) of methyltriphenylphosphonium bromide in THF (24 mL) was added 2.52 mL of *n*-butyllithium (2.5 M in hexane) by syringe at -0°C . After 15 min, the reaction mixture was cooled to -78°C . After 15 min at -78°C , a THF (10 mL) solution of tridecan-3-one (1.27 g, 6.0 mmol) was added dropwise by syringe to the suspension. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was quenched by addition of NH_4Cl solution (saturated, 2 mL), and extracted with ether (3*20 mL). The combined organic phase was dried over Na_2SO_4 , the solvent was evaporated in vacuo, and the residue was purified by silica gel chromatography (hexane) to give the product. Colorless oil, 1.13 g, 93% yield. ^1H NMR (600 MHz, CDCl_3): δ 4.70–4.68 (m, 2H), 2.04–2.00 (m, 4H), 1.44–1.39 (m, 2H), 1.31–1.24 (m, 14H), 1.02 (t, $J = 7.4$ Hz, 3H), 0.88 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3): δ 151.91, 107.24, 36.29, 31.92, 29.65, 29.58, 29.47, 29.35, 28.74, 27.88, 22.69, 14.11, 12.39. HR-MS (EI) Calcd for $\text{C}_{14}\text{H}_{28} (\text{M}^+)$: 196.2191, Found: 196.2186

Synthesis of 2-Hexyl-1-octene



[0043] To a suspension of 2.14 g (6.0 mmol) of methyltriphenylphosphonium bromide in THF (24 mL) was added 2.52 mL of *n*-butyllithium (2.5 M in hexane) by syringe at -0 °C. After 15 min, the reaction mixture was cooled to -78 °C. After 15 min at -78 °C, a THF (10 mL) solution of tridecan-7-one (1.27 g, 6.0 mmol) was added dropwise by syringe to the suspension. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was quenched by addition of NH₄Cl solution (saturated, 2 mL), and extracted with ether (3*20 mL). The combined organic phase was dried over Na₂SO₄, the solvent was evaporated in vacuo, and the residue was purified by silica gel chromatography (hexane) to give the product. Colorless oil, 0.91 g, 77% yield. ¹H NMR (600 MHz, CDCl₃): δ 4.69 (m, 2H), 2.01–1.98 (m, 4H), 1.44–1.39 (m, 4H), 1.34–1.25 (m, 12H), 0.89 (t, *J* = 6.9 Hz, 6H); ¹³C NMR (150 MHz, CDCl₃): δ 150.46, 108.30, 36.10, 31.18, 29.14, 27.18, 22.66, 14.10. HR-MS (EI) Calcd for C₁₄H₂₈ (M⁺): 196.2191, Found: 196.2188.

Ethylene Polymerization Experiments

[0044] In a typical experiment, a 150-mL glass pressure vessel (dried in a 120 °C oven overnight prior to use) was loaded with 40 mL of dry toluene, methylcyclohexane, or chlorobenzene inside the glovebox. A large magnetic stir bar was added to the pressure vessel, and it was sealed, taken out of the glovebox, and attached to a high-pressure/high-vacuum line. The pressure vessel was cooled to -78 °C with a dry ice/acetone bath and degassed, then allowed to warm and equilibrate at the desired reaction temperature for 30 min using an external water bath. The solution was saturated with 1 atm of ethylene at the same time. The catalytically active species was freshly generated by mixing measured amounts of precatalyst and co-catalyst in a vial in the glovebox (in 10 mL of methylcyclohexane, chlorobenzene, or toluene) and mixing for 10 min. The catalyst solution was then removed from the glovebox and quickly injected into the rapidly stirring solution using a gastight syringe equipped with a spraying needle. The temperature of the solution in representative polymerization experiments was monitored using a thermocouple. After a measured time, the polymerization was quenched by addition of 0.5 mL of MeOH. All volatiles were removed from the remaining polymerization mixture, and the products were dried under high vacuum at 60 °C overnight until reaching a constant weight.

Ethylene Copolymerization Experiments

[0045] The procedure for ethylene + 1-hexene co-polymerization was similar to that for ethylene homo-polymerization described above. The 150-mL glass pressure vessel was loaded with 35 mL of dry toluene, methyl cyclohexane, or chlorobenzene and 5 mL of 1-hexene inside the glovebox. The procedures for catalyst preparation, injection into the polymerization flask, and polymer workup were the same as described above.

Hydrogenation of HBPE Sample to Saturated HBPE

[0046] To a 150-mL glass pressure vessel was added unsaturated HBPE (19.3 g), Pd/C (0.15 g), 60 mL of pentane and a stir bar. The vessel was attached to a high-pressure/high-vacuum line. The pressure vessel was cooled to -78 °C with a dry ice/acetone bath and degassed, warmed to room temperature and filled with 5.0 atm of H₂. The reaction immediately started consuming H₂. The reaction was complete after overnight reaction (no H₂ consumption). The reaction solution was filtered through silica gel. The product was then dried under high vacuum at 60 °C for 6 h until reaching a constant weight under high vacuum. The product was obtained in quantitative yield. ¹H NMR indicated complete hydrogenation of the olefinic double bonds in the unsaturated HBPE.

