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CA 2479856 A1 1998/12/30

(21) 2 479 856

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(22) Date de dépôt/Filing Date: 1998/06/22

(41) Mise à la disp. pub./Open to Public Insp.: 1998/12/30

(62) Demande originale/Original Application: 2 294 070

(30) Priorité/Priority: 1997/06/20 (08/880,151) US

(51) Cl.Int.^{7}/Int.Cl.^{7} C08F 210/02, C08F 4/642, C08F 212/08, C10M 107/06, C08F 210/06, C10M 107/02, C08F 2/00

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(54) Titre : COPOLYMERES D'ETHYLENE ET D'ALPHA-OLEFINE, PROCEDES ET UTILISATIONS
(54) Title: ETHYLENE-ALPHA-OLEFIN POLYMERS, PROCESSES AND USES

(57) Abrégé/Abstract:
A novel series of copolymers and terpolymers, useful as base oils for synthetic lubricants, are produced by polymerization of ethylene, an alpha-olefin, and optionally a third monomer comprising an alpha-olefin of 3 to 20 carbon atoms, in the presence of a combination catalyst comprising a compound of a transition metal of Group IVb of the Periodic Table and an aluminoxane. The copolymer or terpolymer may be further processed by thermal cracking to yield novel cracked polymers, and the cracked polymers may be hydrogenated. The copolymers or terpolymers may also be hydroisomerized. All the polymers are useful as base oils for lubricating oils and consumer products.

Abstract

A novel series of copolymers and terpolymers, useful as base oils for synthetic lubricants, are produced by polymerization of ethylene, an alpha-olefin, and optionally a third monomer comprising an alpha-olefin of 3 to 20 carbon atoms, in the presence of a combination catalyst comprising a compound of a transition metal of Group IVb of the Periodic Table and an aluminoxane. The copolymer or terpolymer may be further processed by thermal cracking to yield novel cracked polymers, and the cracked polymers may be hydrogenated. The copolymers or terpolymers may also be hydroisomerized. All the polymers are useful as base oils for lubricating oils and consumer products.

ETHYLENE-ALPHA-OLEFIN POLYMERS, PROCESSES AND USES

Field of the Invention

This invention relates to ethylene-olefin polymers, processes for their production, and uses thereof as low molecular weight liquid, solid or wax-like products.

Background of the Invention

Increasing demand in the oil industry has created a need for a high performance synthetic base oils with low volatility and high oxidative stability. Currently, poly-alpha-olefins (PAO) are used as synthetic base oils but costs are high. This has created a demand for a low cost alternative to PAO such as synthetic hydrocarbons with equivalent or better properties. The present invention is based, in part, on the surprising and unexpected discovery that synthetic base oils may be formulated directly into motor oils or fractionated into different viscosity grade oils with properties equivalent to commercial PAO.

Various prior art publications are available relating to poly-alpha-olefin polymers. Reference may be made to U.S. Patents 4,668,834, 4,542,199, 5,446,221, 4,704,491, 4,377,720, 4,463,201, 4,769,510, 4,404,344, 5,321,107, 5,151,204, 4,922,046, 4,794,096, 4,668,834, 4,507,515, and 5,324,800. Many of these prior art patents involve polymerization of ethylene or poly-alpha-olefins using a catalyst combination comprising a transition metal complex and an aluminoxane.

The present invention provides polymers of poly-olefins which have a high viscosity index, low pour point, low cold cranking viscosity, high fire point and excellent oxidation stability.

Summary of the Invention

An object of the present invention is to provide a novel polymer useful, for example, as a base oil for lubricating oils and consumer products.

According to one aspect of the invention there is provided a cracked liquid copolymer of ethylene and an olefin, said copolymer being characterized by:

(a) mol % of ethylene from 50 to 75%;

(b) number average molecular weight of < 2000;

(c) molecular weight distribution of < 2;

(d) random monomer distribution; and

(e) a head-to-tail molecular structure.

According to another aspect of the invention there is provided a process for the production of a cracked copolymer, comprising the steps of:

(a) polymerizing ethylene and at least one olefin in the presence of a single-site catalyst comprising a compound of a transition metal of Group IVb of the Periodic Table and an aluminoxane to produce a precursor copolymer; and

(b) cracking at least a portion of the precursor copolymer to produce a cracked copolymer at a temperature above 300°C.

Also disclosed herein is a process for the production of an ethylene-olefin copolymer, comprising the steps of:

a) polymerizing ethylene and at least one olefin in the presence of a co-catalyst combination comprising a compound of a transition metal of Group IVb of the Periodic Table and an aluminoxane to produce a copolymer; and optionally,

b) subjecting at least a portion of said copolymer to thermal cracking to produce a cracked hydrocarbon, or

hydroisomerizing said copolymer to produce an isomerization hydrocarbon product.

The present description also includes novel copolymers obtained from the polymerization process and the novel thermally cracked product. Hydrogenation of the polymer obtained from the thermal cracking process may produce a hydrogenated copolymer.

A copolymer produced by the reaction of ethylene and an olefin may be characterized as follows:

(a) mole % ethylene of from 50 to 75%;

(b) number average molecular weight of < 2000;

(c) molecular weight distribution of < 2.5;

(d) bromine number of < 53;

(e) a head to tail molecular structure; and

(f) a pour point of below about 0°C.

Also disclosed herein is a process for the production of a terpolymer by reaction under polymerization conditions of ethylene, at least one olefin monomer different from ethylene, and at least one third monomer comprising an ethenically unsaturated hydrocarbon such as an olefin having a carbon chain length of greater than three, in the presence of a catalyst combination comprising a compound of a transition metal of Group IVb of the Periodic Table and an aluminoxane. Also provided is the novel terpolymer produced as a result of this process. This novel terpolymer may also be thermally cracked and hydrogenated, or hydroisomerized.

A hydrogenated cracked terpolymer produced according to the invention may have a bromine number ranging from 0 to 1.5.

Detailed Description of the Invention

The present invention relates in one embodiment to a process for producing copolymers of ethylene and an olefin polymer, comprising polymerizing ethylene and one or more olefin monomers having 3 to 20 carbon atoms under polymerization conditions in the presence of a catalyst combination comprising a compound of a transition metal of Group IVb of the Periodic Table and an aluminoxane. In a further embodiment, this obtained copolymer is subjected to thermal cracking or hydroisomerization, and optionally, the cracked polymer is subjected to hydrogenation.

This invention further concerns a process for producing an ethylene-olefin polymer, comprising the steps of: polymerizing ethylene and one or more olefin monomers having 3 to 20 carbon atoms in the presence of a catalyst combination comprising a compound of a transition metal of Group IVb of the Periodic Table, and an aluminoxane, and hydroisomerizing the obtained polymer.

By ethylene-olefin polymer, there is meant a copolymer obtained by reaction of an ethylene monomer and one or more additional olefin monomers of suitable reactivity. The ethylene-olefin polymer may be, for example, a copolymer, a terpolymer, a tetrapolymer, etc., depending on the number of monomers reacted in the process.

In one embodiment of the process of this invention, the starting material to be fed to the polymerization reaction system is a mixture of ethylene (ethene) and one or more olefins having about 3 to 20 carbon atoms. The content of ethylene in the starting material is preferably about 2 to 80 mole%, preferably about 4 to 55 mole%, and the content of the olefin is preferably about 20 to 98 mole%, preferably about 35 to 96 mole%.