Tribology Experiments on HBPE Sample vs. PAO4

Viscosity and Viscosity Index

[0047] HBPE was compared with standard PAO4 at the same dynamic viscosity to assess the tribological merit of the saturated HBPE. Dynamic viscosity, as the measure of the resistance to shear stress, is a key property affecting both lubrication film thickness and friction. A high dynamic viscosity value would not only yield a higher film thickness but also a higher friction because of the higher shear stress. The kinematic viscosity should first be measured in order to determine the dynamic viscosity. A Canon constant temperature bath was used to evaluate the kinematic viscosities of saturated HBPE and PAO4 samples at 40 °C and 100 °C. Viscosity information at more temperature points can be extrapolated using the well-known Walther equation:

$$\log\log(\nu + 0.7) = A - B \log T,$$

where *A* and *B* are constants to be determined in the simultaneous solving of the equations at 40 °C and 100 °C, *T* is the absolute temperature in Kelvin, and *ν* is the kinematic viscosity. The dynamic viscosity is calculated by multiplying the kinematic viscosity by the density. Using

this equation, along with the density information at 40°C and 100°C, a routine was written to determine the required temperatures at which the saturated HBPE and PAO4 render the same viscosities within 0.4 cP of accuracy. FIG. 4A (Viscosity and viscosity index (VI) of saturated HBPE and PAO4 oil) shows viscosities of the oils and the respective temperatures needed to match the viscosities. The routine determined that at the temperatures 62 °C and 35 °C for the saturated HBPE and PAO4, respectively, each had a dynamic viscosity of 21 cP.

Elastohydrodynamic Lubrication (EHL) Evaluation at the Same Viscosity

[0048] A PCS EHL system was used for film thickness measurements. Each film thickness test used a ball of 19.55 mm diameter on a glass disc under the normal load of 20N. The elastic moduli of the steel ball and optically smooth glass disc are 210 GPa and 75 GPa, respectively, yielding a baseline contact pressure of 540 MPa. Both oils were tested under the speed range of 20 mm/s to 4.3 m/s under pure rolling conditions where the steel ball rotates at the same speed as the glass disc. The tests were commenced after the temperature stabilized and was maintained consistent.

Friction Evaluation at the Same Viscosity

[0049] A CETR pin-on-disc high-temperature tribometer was used for a comparative study of the induced friction resulting from the surface-lubricant-surface interface. A polished 9.53 mm diameter M-50 steel ball was used in contact with a polished 52100 steel disc. Speeds of 1 mm/s, 10 mm/s, and 100 mm/s were chosen for the speed-ramp tests to capture the boundary, mixed, and hydrodynamic lubrication regimes. Each speed was tested for 15 minutes with a smooth transition to the next speed. A load of 5N was applied to the disc, yielding a contact pressure of 820 MPa.

Molecular Weight Calculation and Branching Analysis from ¹H NMR

[0050] M_n and branching density based on ¹H NMR were analyzed according to literature procedures, and all equations are listed below. (Wiedemann, T., *et al.*, *J. Am. Chem. Soc.* **2014**, *136*, 2078-2085) Since all polymers have very low M_n , $N_{Me\ groups}/1000\ C$ was corrected for methyl end groups in the chain, which should not be counted as branches. Since most polymers in the present study had >99% terminal double bonds, $N_{Me\ groups}/1000\ C$ were therefore corrected with one methyl group for each chain.

$$N_{Me\ groups/1000C} = 2 \times I_{Me} / (3 \times I_{tot}) \times 1000$$

$$N_{Branches/1000C} = N_{Me\ groups/1000C} - 1000 \times 14 / M_n$$

Branching Analysis from ^{13}C NMR

[0051] Percentages of different branch lengths were calculated from ^{13}C NMR (Table 3). The branching densities of polyethylene and poly(ethylene-co-1-hexene) samples were analyzed based on modified methods of Galland *et al.*, assuming one double bond per macromolecule. (Galland, G. B., *et al. Macromolecules* **1999**, 32, 1620-1625). The percentages were estimated by analyzing those ethyl, butyl, and long chain branches that are not influenced by proximate olefinic double bonds, assuming the percentages of 2-alkyl branches, including ethyl, butyl and long chain branches, are similar to those that are not influenced by olefin double bond². In this analysis, peak symbol and numbering are the same as in Galland et al. (1999). In this analysis, N_E , N_B , and $N_{L, \text{total}}$ represent the branching content of ethyl, *n*-butyl, and long chain ($C \geq 6$) branches, respectively. I_n represents the integral of the *n*-peak. Therefore, a few modifications were made, as shown below. Ethyl, *n*-butyl, and long chain branch content calculations are shown below:

$$N_E = (I_1 + I_{10} + I_{33})/3$$

$$N_B = I_8.$$

[0052] As for long chain branches $N_{L, \text{total}}$, according to Galland method, $I_{31} = k(N_B + N_A + N_L)$; $N_B = I_8$; $I_{21} = kN_A$, and $I_{21} = 0$ for all the samples; $I_{19} = k2N_{L(1,4)}$, and $I_{19} = 0$ for all the samples, indicating no paired long chain branches, thus,

$$N_{L, \text{total}} = I_{31} - I_8 + I_{19}/2 = I_{31} - I_8.$$

[0053] While the above Galland equation provides reasonable results for ethylene homopolymer samples, it does not give reasonable $N_{L, \text{total}}$ data for ethylene copolymer samples. The integral of I_{31} (butyl, amyl, and long chain branches) is often smaller than that of I_8 (butyl), which indicates that the large ratio of butyl branches is not proportionally reflected in I_{31} and I_8 . Thus, in calculating $N_{L, \text{total}}$ for the present ethylene copolymer samples, I_{19} and I_{20} were used instead of I_8 and I_{31} . According to the Galland method, $I_{20} = k(N_L + 2N_{L(1,4)})$ and $I_{19} = k2N_{L(1,4)}$, for which N_L means unpaired or isolated long chain branches. Thus, long chain branches of copolymer samples were analyzed based on the following equation:

$$N_{L, \text{total}} = N_L + N_{L(1,4)} = I_{20} - I_{19}/2 \quad (I_{19} = 0 \text{ for all the samples}).$$

Percentages of ethyl, *n*-butyl, and LCB ratios are then calculated from the above N_E , N_B , and N_L values.

Table 2. ^{13}C NMR Peak Assignments

peak no.	I ₁	I ₈	I ₁₀	I ₁₆	I ₁₉	I ₂₀	I ₃₁	I ₃₃
δ (ppm)	11.10	23.42	26.83	30.00	31.50	32.23	38.24	39.72
assignment	1B ₂	2B ₄	2B ₂	δB_{1-n}	1,4- α' B _n	3B _n , 1,4-3B _n	brB ₄ , brB _n	brB ₂

[0054] Polymer End-Group Analysis

[0055] End-group analysis was based on ^1H NMR. Vinyl, vinylidene groups, and internal double bonds were assigned and quantified according to the literature. (Wiedemann, T., *et al.*, *J. Am. Chem. Soc.* **2014**, *136*, 2078-2085.)

Table 3. End Group Analysis of Samples in Table 1.

Entry	Solvent	T _p /°C	t/min	Vinyl/%	Vinylidene/%	Internal/%
1	PhCl	25	30	98	2	0
2	T	25	30	80	16	4
3	MeCy	25	30	-	-	-
4	MeCy	25	30	18	81	1
5	MeCy	25	20	26	73	1
6	MeCy	25	10	35	64	1
7	MeCy	40	30	19	79	1
8	MeCy	60	30	14	84	2
9	MeCy	80	30	39	60	1
10	T	25	20	71	13	16
11	MeCy	25	4	38	61	1
12	MeCy	25	8	27	68	5
13	MeCy	25	20	17	82	1

Viscosity and Viscosity Index Test

[0056] The kinematic viscosity (KV) of the samples at 40 °C and 100 °C was determined as per ASTM D2270. Viscosity index was calculated from KV at 40 °C and 100 °C.

Table 4. Viscosity and Viscosity Index to Compare with Commercial Lubricant Oils^a

Sample	Viscosity (40 °C, cSt)	Viscosity (100 °C, cSt)	Viscosity Index
A	57.3	10.1	166
B	230	16	57
PAO4	22.3	4.8	130
Synthetic	80.1	13	165
Blended 5W30	74.4	12.1	158

^a **Sample A:** ethylene copolymer from Table 1, entry 13; **Sample B:** ethylene homopolymer from Table 1 entry 4. PAO4, Synthetic and Blended 5W30 are all lubricant oils directly from lubricant companies.

GC-MS Analysis

[0057] GC-MS analysis was performed on several of the ethylene polymerization reaction mixtures. To these, a known amount of *n*-heptane was added as internal standard after the reaction was quenched, and a small amount of the reaction product was diluted with *p*-xylene for GC-MS analysis. Note that C₆-C₁₄ α -olefins are detected. Negligible butene products and only small quantities of higher oligomers (C_n⁼, n $\geq$ 16) are detected and are therefore not included in Tables 6 and 7 below. The structures of these olefin isomers were identified with the NIST database in the computer of the in-house GC-MS. 1-Hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 2-ethyl-1-dodecene, 2-hexyl-1-octene were confirmed by comparing with standard samples (same retention times and MS fragmentation patterns).

[0058] To summarize these results: (i) $\leq$ 10.3 wt.% of volatile oligomers were produced in the catalytic reaction for HBPE; (ii) only 0.5 wt.% of volatile α -olefins were detected in the 6 min reaction (Entry 3, Table 6), suggesting that, at the early stage of the reaction, most α -olefins are captured and enchainned by the cationic Zr catalyst. When polymerizations were conducted for longer times (30 min, Entry 1, Table 6), only 3.7 wt.% of volatile α -olefins were detected, evidencing a strong binding/enchainment preference over dissociation into unbound species in solution; (iii) besides α -olefins, there are non-negligible quantities of branched olefin isomers as shown in Table 6 in FIG. 6, which parallels the branch formation process in the production of the final HBPE products.

Table 7. Compositions of decenes, dodecenes, and tetradecenes by GC-MS analysis^e

entry	a1 in C10 ⁼ %	a2 in C10 ⁼ %	a3 in C10 ⁼ %	b1 in C12 ⁼ %	b2 in C12 ⁼ %	b3 in C12 ⁼ %	p1 in C14 ⁼ %	p2 in C14 ⁼ %	p3 in C14 ⁼ %	p4 in C14 ⁼ %
1	23	68	9	30	41	29	18	48	14	20
2	71	21	8	71	16	3	72	14	10	4
3	33	47	20	83	10	17	62	23	5	7

^a Conditions: catalyst, CGCZrMe₂, 10 μ mol; cocatalyst, B_{1,n-octyl}, 10 μ mol; ethylene, 1 atm; rxn temp., temperature of bath surrounding reactor; MeCy, 50 mL; ^b Kg·(mol of metal)⁻¹·h⁻¹·atm⁻¹. ^c Yield of volatile C6⁼ to C14⁼ oligomers. Oligomer qualitative and quantitative

analysis by GC-MS using *n*-heptane as internal standard. Includes hexenes (C₆=), octenes (C₈=), decenes (C₁₀=), dodecenes (C₁₂=) and tetradecenes (C₁₄=). ^d wt.% of each oligomer class, analyzed by GC-MS. ^e isomeric decenes, dodecenes, and tetradecenes were analyzed respectively.