Specific examples of the one or more olefins having 3 to 20 carbon atoms which may be used as a starting material in the process of this invention are 1-propene (propylene), 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-

eicocene, styrene and α-methylstyrene, 2-methyl-1-butene, 2-methyl-1-hexene, 3-methyl-1-butene, 4-methyl-1-pentene, 2-methyl-1-pentene, 2-methyl-1-propene.

In an important embodiment of the invention,. liquid copolymers and terpolymers are provided. Generally, liquid copolymers and terpolymers are produced when the amount of ethylene used in the polymerization reaction is less than about 60 mole percent. However, liquid polymers may also be produced using higher amounts of ethylene if a comonomer is used which introduces longer side chains (e.g., C_6 and up) into the polymer.

In a further embodiment, semi-solid (low melting solids) and solid polymers are also provided. Such polymers are usually produced when the ethylene content is more than about 75 mole percent. However, solid and semi-solid polymers can be produced when the ethylene content is higher than 75% depending on the other comonomers.

The catalyst combinations used in the polymerization processes of the present invention are well known as catalysts for such polymerization reactions. Such catalysts comprise preferably the combination of (a) metallocene compounds which are compounds of a transition metal of Group IVb of the Periodic Table and (b) an aluminoxane.

Such metallocene compounds are preferably tri- and tetravalent metals having one or two hapto η^5-ligands selected from the group comprising cyclopentadienyl, indenyl, fluorenyl with the maximum number of hydrogen substituted with alkyl, alkenyl, aryl, alkylaryl, arylakyl or benzo radicals to none. When there are two η^5-ligands, they may be the same or different which are either connected by bridging groups, selected from the group comprising, C_1-C_4 alkylene, R_2Si, R_4Si_2, R_2Si-O-Si-R_2, R_2Ge, R_2P, R_2N with R being hydrogen, alkyl or aryl radicals, or the two η^5-ligands are not connected. The non-hapto ligands are either halogen or R, there are two or one such ligands for the tetravalency or trivalency transition metal, respectively. Where there is only one hapto η^5-ligands, it can be selected from the group

comprising cyclopentadienyl, indenyl, fluorenyl with from the maximum number of hydrogen substituted with R or benzo radicals or to none. The transition metal will have three or two non-hapto ligands in the +4 and +3 oxidation state, respectively. One hydrogen of the hapto ligand may be substituted with a heteratom moiety selected from the group NR, NR_2, PR, PR_2 which are connected by C_1-C_4 alklene, R_2Si, R_4Si_2 to the η^5-ring. The appropriate number of non-hapto ligands is three for tetravalent metal in the case of coordinate bondings NR_2 or PR_2 moiety and one less non-hapto ligands for the trivalent metal. These numbers are decreased by one in the case of covalent bonding NR or PR moieties.

Illustrative but not limiting examples of titanium compounds comprise bis-(cyclopentadienyl) dimethyl-titanium, bis-(cyclopentadienyl) diisopropyltitanium, bis(cyclopentadienyl) dimethyltitanium, bis(cyclopenta-dienyl) methyltitanium monochloride, bis(cyclopenta-dienyl) ethyltitanium monochloride, bis(cyclopentadienyl) isopropyltitanium monochloride, bis(cyclopentadienyl) titanium dichloride, dimethylsilylene (1-η^5-2,3,4,5-tetramethylpentadienyl) (t-butylamido) titanium dichloride, 2-dimethyl aminoethyl-η^5-cyclopentadienyl titanium dichloride.

Illustrative but not limiting examples of zirconium compounds comprise as bis(isopropylcyclopentadienyl)-zirconium dichloride, bis(cyclopentadienyl)dimethyl-zirconium, bis(cyclopentadienyl)-diethylzirconium, bis-(methylcyclopenta-dienyl) diisopropylzirconium, bis(cyclopentadienyl) methylzirconium monochloride, bis-(cyclopentadienyl)ethylzirconium monochloride, bis(cyclo-pentadienyl)zirconium dichloride, rac-ethylene bis-(1-η^5-indenyl) zirconium dichloride, rac-ethylene bis(1-η^5-indenyl) zirconium dichloride, rac-ethylene bis(1-η^5-4,5,6,7-tetrahydroindenyl) zirconium dichloride and isopropylidene-(1-η^5-cyclopentadienyl) (9-η^5-fluoronyl) zirconium dichloride.

Specific examples of hafnium compounds comprise bis(cyclo-pentadienyl)dimethylhafnium,

bis(cyclopentadienyl)methylhafnium monochloride, and bis(cyclopentadienyl)hafnium dichloride.

The aluminoxane co-catalyst useful in the catalysts of the present invention are polymeric aluminum compounds which can be represented by the general formulae $(R\text{-}Al\text{-}O)_n$ which is a cyclic compound and $R(R\text{-}Al\text{-}O\text{-})_nAlR_2$, which is a linear compound. In the general formula R is a C_1-C_5 alkyl group such as, for example, methyl, ethyl, propyl, butyl and pentyl and n is an integer from 1 to about 20. Most preferably, R is methyl and n is about 4. Generally, in the preparation of alumoxanes from, for example, aluminum trimethyl and water, a mixture of the linear and cyclic compounds is obtained.

The proportion of the catalyst comprising a compound of a transition metal of Group IVb of the Periodic Table may be, for example, 10^{-8} to 10^{-2} gram-atom/liter, preferably 10^{-7} to 10^{-3} gram-atom/liter, as the concentration of the catalyst comprising a compound of a transition metal in the polymerization reaction. The proportion of the aluminoxane used may be, for example, 10^{-4} to 10^{-1} gram-atom/liter, preferably 10^{-3} to $5x10^{-2}$ gram-atom/liter, as the concentration of the aluminum atom in the polymerization reaction. The ratio of the aluminum atom to the transition metal in the polymerization reaction system may be, for example, in the range of 25 to 10^6, preferably 50 to 10^4. The molecular weight of the polymer may be controlled by using hydrogen, and/or by adjusting the polymerization temperature, or by changing the monomer concentrations.

The copolymerizations and terpolymerizations could also be performed using other co-catalysts, without R_3Al (*Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 32, 2387-2393 (1994)).

While the above description represents preferred catalysts for use in the invention, equivalent catalysts and combinations may also be used to effect the olefin polymerization.

The polymerization reaction in the process of this invention may be carried out in absence of a solvent or in a hydrocarbon solvent. Examples of a hydrocarbon solvent suitable for this purpose are aliphatic hydrocarbons such as butane, isobutane, pentane, hexane, octane, decane, dodecane, hexadecene and octadecane; alicyclic hydrocarbons such as cyclopentane, methylcyclopentane, cyclohexane and cyclooctane; aromatic hydrocarbons such as benzene, toluene and xylene; and petroleum fractions such as gasoline, kerosene, lubricant base stocks and light oils. The starting olefins may themselves serve as the hydrocarbon medium. Among these hydrocarbon media, the aromatic hydrocarbons and the starting olefins may be preferably used in the process of this invention.

The polymerization temperature in this first step of the process of the invention may range, for example, from about 0°C to about 200°C, preferably from about 40°C to about 120°C.