[0059] As for the fraction of added 1-hexene consumed in entry 13 of Table 1, GC-MS analysis was performed immediately after quenching the reaction mixture with a small amount of methanol (MeOH). For an internal standard, *n*-heptane was used for quantification. The results indicate that most of the 1-hexene was consumed in the catalytic process (97% conversion). Entry 12 demonstrates the catalytic tunability of the HBPE product microstructure by introducing a comonomer.

[0060] Solvent effects (MeCy vs. toluene) on catalytic activity and branch formation selectivity were analyzed at similar conversion levels to minimize the influence of comonomer concentration changes over the course of these polymerizations.

[0061] The word "illustrative" is used herein to mean serving as an example, instance, or illustration. Any aspect or design described herein as "illustrative" is not necessarily to be construed as preferred or advantageous over other aspects or designs. Further, for the purposes of this disclosure and unless otherwise specified, "a" or "an" means "one or more."

[0062] The foregoing description of illustrative embodiments of the invention has been presented for purposes of illustration and of description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed, and modifications and variations are possible in light of the above teachings or may be acquired from practice of the invention. The embodiments were chosen and described in order to explain the principles of the invention and as practical applications of the invention to enable one skilled in the art to utilize the invention in various embodiments and with various modifications as suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended hereto and their equivalents.

WHAT IS CLAIMED IS:

1. A branched polyolefin having a number average molecular weight of no greater than 2100 g/mol and a branch density of at least 40 branches/1000 C, wherein the branches comprise ethyl branches and butyl branches, less than 30% of the branches are odd-numbered branches, and at least 60% of the end groups on the branches are vinylidene groups, and further wherein internal double bonds make up no greater than 10% of the total polyolefin unsaturation.
2. The branched polyolefin of claim 1, wherein the polyolefin is a polyethylene homopolymer.
3. The branched polyolefin of claim 1, wherein the polyolefin is a polyethylene copolymer.
4. The branched polyolefin of claim 3, wherein the polyolefin is a copolymer of ethylene and an α -olefin co-monomer.
5. The branched polyolefin of claim 4, wherein the copolymer is an ethylene-1-hexene copolymer.
6. The branched polyolefin of claim 1, wherein the branches further comprise alkyl branches comprising at least 6 carbon atoms in an alkyl chain.
7. The branched polyolefin of claim 1, wherein at least 20% of the branches comprise alkyl branches comprising at least 6 carbon atoms.
8. The branched polyolefin of claim 1, less than 15% of the branches are odd-numbered branches.
9. The branched polyolefin of claim 1, less than 5% of the branches are odd-numbered branches.
10. The branched polyolefin of claim 1, wherein none of the branches are odd-numbered branches.

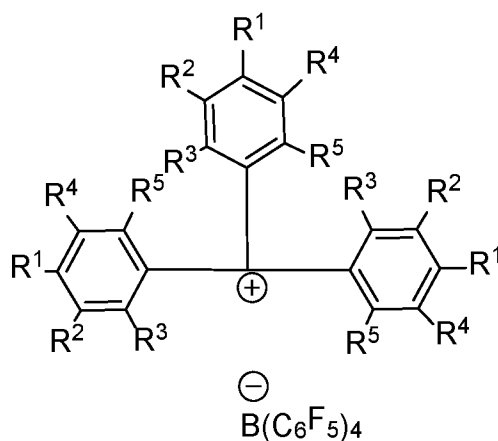
11. The branched polyolefin of claim 1, wherein at least 70% of the end groups on the branches are vinylidene groups.
12. The branched polyolefin of claim 11, no greater than 25% of the end groups on the branches are vinyl groups.
13. The branched polyolefin of claim 1 having a number average molecular weight of no greater than 1200 g/mol and a branch density of at least 60 branches/1000 C.
14. The branched polyolefin of claim 13 having a number average molecular weight in the range from 400 to 1200 g/mol and a branch density in the range from 60 to 100 branches/1000 C.
15. A branched polyethylene homopolymer having a number average molecular weight of no greater than 1000 g/mol and branch density of at least 50 branches/1000 C, wherein the branches comprise a combination of ethyl branches, n-butyl branches, and alkyl branches comprising at least 6 carbon atoms in an alkyl chain, and further wherein and at least 70% of the end groups of the branches are vinyl groups, vinylidene groups, or a combination thereof.
16. A branched copolymer of ethylene and 1-hexene having a number average molecular weight of no greater than 1000 g/mol and branch density of at least 70 branches/1000 C, wherein the branches comprise a combination of ethyl branches, n-butyl branches, and alkyl branches comprising at least 6 carbon atoms in an alkyl chain.
17. A method for olefin oligomerization, the method comprising combining olefin monomers with a single-site organozirconium complex and a perfluoroarylborate compound in a non-polar non-coordinating solvent or a halogenated solvent, whereby the single-site organozirconium complex and the perfluoroarylborate compound mediate the oligomerization of the olefin monomers into an olefin oligomer.
18. The method of claim 17, wherein the olefin monomers include ethylene.
19. The method of claim 1, wherein the olefin monomers comprise α -olefin monomers.

20. The method of claim 19, wherein the α -olefin monomers comprise 1-hexene monomers.

21. The method of claim 17, wherein the non-polar non-coordinating solvent is methylcyclohexane.

22. The method of claim 17, wherein the branches have end groups comprising vinyl groups, vinylidene groups, or a combination thereof, the method further comprising reacting the end groups with one or more reactants to form functionalized end groups.

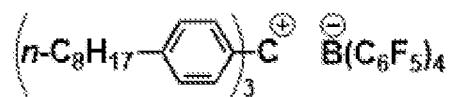
23. The method of claim 17, wherein the perfluoroarylborate compound has the structure:



where:

each R^1 , R^2 , R^3 , R^4 , and R^5 is independently chosen from H, F, Cl, substituted or unsubstituted (C_4 – C_{40})alkyl, substituted or unsubstituted (C_4 – C_{40})alkenyl, and substituted or unsubstituted (C_4 – C_{40})cycloalkyl, wherein the substituted (C_4 – C_{40})alkyl and substituted (C_4 – C_{40})cycloalkyl are substituted with one or more R^S , where each R^S is chosen from (C_1 – C_{20})alkyl and halogen;
provided that at least one of R^1 , R^2 , R^3 , R^4 , or R^5 is chosen from substituted or unsubstituted (C_4 – C_{30})alkyl and substituted or unsubstituted (C_4 – C_{40})cycloalkyl.

24. The method of claim 23, wherein the perfluoroarylborate compound have the structure:



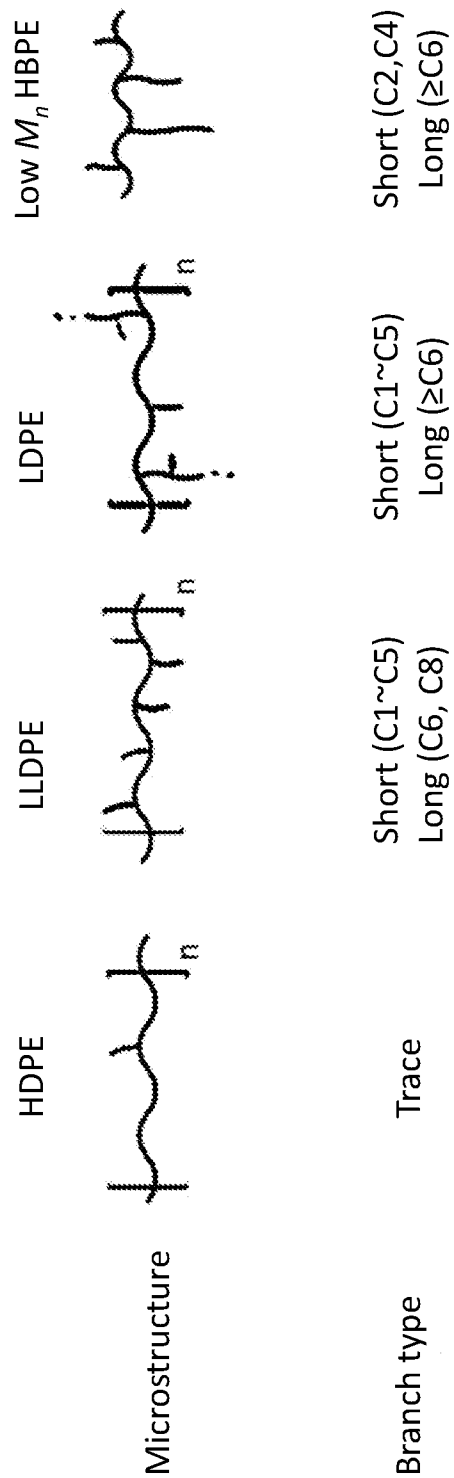
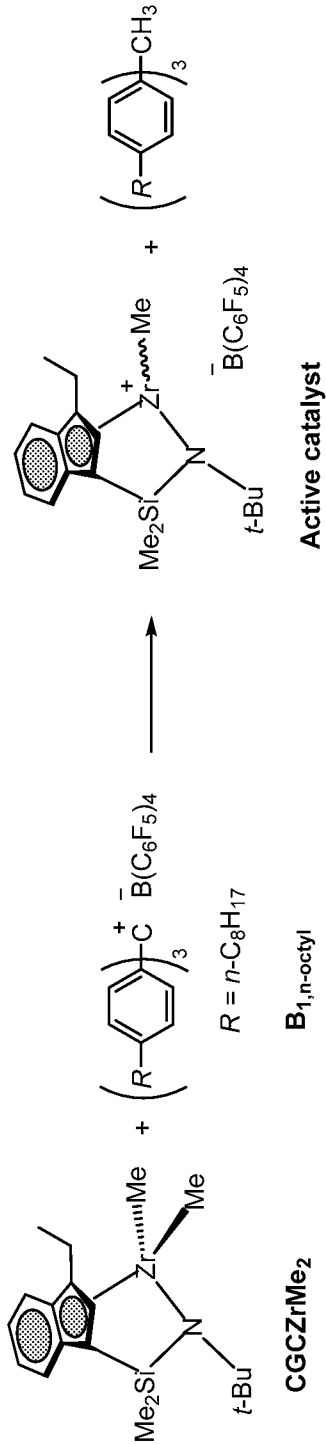