When the polymerization reaction in the process of this invention is carried out in the absence of hydrogen, a liquid copolymer having a high bromine value is obtained which contains unsaturation (double bonds). This copolymer is usually a high molecular weight copolymer. When the polymerization is carried out in the presence of hydrogen, a liquid polymer having a low bromine value or a bromine value of substantially zero may be obtained. Some unsaturation may be present. The hydrogen is used to control (lower) the molecular weight of the copolymer. Excess solvent may be removed by evaporation and a light copolymer (boiling point below 371°C (700°F) in ASTM D-2887 Simulated Distillation) is recovered by distillation under vacuum.

The product resulting from this copolymerization reaction of ethylene monomer and an olefin monomer different from ethylene is a copolymer suitable as a base oil for synthetic lubricants. The polymer may be characterized as containing from 50 to 75 mole % ethylene, having a number average molecular weight in excess of 1000, a molecular weight distribution in excess of 2,

a bromine number in excess of 2, and a molecular structure which is head to tail with a random monomer distribution.

In a further aspect, the present invention provides vinylidene olefin polymers, copolymers, and terpolymers from vinylidene monomers alone or copolymerized with other non-vinylidene monomers. Vinylidene monomers are characterized by the formula:

$$CH_2=CR_1R_2$$

wherein R_1 and R_2 are independently selected from the group consisting of C_1-C_{20} aliphatic groups, alicyclic groups and aromatic groups. Preferred vinylidene monomers are 2-methyl propene (isobutylene) and 4-methylpentene. Homopolymers of vinylidene monomers may be produced or a vinlidene monomer may be reacted with one or more comonomers which may be a second vinylidene monomer or an alpha-olefin. Suitable alpha-olefin comonomers comprise ethene, propene, styrene, ethylidene, norbornene, non-conjugated dienes, norbornene, and the like.

These vinylidene polymers are produced in generally the same manner and under the same conditions as the other polymers of the invention. However, it is preferred to use a tri-catalyst system comprising a catalytic amount of triisobutyl aluminum (TIBA), a TeCl catalyst, ([C_5Me_4) $SiMe_2$-$_3$N(T-Bu]$TiCl_2$,, and a borate, triphenyl carbenium tetrakis (pentafluorophenyl) borate. The monomers are contacted with this catalyst system at a termperature ranging from about 20°C to 40°C, a polymerization pressure of about 0.34 to 1.7 atm (5 to 25 psig) and a residence time of about 0.5 to 2 hours, and preferably in the presence of hydrogen. Preferred ratios of reactants comprise olefin to vinylidene olefin ranging from about 5-50 mole % olefins to 50-95 mole % vinylidene olefin, and optionally about 0-2 percent hydrogen.

In a preferred further embodiment of the invention, a third monomeric reactant different from ethylene and the olefin polymer, may be included in the initial polymerization reaction to form a terpolymer product. This third component

must contain unsaturation so that polymerization can occur and is selected from the group consisting of olefins having 4 to 20 carbon atoms.

Preferred reactants are olefins of 4 to 12 carbon atoms such as 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene, 1-undecene and 1-dodecene, 2-methyl-1-pentene, styrene, ∝-methylstyrene, 2-methyl-1-butene, 3-methyl-1-butene, 4-methyl-1-pentene, 2-methyl-1-pentene, 2-methyl-1-propene.

In conducting the reaction with the third monomeric reactant, it is preferred to use about 0.1 up to 40 mole percent, preferably about 1 to 20 mole percent of the third monomer, based on the total composition.

The terpolymer produced in this embodiment of the invention may be characterized as a liquid terpolymer of ethylene, a first olefin different from ethylene, and a second olefin different from ethylene and the first olefin, preferably having 4 to about 20 carbon atoms; and characterized by:

(a) mole % ethylene of from 10 to 80%;

(b) mole % of said first olefin of from 14 to 80%;

(c) mole % of said second olefin of from 1% to 10%;

(d) number average molecular weight of 300-10,000;

(e) molecular weight distribution of < 2.5; and a

(f) bromine number in the range of 0 to 53.

The terpolymer resulting from reaction using the third monomer reactant is also useful as a synthetic base oil for synthetic lubricants and as a white oil for use in cosmetics and medicines. The third monomer provides a beneficial effect by lowering the pour point of the final base oil.

The presence of the third monomer during the polymerization reaction may require a change in catalyst or polymerization reaction conditions. Obviously, other and additional different monomers may be included in the reaction to produce tetrapolymers, etc.

In a further embodiment of the invention, the intermediate copolymer or terpolymer resulting from the polymerization reaction, is subjected to cracking, preferably thermal cracking. As noted above, once the polymerization reaction is completed, excess solvent is removed and those polymers having boiling points below about 371°C (700°F) in ASTM D-2887 Simulated Distillation are recovered by distillation. The catalyst may be washed from the copolymer or terpolymer with an aqueous base (e.g., 1M NaOH) or acid (e.g., 1M HCl). The resulting copolymer or terpolymer product is then subjected to cracking, preferably under thermal conditions but catalytic cracking could be used as is known in the art. The thermal cracking process is carried at a temperature range of from about 250°C to about 550°C, preferably from about 350°C to about 450°C.

The pressure in the cracking step of the invention may range, for example, from about 0.1 to 30 mm Hg vacuum pressure, preferably from about 0.2 to about 10 mm Hg vacuum pressure.

The cracked product in liquid form may optionally be washed with an aqueous base or aqueous acid, and water. Preferably, the cracked feed is washed with aqueous 1M NaOH, followed by large quantities of water.

As a result of the thermal cracking process, there is produced a copolymer or terpolymer or segments thereof which contain unsaturation (double bonds). The thermally cracked polymeric product is also useful as a synthetic base oil for synthetic lubricants.

The cracked liquid copolymer may be described as a liquid copolymer of ethylene and an olefin, said copolymer being characterized by:

(a) mole % ethylene of from 10 to 75%;

(b) number average molecular weight of < 2000;

(c) molecular weight distribution of < 2;

(d) bromine number of < 53; and

(e) a head to tail molecular structure.

The cracked liquid terpolymer may be described as a liquid terpolymer of ethylene, a first olefin, and a second olefin having 3 to about 20 carbon atoms; said terpolymer being characterized by:

(a) mole % ethylene of from 10 to 80%;

(b) mole % of said first olefin of from 14 to 80%;

(c) mole % of said second olefin of from 1% to 10%;

(d) number average molecular weight of 300-10,000;

(e) molecular weight distribution of < 2.5; and a

(f) bromine number in the range of 0 to 53.

In the thermal cracking process, the polymer appears to crack or separate substantially in the center of the polymer. These are narrow molecular weight range products particularly useful as 2, 4 and 6 centistoke oils. For example, in a polymer having a number average molecular weight of about 1200, the resulting cracked products will have two segments of about 600 number average molecular weight each. Also, after cracking, the segments will not exclusively exhibit vinylidene unsaturation but rather will have allyl unsaturates and some internal double bonds .

The bromine number of a preferred hydrogenated cracked hydrocarbon product will range from 0 up to 1.0, the kinematic viscosity at 100°C will range from 2 to 16 cSt, the viscosity index will range from 140 to 160, and the pour point will be below 0°C.

In a further embodiment, the cracked product is then hydrogenated by reaction with hydrogen gas in the presence of a catalytic amount (0.1 to 5 wt.%) of a catalyst. Examples of suitable hydrogenating catalysts are metals of Group VIII of the Periodic Table such as iron, cobalt, nickel, rhodium, palladium and platinum. These catalysts are deposited on alumina, on silica gel, or on activated carbon in preferred embodiments. Of these catalysts, palladium and nickel are preferred. Palladium on activated carbon and nickel on kieselguhr are especially preferred. The hydrogenation reaction is carried out in the presence or absence of solvents. Solvents are necessary only

to increase the volume. Examples of suitable solvents are hydrocarbons such as pentane, hexane, heptane, octane, decane, cyclohexane, methycyclohexane and cyclooctane aromatic hydrocarbons such as toluene, xylene or benzene. The temperature of the hydrogenation reaction may range, for example, from about 150°C to about 500°C, preferably from about 250° to about 350°C. The hydrogenation reaction pressure may be, for example, in the range of 250-1000 psig hydrogen. The hydrogenated polymeric product is then recovered by conventional procedures. In the hydrogenated product, the double bonds formed in the cracking step have been hydrogenated so that the polymer is a separate type of product. The hydrogenated product will have a number average molecular weight ranging from about 300 to 1000 and a kinematic viscosity @ 100°C of about 6-16 centistokes.

In a further embodiment of the present invention, the resulting ethylene-olefin polymer or terpolymer can be hydroisomerized in the presence of a catalytic amount (0.1 to 5 wt.%) of an acidic hydroisomerization catalyst. The hydroisomerization temperature used in this process ranges from about 250°C to about 550°C, preferably from about 150°C to about 300°C.

The pressure in the hydroisomerization process may range, for example, from about 17 to 68 atm (250 to 1000 psig) hydrogen pressure, preferably from about 20.4 to about 34 atm (300 to about 500 psig) hydrogen pressure. In the resulting hydroisomerized product, the carbon moieties have been rearranged into a different molecular structure.

Examples of the acidic hydroisomerization catalysts include transition metals of Groups VI to VIII of the Periodic Table, their oxides, or the combination of metal and metal oxide supported on acidic molecular sieves. The metals include Pd, Ni, Pt, Mo. Metal oxides include PdO, NiO, MoO_3. Molecular sieves include synthetic zeolites, such as zeolite A, L, X, Y, and natural zeolites, such as mordentie, chabazite, eriomite, and clinoptilolite. Preferred

hydroisomerization catalysts include Pd supported on acidic zeolite X, Ni/MoO_3 on zeolite and Ni/NiO on zeolite.

The polymer products of the invention are useful as synthetic lubricating base oils. The base oils of the invention are comparable or improved in lubricating properties, but are less expensive to produce, than poly-alpha-olefins which are currently used commercially as synthetic lubricants.

The synthetic base oils of the invention may be formulated with from about 0.1% up to about 5 wt.% of one or more conventional lubricating oil additives. Such addi-tives comprise detergent packages, pour point depressants, viscosity index improvers and other additives such as anti-oxidants, additives with a detergent action, viscosity increasing compounds, anti-corrosives, anti-foaming agents, agents to improve the lubricating effect and other compounds which are usually added to lubricating oils.

The following examples are presented to further illustrate the invention but are not considered to limit the scope of the invention in any manner whatsoever.

EXAMPLE 1

Preparation of ethylene-propylene polymer

A 4-liter autoclave reactor (using two 2-liter autoclave reactors connected in series) was thoroughly purged with nitrogen and was charged with 300 ml of dried toluene (dried over potassium). Ethylene, propylene and hydrogen were simultaneously and continuously fed through a mass flow controller into the bottom of the reactor at a ratio of 2000 cc/min, 1900 cc/min, and 240 cc/min, respectively. Methylaluminoxane 1.5 mg-atom/hour based on Al content in toluene solution and bis(isopropyl-cyclopentadienyl)zirconium dichloride $15x10^{-3}$ mg-atom/hour based on Zr content in toluene solution were simultaneously and continuously pumped into the reactor. The ethylene and propylene were polymerized at 50°C and 1.02 atm(15 psig) pressure. Throughout the reaction run, the temperature was maintained at +/-2°C by a heat transfer fluid

being circulated through a coil tubing inside the reactor. The excess monomers and hydrogen were continuously vented out at 11.33 x 10^{-3} m^3 (0.4 cubic feet) per hour to maintain a constant gas concentration in the reactor.

The resulting polymer solution was continuously transferred from the reactor to a collection vessel. The pressure was controlled by a back-pressure valve 1.02 atm (15 psig). The product, along with toluene, was withdrawn from the collector, and the toluene was removed on a rota-evaporator. The product was washed with aqueous 1M NaOH, followed by washing with a large quantity of water. A clear liquid polymer (245 grams per hour) was obtained. The obtained liquid polymer had a kinematic viscosity of 40 cSt at 100°C and viscosity index of 173, Mn of 1400, Mw/Mn of 2.44, bromine number of 4.7. The obtained copolymer contained 62 mole % ethylene.

EXAMPLE 2

The procedure was essentially the same as Example 1, except the polymerization conditions and the feed ratio of ethylene/propylene were changed. The results and properties of the product are summarized in Table 1.

TABLE 1

Polymerization conditions and products properties		
Example	**1**	**2**
Reactor Vol., L	4	2
Propylene, cc/min	1990	2000
Ethylene, cc/min	2000	1400
Hydrogen, cc/min	240	20
MAO, Al mg-atom /h	1.5	1.5
(i-PrCp)$_2$ZrCl$_2$, Zr mg-atom/h	$1.5x10^{-3}$	$1.5x10^{-3}$
Polymerization Temperature, °C	50	90
Polymerization Pressure, atm (psig)	1.02 (15)	2.04 (30)
Mn	1400	1300
Mw/Mn	2.37	2.41
Ethylene mole % in Copolymer	62	63
Yield, grams/hour	245	153
Simulated Distillation % off at 371°C (700°F)	10	8.6
Kinematic Viscosity @ 100°C, cSt	40	33
Viscosity Index	173	176
Bromine Number	4.7	8.5

EXAMPLE 3

Thermal Cracking

The light polymers produced in Example 1 (boiling point below 371°C (700°F) in ASTM D-2887 Simulated Distillation) were distilled under vacuum. The remaining viscous oils (500 grams) were placed in a round-bottom flask connected to a short-path distillation column and a receiver. The contents were heated at 350° to 450°C at 0.2 to 2 mm Hg vacuum pressure. The liquid polymers were thermally cracked inside the flask. Once the polymer pyrolized, the cracked polymers were simultaneously evaporated at this temperature range under reduced pressure, and condensed in the receiver to give 420 grams of clear oil. About 15 grams of polymer were left in the flask with the remaining catalysts. The condensed cracked product was characterized by Mn, 797; Mw/Mn, 1.34; kinematic viscosity at 100°C, 7.29 cSt; VI, 160; bromine number, 18.9.

EXAMPLE 4

Hydrogenation

Method A

A portion of the cracked product from Example 1 and 1 weight percent of Pd/C powder were placed in a Zipperclave reactor and filled with 34 atm (500 psig) hydrogen. After agitation for 7 hours at 250°C, the reactor was cooled at room temperature. The catalyst was filtered through a filter agent available under the trade designation "cellite" under reduced pressure to give a clear colorless liquid oil having a bromine number of less than 0.1. C-13 NMR: peak at δ 11.4 ppm. proves the presence of iso-butyl groups.