FIG. 1

FIG. 2



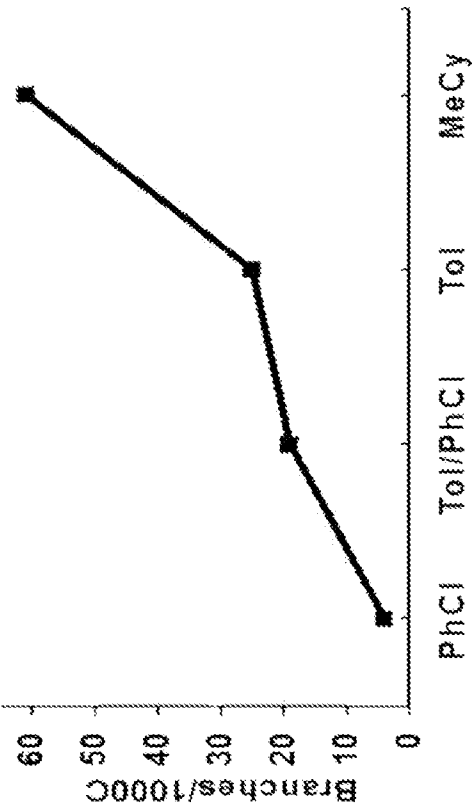


FIG. 3A

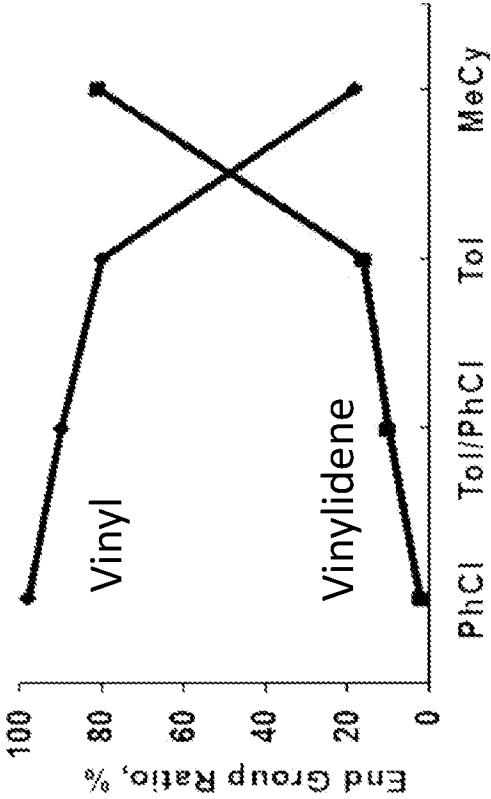


FIG. 3B

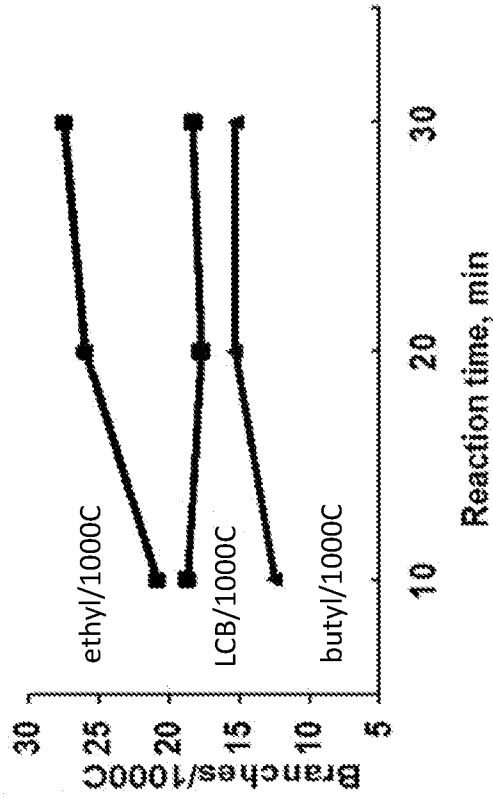


FIG. 3C

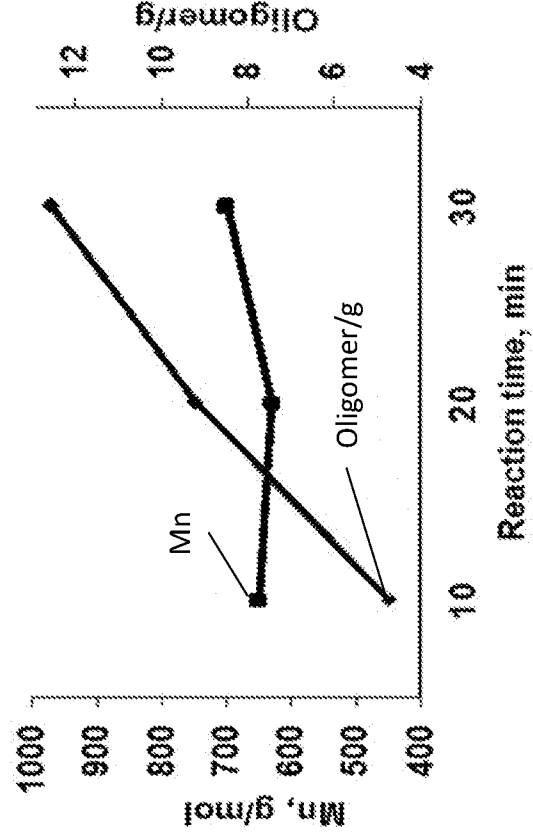


FIG. 3D

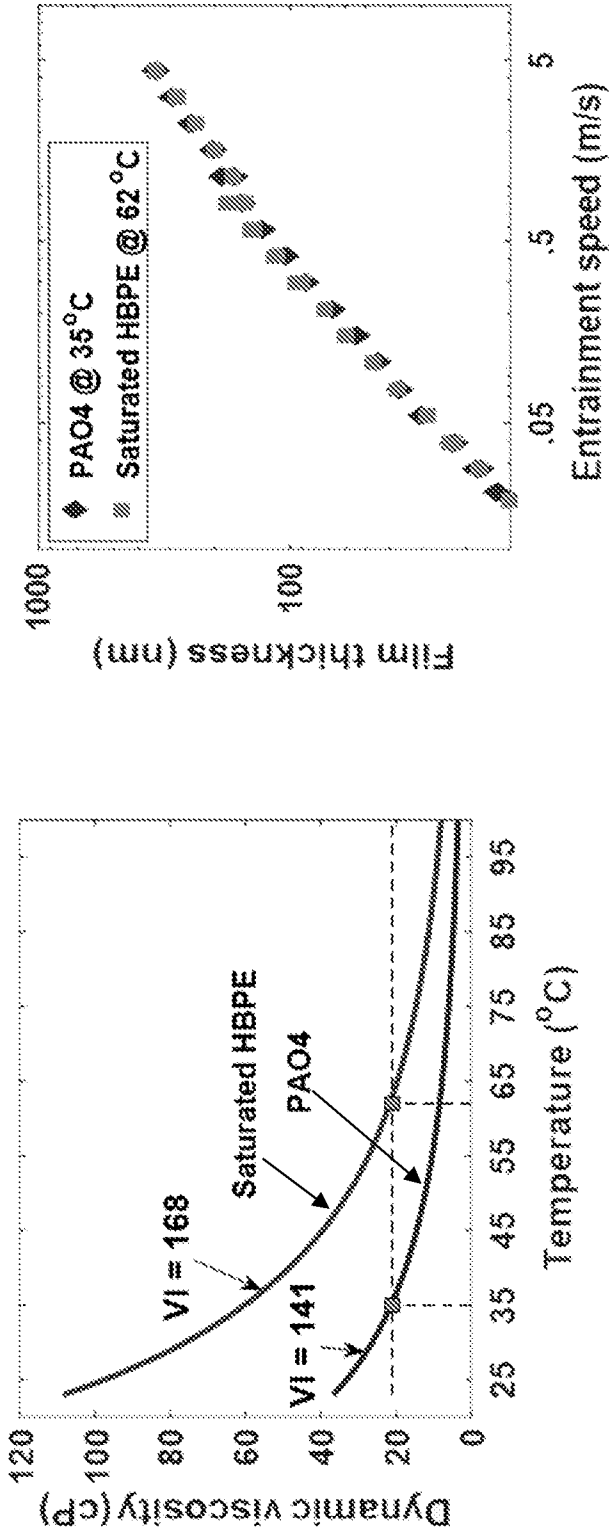


FIG. 4A

FIG. 4B

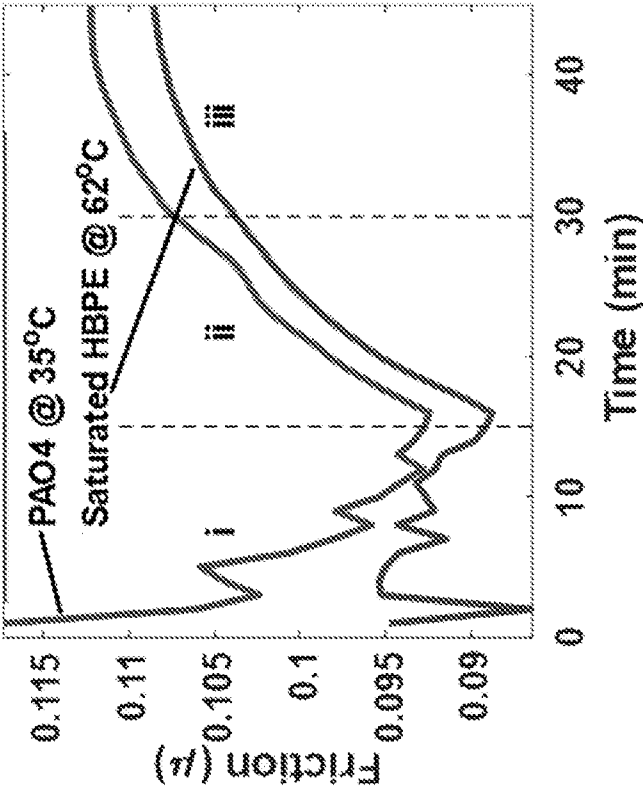


FIG. 4C

Table 1. Ethylene Polymerization Data

Entry	monomer	solvent	T/°C	t/min	poly. (g)	act. ^b	M _n (g/mol) ^c	branches /1000C ^d	ethyl/% ^e	n- butyl/% ^e	LCB/% ^e
1	E	PhCl	25	30	16.96	3393	2080	36	20	14	66
2	E	Tol	25	30	3.96	790	408	22	45	16	39
3 ^f	E	MeCy	25	30	0	0	-	-	-	-	-
4	E	MeCy	25	30	12.57	2516	690	61	45	25	30
5	E	MeCy	25	20	9.24	2773	646	57	44	26	30
6	E	MeCy	25	10	4.74	2842	588	48	42	22	36
7	E	MeCy	40	30	10.29	2058	850	60	40	26	34
8	E	MeCy	60	30	7.75	1549	1140	51	33	23	43
9	E	MeCy	80	30	5.59	1118	1020	38	27	19	54
10	E+H	Tol	25	20	3.30	987	460	48	11	49	40
11	E+H	MeCy	25	4	3.09	4627	470	87	16	64	20
12	E+H	MeCy	25	8	5.52	4132	480	93	16	62	22
13	E+H	MeCy	25	20	11.54	3461	600	79	19	44	37

Conditions: catalyst, **CGCZr**, 10 μmol; cocatalyst, **B_{1,n-octyl}**, 10 μmol; ethylene, 1 atm; T, temperature of water bath surrounding the reactor; reaction solution for ethylene polymerization: PhCl, toluene or MeCy, 50 mL; solution for ethylene (E)/1-hexene (H) copolymerization: toluene or MeCy, 45 mL and 1-hexene, 5 mL; ^b Unit is kg·(mol of metal)⁻¹·h⁻¹·atm⁻¹. ^c M_n calculated from ¹H NMR intensity ratio of unsaturated end groups vs overall integral. ^d Branches/1000 C calculated from ¹H NMR intensity ratio of methyl groups vs overall integral. ^e Percentages of different branch lengths calculated from ¹³C NMR spectra. LCB = Long chain branch = n-hexyl and longer branches. ^f Ph₃C⁺B(C₆F₅)₄⁻ (**B_{1,n}**) used as cocatalyst. No activity likely due to insolubility of cocatalyst in MeCy.

FIG. 5

Table 6. GC-MS analysis of ethylene homopolymerization reaction mixtures.