Method B

A stainless steel column 1.27 cm x 0.61 m(1/2 in x 2 feet)was filled with 45.9 grams of Ni-Kieselguhr pellets. A portion of the

cracked oils from Example 2 were continuously pumped upward at a rate of 1.5 ml/min. through the column at 350°C (inside temperature) and 51.05 atm (750 psig) hydrogen. The hydrogen also flowed upward through the column from a separate line. The hydrogenated products were collected at the other end of column to give a clear colorless liquid oil having a bromine number of less than 0.1. The C-13 NMR: peak at δ 11.4 ppm. proves the presence of iso-butyl groups.

EXAMPLE 5

Hydroisomerization

Method A

Hydroisomerization on a portion of the cracked product of Example 1 was performed in the same equipment using the same procedure as described in Method B of Example 4, except the Ni-Kieselguhr catalyst was replaced by 32 grams of Pd supported acidic molecular sieve (an x-type zeolite). The Pd supported zeolite was prepared by the treatment of molecular sieve X13 (50 grams) with NH_4Cl (13 grams) and $Pd(NH_3)_2Cl_2$ (1 gram) in aqueous solution at 90°C. After the separation of the water, the treated zeolite was then calcined at 450° for 4 hours. The hydroisomerization was carried out at 280°C and 23.8°C (350 psig) of hydrogen pressure. The hydroisomerized product is a clear colorless liquid having a bromine number of <0.1; C-13 NMR showed the characteristic internal ethyl group at δ 10.9 ppm and the characteristic terminal ethyl group at δ 11.4 ppm. High resolution C-13 NMR also revealed that there are at least six different methyl-carbon signals at 14.16, 14.21, 14.42, 14.45, 14.58, and 14.63 ppm.

Method B

Method A was repeated on a portion of the cracked product of Example 1 but using the commercially available Pd

supported zeolite. There was obtained an isomerized colorless liquid having a bromine number of <0.1.

EXAMPLE 6

The hydrogenated cracked oil obtained in Example 4 was formulated by the addition of commercial additives into a 5W30 grade motor oil. The formulation and the resulting physical properties are shown in Table II and compared with a commercial synthetic 5W-30 oil made from poly-alpha-olefins. In Table II, DI is a detergent inhibitor package and a VI improver is a viscosity index improver.

TABLE II

	5W30 From Example 4	Commercial Synthetic 5W -30
Components	Wt %	Wt %
Synthetic Basestock - Example 4	71.29	0
Synthetic Ester	11.39	12.06
PAO 8	0	39.17
PAO 4	0	30.79
DI Package	11.40	11.56
VI Improver	5.82	6.32
Pour Point Depressant	0.1	0.1
Physical Properties		
Kinematic Viscosity @ 100°C	11.6 cSt	11.3 cSt
Kinematic Viscosity @ 40°C	64.5 cSt	65.3 cSt
Viscosity index	177	166
Cold Cranking Simulator, -25°C	2628 cP	2486 cP
Minirotary Viscometer TP-1 @-30°C	6600 cP	5400 cP
Minirotary Viscometer TP-1 Y.S. @-30°C	0	0
Scanning Brookfield Viscosity at 30,000 cP	-39.9°C	<-40°C
Pour Point, °C	-54°C	<-57°C
Simulated Distillation, % off at 371°C (700°F)	10.90%	2.60%
Noack	11.89%	N.D.
4-Ball Wear Scar, mm	0.37	0.38
Friction Coefficient @ 100°C	0.11	0.11

The data in Table II shows that the motor oil formed from the base oil of Example 4 is comparable in characteristics and performance to the more expensive synthetic PAO oil.

EXAMPLE 7

The hydrogenated cracked oil obtained in Example 4 was further fractionated into 2 cSt, 4 cSt and 6 cSt base oils. Their physical properties are shown in Table III.

TABLE III

Property	2 cSt Oil	4 cSt Oil	6 cSt Oil
Viscosity, cSt			
100°C	1.9	4.05	6.1
40°C	5.98	17.3	31.6
Viscosity Index	106	137	145
Cold Cranking Simulator, -25°C	N.D.	670	1930
Pour Point, °C	<-60	-27	-27
Flash Point, °C	146	207	246
Fire Point, °C	N.D.	259	282
Sp. Gr.	0.797	0.815	0.823
Bromine Number	<0.1	<0.1	<0.1
GPC, Mn	326	606	761
GPC, Mw/Mn	1.07	1.05	1.15
NOACK, wt%	99.6	15.2	7.1
Simulated Distillation, % off at 371°C(700°F)	96.5	0	1.2

1%	561	730	694
5%	577	752	747
10%	592	761	786
20%	604	775	838
50%	637	804	883
90%	680	820	927
95%	693	853	972
99%	730	869	1101
PDSC Oxidation Test 34 atm O_2 (500 psig O_2)	20	18.4	18.8
Base oil. @ 165°C, minutes	25.8	49.9	50.1
Containing 10% Dl, @ 195°C, min			

EXAMPLE 8

Ethylene/Propylene/1-Butene Terpolymer

This experiment was carried out in a similar manner as Example 1, except that the reaction was a batch reaction. A 1-liter autoclave reactor was thoroughly purged with nitrogen and then charged with 300 ml of dried toluene. Through the mass flow controller, ethylene, propylene, 1-butene and hydrogen were fed into the reactor at a ratio of 4000 cc/min, 3600 cc/min, 400 cc/min, and 400 cc/min, respectively. Methyl aluminoxane in toluene solution, 46.9 mg-atom, as aluminum atom, and 0.015 mg-atom, as Zr atom, of bis(isopropylcyclopentadienyl)zirconium dichloride in toluene solutions were injected at 50°C and 1.02 atm (15 psig) pressure. After 3 hours, the reaction was quenched with 1% aq. HCl, then washed with aqueous 1 M NaOH, followed by a large quantity of water. After stripping off toluene, the reaction gave 348 grams of liquid terpolymer. The polymerization conditions and physical properties of the reactor product are summarized in Table IV. The crude reactor product was thermally

cracked as described in Example 3, followed by distilling off the light polymer through a Vigreux column. The residue was hydrogenated with 1 wt% of 10% Pd on active carbon. The final hydrogenated liquid terpolymer had a kinematic viscosity at 100°C of 9.6 cSt and viscosity index of 158; Mn of 1006, Mw/Mn of 1.24. The composition of the terpolymer, determined by C-13 NMR, was 72 mole % of ethylene, 25 mole % of propylene, and 3 mole % of butene. The physical properties are summarized in Table V.

EXAMPLE 9

The liquid terpolymer was prepared in the same manner as in Example 8, except that the reactor was fed ethylene, propylene, 1-butene and hydrogen at a rate of 4000 cc/min, 3980 cc/min, 995 cc/min, and 540 cc/min, respectively. The polymerization conditions and physical properties of the product are summarized in Table IV.

The reactor product was cracked and hydrogenated in the same manner as in Example 8 to give a colorless liquid of kinematic viscosity at 100°C of 9.9 cSt and viscosity index of 150. The composition and the physical properties of terpolymer are summarized in Table V.