entry	rxn temp. °C	t/ min	HBPE yield (g)	Oligomer, g ^c	Oligomer/ product yield ^c	α -olefin, g ^c	α -olefin product yield ^c	C6= wt% ^d	C8= wt% ^d	C10= wt% ^d	C12= wt% ^d	C14= wt% ^d
1	25	30	12.57	1.298	10.3%	0.459	3.7%	16	11	22	23	27
2	80	30	5.59	0.150	2.7%	0.115	2.1%	18	20	24	22	16
3	25	6	2.26	0.018	0.8%	0.012	0.5%	14	19	27	24	17

FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2019/016762

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C08F 290/04; C08F 10/00; C08F 216/38; C08F 220/12; C10L 1/198 (2019.01)

CPC - C08F 290/042; C08F 10/00; C08F 216/38; C08F 220/12; C10L 1/198 (2019.02)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

USPC - 525/331.7; 526/320; 526/348.3; 526/348.8 (keyword delimited)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	LIU et al., Synthesis, Characterization, and Heterobimetallic Cooperation in a Titanium–Chromium Catalyst for Highly Branched Polyethylenes, Journal of the American Chemical Society, Vol. 153, 27 May 2013, Pgs. 8830-8833	1-16
A	US 2002/0161156 A1 (NKANSAH et al) 31 October 2002 (31.10.2002) entire document	1-16
A	PATIL et al., Rheology of Polyethylenes with Novel Branching Topology Synthesized by a Chain-Walking Catalyst, Macromolecules, Vol. 38, No. 25, 12 November 2005, abstract	1-16
A	US 6,017,859 A (ROSSI et al) 25 January 2000 (25.01.2000) entire document	1-16
P, A	GAO et al., Highly branched polyethylene oligomers via group IV-catalysed polymerization in very nonpolar media, Nature Catalysis, 01 January 2019, abstract	1-16

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“E” earlier application or patent but published on or after the international filing date

“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search

30 April 2019

Date of mailing of the international search report

23 MAY 2019

Name and mailing address of the ISA/US