EXAMPLE 10

Ethylene/Propylene/1-Decene Terpolymer

The liquid terpolymer was prepared in the same manner as Example 8, except that into the reactor was injected 25 mL of 1-decene and ethylene, propylene, and hydrogen at a rate of 4000 cc/min, 3980 cc/min, and 480 cc/min, respectively. The reaction ran for 3 hours and gave 444 grams of liquid terpolymer. The polymerization conditions and physical properties of the product are summarized in Table IV.

The reactor product was cracked and hydrogenated in the same manner as Examples 3 and 4 to give a colorless liquid

having a kinematic viscosity at 100°C of 9.8 cSt and viscosity index of 159. The terpolymer contained 4.2% by weight of 1-decene. The physical properties, summarized in Table V, show the terpolymer has a better (lower) pour point than the copolymer in comparative Example A.

Comparative Example A

The same procedure as Example 10 was followed, except the polymerization was conducted without adding a third olefin. The physical properties of the reactor product and the final hydrogenated cracked liquid terpolymer are outlined in Tables IV and V.

EXAMPLE 11

Ethylene/Propylene/1-Hexene Terpolymer

Ethylene, propylene, and hydrogen were mixed in ratio of 47:53.3:5.2 in a 7 L cylinder to a total pressure of 7.16 atm (105.2 psig). The temperature of the cylinder was heated to and maintained at 50°C for at least 2 hours to mix the gases. Into a 0.5 L autoclave reactor was placed 100 ml of toluene, followed by the gas mixture at 50°C, 1.02 atm (15 psig) pressure. Two ml of 1-hexene, dried over 4A molecular sieves, was injected into the reactor, followed by the injection of 15 mg-atom, as aluminum atom, of methyl aluminoxane and 0.015 mg-atom, as zirconium atom, of Bis(i-propylcyclopentadienyl) zirconium dichloride in toluene solution. After 3 hours, the polymerization product was quenched with 1% HCl/MeOH, washed with 100 ml 0.5 M aq.NaOH, then water. The solvent was rota-evaporated to give 156 grams of liquid terpolymer. The terpolymer contained 0.9% 1-hexane by weight.

The crude reactor product was cracked in the same manner as described in Example 3. A heart cut of terpolymer was collected overhead at a temperature of 150°C to 275°C at 1.5 mm Hg vacuum. The product, 114 grams (82%), was hydrogenated with 1 wt.% of Pd/C as described in Example 4 to give a

colorless liquid polymer. The physical properties of the final hydrogenated liquid terpolymer are outlined in Table VI.

EXAMPLE 12

Example 11 was repeated, except that 4 ml 1-hexene was injected as the third monomer. The physical properties of the final hydrogenated liquid terpolymer are outlined in Table VI.

EXAMPLE 13

Example 11 was repeated, except that 20 ml 1-hexene was injected as the third monomer. The physical properties of the final hydrogenated liquid terpolymer are outlined in Table VI.

Comparative Example B

For comparison, the ethylene/propylene copolymer was prepared without adding 1-hexene using the same procedure as described in Example 11. The physical properties of the final hydrogenated liquid copolymer are outlined in Table VI.

TABLE IV

Conditions and Properties of the Reactor Products				
Experiment	**Comparative Ex. A**	**8**	**9**	**10**
Reactor Volume	1 L	1 L	1 L	1 L
Solvent, ml	300	300	300	300
T, °C	50	50	50	50
Pressure, atm (psig)	1.02 (15)	1.02 (15)	1.02 (15)	1.02 (15)
Feed: Monomers				
Ethylene, cc/min	4000	4000	4000	4000
Propylene, cc/min	3980	3600	3980	3980
1-Butene, cc/min	0	400	995	0
1-Decene, ml	0	0	0	25
Hydrogen, cc/min	480	400	540	480
Catalysts				
MAO, Al mg-atom	31.3	46.9	62.6	31.3
$(i\text{-}PrCp)_2ZrCl_2$, Zr mg-atom/h	0.01	0.015	0.02	0.01
Time, hours	3	3	3	3
Yield, grams	311	348	394	444
Kin. Vis., at 100°C, cSt	113	86	53	43
Kin. Vis., at 40°C	1101	897	496	302
Viscosity Index	202	181	172	200
C_2, **mole % in polymer**	72	71.5	67	N/A
C_3, **mole % in polymer**	28	25.4	27	N/A
C_4, **mole % in polymer**	0	3	6	0
Mn	2196	2339	1784	2129
Mw/Mn	2.27	2	2.14	2.02
Bromine Number	2.8	2.1	2.5	22
Sim. Dist.% off at 371°C (700°F)	3.8	4.3	6.4	6.5

TABLE V

Physical Properties of the Hydrogenated Liquid Terpolymer				
Experiment	**Comparative Ex. A**	**8**	**9**	**10**
Feed: Monomers				
Ethylene, cc/min	4000	4000	4000	4000
Propylene, cc/min	3980	3600	3980	3980
1-Butene, cc/min	0	400	995	0
1-Decene, ml	0	0	0	25
Hydrogen, cc/m	480	400	540	480
Mole % of C_2	72	72	67	N.D.
Mole % of C_3	28	25	27	N.D.
Mole % of C_4	0	3	6	0
Wt % of C_{10}				4.2
Kinematic Viscosity				
at 100°C, cSt	11.4	9.6	9.9	9.8
at 40° C, cSt	66.1	55.8	60.3	56.5
Viscosity Index	166	158	150	159
Pour Point, °C	-3	-12	-24	-12
Simulated Dist., % off @ 371°C (700°F)	3.6	2.2	5.1	3.1
Mn	1086	1006	1001	1028
Mw/Mn	1.34	1.24	1.31	1.25
Bromine Number	0.1	0.1	0.1	0.1

TABLE VI

Physical Properties of the Hydrogenated $C_2/C_3/C_6$ Liquid Polymer				
	Example 11	**Example 12**	**Example 13**	**Comparative Ex. B**
Wt % of 1-hexene in polymer	0.9	1.5	7.5	0
Overhead temperature,	150-275°C/1.5mm	150-235°C/1.5mm	150-340°C/1.5mm	150-280°C/1.5mm
Wt% cut of distillate	82%	77%	80%	85%
Bromine Number	0.12	0.16	0.07	0.07
Kin. Vis., @ 100°C	6.3 cSt	6.0 cSt	8.6 cSt	7.8 cSt
40°C	31 cSt	29.4 cSt	48.1 cSt	42.7 cSt
Viscosity Index	161	157	156	157
Simulated Distillation, °C (°F)				
1% BP	206 (403)	217 (423)	245 (473)	218 (424)
50% BP	502 (936)	492 (918)	513 (955)	486 (907)
Final BP	644 (1191)	616 (1141)	675 (1247)	631 (1167)
% Off @ 371°C (700°F)	12.4	9.7	9.4	13.7
Mn	853	805	856	856
Mw/Mn	1.27	1.22	1.43	1.43
Pour Point, °C	-30°C	-33°C	-42°C	-27°C
Cold Cranking Simulator				
@ -20°C, cP	937	885	1903	980
@ -25°C, cP	1520	1404	3219	1585

EXAMPLES 14-17

Ethylene/Propylene/1-Butene Terpolymer

These examples were carried out in a manner similar to Example 8, except that the feed rates of the monomers were as set forth below in Table VII. Also set forth in Table VII are physical and chemical characteristics of the terpolymers produced.