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PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2019/016762

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Extra Sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-16

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2019/016762

Continued from Box No. III Observations where unity of invention is lacking

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees need to be paid.

Group I: claims 1-16 are drawn to branched polyolefins, branched polyethylene homopolymers, and branched copolymers of ethylene and 1-hexene.

Group II: claims 17-24 are drawn to methods for olefin oligomerization.

The inventions listed in Groups I and II do not relate to a single general inventive concept under PCT Rule 13.1, because under PCT Rule 13.2 they lack the same or corresponding special technical features for the following reasons:

The special technical features of Group I, branched polyolefins, branched polyethylene homopolymers, and branched copolymers of ethylene and 1-hexene, are not present in Group II; and the special technical features of Group II, methods for olefin oligomerization, are not present in Group I.

Additionally, even if Groups I and II were considered to share the technical features of a branched polyolefin, these shared technical features do not represent a contribution over the prior art as disclosed by "Rheology of Polyethylenes with Novel Branching Topology Synthesized by a Chain-Walking Catalyst" to Patil et al.

"Rheology of Polyethylenes with Novel Branching Topology Synthesized by a Chain-Walking Catalyst" to Patil et al. teach a branched polyolefin (Abstract,...polyethylenes...short-chain branching (92-97 branches per 1000 carbons...)).

The inventions listed in Groups I and II therefore lack unity under Rule 13 because they do not share a same or corresponding special technical feature.