TABLE VII

Example	14	15	16	17
Feed				
Ethylene, ml/min	3600	3880	4000	4000
Propylene, ml/min	4000	4000	3000	3200
1-Butene, ml/min	200	200	1000	800
Hydrogen ml/min	312	240	480	600
Products				
Composition				
Ethylene, % mole	65.2	69.7	73.6	73.5
Propylene, % mole	33.2	28.9	19.9	21.3
Butene,% mole	1.4	1.3	6.4	5.1
Pour Point, °C	-33	-21	-9	-6
Mn	2477	2694	2547	2055
Mw/Mn	2.12	2.23	2.01	2.16
Bromine Number	2.3	3.2	1.3	1.0
Kin. Vis. at 100°C, cSt	107	188	106	70.4
at 40°C, cSt	1140	2286	1096	625
Viscosity Index	189	204	193	191
% Unsaturation	35.6	53.9	20.7	12.8

Example 18

A 1-liter autoclave reactor was thoroughly purged with nitrogen and then charged with 200 ml of toluene. Through mass flow controller, ethylene, propylene, 1-butene and hydrogen were fed into the reactor at a ratio of 4000 ml/min, 312 ml/min, 135 ml/min, and 89 m./min, respectively. The molar ration of ethylene/propylene/1-butene were 90/7/3. Methyl aluminoxane in toluene solution, 30 mg-atom, as aluminum atom, and 0.03 mg-atom, as Zr atom, of bis(cyclopentadienyl)zirconium dichloride in toluene solution were injected at 50°C, 2.04 atm (30 psig) pressure. After 1 hour, the reactor was dismounted. The solid polymer was washed in a blender with 5% aq.HCl. The solid polymer was filtered, re-washed with water. The filtered solid was then oven dried overnight at 50°C/10 mm Hg. total 233 grams of a white powder was obtained. Drop melting point 103.8°C; DSC melting point, 103°C.

Example 19

The solid terpolymer was prepared in the same manner as in Example 18, except that the fees contain no hydrogen. total 181 grams of white solid was obtained. Capillary melting point, 91-111°C.

Example 20

The slid terpolymer was prepared in the same manner as in Example 18, except that the reactor pressure was maintained at 3.4 atm (50 psig); and the reaction was run for 2 hours. total 423 grams of white fine solid was obtained. Drop melting point, 105°C.

Example 21

The semi-solid terpolymer was prepared in the same manner as in Example 18, except that ethylene, propylene, 1-butene and hydrogen were fed into the reactor at a ratio of

4000 ml/min, 1176 ml/min, 160 ml/min, and 107 ml/min, respectively. The molar ratio of ethylene/propylene/1-butene were 75/22/3. The reaction was run for 2 hours. AFter worked up, 563 grams of white semi-slid was obtained. Drop melting point 64.5°C; Brookfiled viscosity (Spindle TF at 5 RPM; 21°C), 387,000 cP.

Example 22

A rubber semi-slid terpolymer was prepared in the sam manner as in Example 21, except that the fees contain no hydrogen. The reaction was run for 2 hours. After worked up, 303 grams of a rubber semi-slid was obtained. Drop melting point, 103.3°C.

EXAMPLE 23

Preparation of ethylene-isobutene copolymer

At 250 ml pressure reaction bottle with a magnetic stir bar was thoroughly purged with argon and was charged with 50 ml of dried toluene (distilled over potassium). Ethylene, isobutene and hydrogen were premixed in a 7 Liter cylinder at a ratio of 8%, 82%, and 10%, respectively, and then heated at 70°C overnight. The gas mixture was fed into the reaction bottle at 25°C under a pressure of 10 psig. Then 1.5 ml of 0.05 M triisobutylaluminum (TIBA) in toluene solution was injected into the bottle with a syringe followed by 1 ml of 3.75×10^{-3} M Dow Insite® catalyst ($[(C_5Me_4)SiMe_{2-3}N(t\text{-}Bu)]TiCl_2$, Me = methyl) in toluene solution and finally 1 ml of 3.75×10^{-3} M triphenylcarbenium tetrakis(pentaflucrophenyl)borate ($Ph_3CB(C_6F_5)_4$) in toluene solution as cocatalyst. Polymerization of ethylene and isobutene was initiated upon injection of cocatalyst solution. Throughout the reaction run, the temperature was maintained by a constant temperature bath with a circulator. The excess monomers and hydrogen were continuously vented at a rate of about 10 ml/min to maintain a constant gas concentration in the reaction bottle.

After one hour the reaction was quenched by injecting 10 ml of 2% acidic methanol into the bottle and the resulted solution was stirred for an extra hour. The product, along with toluene, was then washed with 3 x 200 ml of deionized water in a 500 ml separatory funnel. the organic layer was filtered through a filter agent available under the trade designation "cellite" to get a clear solution. Toluene was subsequently removed into a rota-evaporator to obtain an opaque, viscous liquid. Activity of the polymerization was 1.97×10^{5} g of polymer/(mol Ti-hr). Quantitative ^{13}C NMR analysis of the liquid showed an ethylene-isobutene copolymer was formed and it contained 46% of ethylene.

EXAMPLE 24

The procedure was essentially the same as Example 23, except that polymerization conditions and the feed ratio of ethylene/isobutene were changed and the gas phase of the reaction system was nonvented. The polymerization conditions are summarized in Table VIII. Waxy solid material was obtained from the polymerization and ^{13}C NMR analysis of the solid showed formation of ethylene-isobutene copolymer.

TABLE VIII

Polymerization conditions		
Example	23	24
Ethylene in feed, %	8	9
Isobutene in feed, %	82	91
Hydrogen in feed, %	10	0
Polymerization Temperature, °C	25	25
Polymerization Pressure, atm (psig)	0.68 (10)	0.68 (10)
Polymerization Time, hr.	1	1
Toluene, ml.	50	50
TIBA	1.5 ml of 0.05M	1.5 ml of 0.05M

Insite® catalyst	1 ml of 3.75 x 10^{-3}M	2 ml of 7.5 x 10^{-3}M
$Ph_3CB(C_6F_5)_4$	1 ml of 3.75 x 10^{-3}M	2 ml of 7.5 x 10^{-3}M
Activity, g of polymer/(mol Ti - hr)	1.97×10^5	2.4×10^5

EXAMPLE 25

Preparation of propylene-isobutene copolymer

The procedure was essentially the same as Example 23. A propylene, isobutene and hydrogen gas mixture at a ratio of 9%, 82%, and 9%, respectively, was fed into the reaction bottle containing 50 ml of toluene at 60°C under a pressure of 20 psig. 2 ml of 0.05 M TIBA , 4 ml of 15 x 10^{-3} M Insite® catalyst and 4 ml of 15 x 10^{-3} M $Ph_3CB(C_6F_5)_4$ solutions were used to initiate polymerization. The gas phase of the reaction system was continuously vented at a rate of about 20 ml/min. After one hour of reaction, a clear liquid was obtained with an activity of 0.73 x 10^5 g of polymer/(mol Ti - hr). The liquid has M_w of 3,316 and M_w/M_n of 3.00. ^{13}C NMR analysis of the liquid showed formation of propylene-isobutene copolymer.

EXAMPLE 26

The procedure was essentially the same as Example 25 except a monomer gas mixture at a ratio of 26%, 65%, and 9% for propylene, isobutene and hydrogen, respectively, was fed into the reaction bottle and 3 ml of 0.05 M TIBA was used to initiate polymerization. one hour of reaction a clear liquid was obtained with an activity of 0.53 x 10^5 g of polymer/(mol Ti - hr.). ^{13}C NMR analysis of the liquid showed formation of propylene-isobutene copolymer.

EXAMPLE 27

Preparation of ethylene-propylene-isobutene terpolymer

The procedure was essentially the same as Example 23. An ethylene, propylene, isobutene and hydrogen gas mixture at a ratio of 9%, 4%, 78% and 9%, respectively, was fed into the reaction bottle containing 50 ml of toluene at 40°C under a pressure of 1.36 atm (20 psig). 2 ml of 0.05 M TIBA, 2 ml of 3.75×10^{-3} M Insite® catalyst under 2 ml of 3.75×10^{-3} M $Ph_3CB(C_6F_5)_4$ solutions were used to initiate polymerization. The gas phase of the reaction system was continuously vented at a rate of about 20 ml/min. After one hour of reaction a clear liquid was obtained with an activity of 4.89×10^5 g of polymer/mol Ti - hr). ^{13}C NMR analysis of the liquid showed formation of ethylene-propylene-isobutene terpolymer.

EXAMPLE 28

The procedure was essentially the same as Example 27 except for the monomer gas mixture was at a ratio of 13.4%, 18%, 55.2% and 13.4% for ethylene, propylene, isobutene and hydrogen, respectively. After one hour of reaction a clear liquid was obtained with an activity of 3.47×10^5 g of polymer/(mol Ti - rr). ^{13}C NMR analysis of the liquid showed formation of ethylene-propylene-isobutene terpolymer.

EXAMPLE 29

Preparation of ethylene-styrene-isobutene terpolymer

The procedure was similar to that in Example 23. The reaction bottle was charged with 50 ml of dried toluene and 10 ml of styrene. 0.68 atm (10 psig) of a gas mixture at a ratio of 10% and 90% for ethylene and isobutene, respectively, was fed into the bottle at 50°C. 3 ml of 0.05 M TIBA, 4 ml of 0.015 M Insite® catalyst and 4 ml of 0.015 M $Ph_3CB(C_6F_5)_4$ solutions were used to initiate polymerization. The gas phase of the reaction system was continuously vented at a rate of about 10 ml/min. After one hour of reaction a semi-solid was obtained

with an activity of 2.42 x 10^5 g of polymer/(mol Ti - hr). The product has M_w of 3,127 and M_w/M_n of 3.06. DSC study of the material indicated an ethylene-styrene-isobutene terpolymer was formed.

EXAMPLE 30

The procedure was similar to example 29. 10 psig of a gas mixture at a ratio of 10% and 90% for ethylene and isobutene, respectively, was fed into the bottle containing with 1.04 x 10^{-4} mole of $(C_5Me_5)TiCl_3$ and 10 ml of a α-methylstyrene at 25°C. 3 ml of 0.05 M TIBA and 5 ml of 0.028 M $Ph_3CB(C_6F_4)_4$ solutions were used to initiate polymerization. The gas phase of the reaction system was continuously vented at a rate of about 10 ml/min. AFter one hour of reaction solid product was obtained with an activity of 0.24 x 10^5 g of polymer/(mol Ti - hr). DSC study of the material indicated an ethylene-α-methylstyrene-isobutene terpolymer was formed.

EXAMPLE 31

The procedure was essentially the same as Example 30 except for 1.04 x 10^{-4} mole of Insite® catalyst instead of $(C_5Me_5)TiCl_3$ was used as a catalyst for polymerization. one hour of reaction solid product was obtained with an activity of 0.41 x 10^5 g of polymer/(mol Ti - hr). DSC study of the material indicated an ethylene-α-methylstyrene-isobutene terpolymer was formed.

In addition to their use as base oils, the products of the invention are also useful in applications such as air care, skin care, hair care, cosmetics, household products, cleaners, polishes, fabric care, textile coatings and textile lubricants,automotive products, car cleaners and polishes, fuel additives, oil additives, candles, pharmaceuticals,

suspending agents, sun care, insecticides, gels, hydraulic fluids, transmission fluids, modifier for polymers, biodegradable applications and 2-cycle oils.

The invention has been described with reference to certain preferred embodiments. However, as obvious variations thereon will become apparent to those skilled in the art, the invention is not to be considered as limited thereto.

What is claimed is:

1. A cracked liquid copolymer of ethylene and an olefin, said copolymer being characterized by:

(a) mol % of ethylene from 50 to 75%;

(b) number average molecular weight of < 2000;

(c) molecular weight distribution of < 2;

(d) random monomer distribution; and

(e) a head-to-tail molecular structure.

2. A cracked copolymer according to claim 1, wherein said olefin contains from 3 to 20 carbon atoms.

3. A cracked copolymer according to claim 1, wherein said olefin is propylene.

4. A cracked copolymer according to claim 1, wherein said olefin is 2-methyl-1-propene, 2-methyl-1-butene, 2-methyl-1-pentene, or 2-methyl-1-hexene.

5. A cracked copolymer according to claim 1, wherein said olefin is alpha-methylstyrene.

6. A process for the production of a cracked copolymer, comprising the steps of:

(a) polymerizing ethylene and at least one olefin in the presence of a single-site catalyst comprising a compound of a transition metal of Group IVb of the Periodic Table and an aluminoxane to produce a precursor copolymer; and

(b) cracking at least a portion of the precursor copolymer to produce a cracked copolymer at a temperature above 300°C.

7. A process according to claim 6, wherein said olefin has from about 3 to 20 carbon atoms.

8. A process according to claim 6, wherein the olefin is propylene.

9. The cracked copolymer obtained according to the process of claim 6, which comprises a copolymer or segments thereof and having greater unsaturation than said precursor copolymer.

10. A process according to claim 6, wherein the transition metal is selected from the group consisting of titanium, zirconium and hafnium.

11. A process according to claim 6, wherein the aluminoxane is polymethylaluminoxane.

12. A process according to claim 6, wherein said cracking step is thermal cracking.

13. A process according to claim 6, wherein said cracking step is carried out at a temperature range of about 350°C to about 550°C and a pressure of from about 0.1 to 30 mm Hg vacuum pressure.

14. The process according to claim 6, which comprises the additional step of hydrogenating said cracked copolymer product to produce a hydrogenated product.

15. A process according to claim 14, wherein the hydrogenation is carried out by reaction of the cracked copolymer with hydrogen gas in the presence of a hydrogenation catalyst, a temperature of about 150°C to about 500°C, and a pressure of about 17-68 atm hydrogen.

16. The hydrogenated cracked copolymer produced according to the process of claim 15, wherein the bromine number ranges about 0 to about 1.5.

17. A lubricating oil comprising a polymer of claim 1 as the base oil and effective amount of at least one oil additive.

18. A lubricating oil comprising a polymer of claim 9 as the base oil and an effective amount of at least one oil additive.

19. A lubricating oil comprising a polymer of claim 16 as the base oil and an effective amount of at least one oil additive.