

1 **HIGH VISCOSITY POLYALPHAOLEFINS**
2 **PREPARED WITH IONIC LIQUID CATALYST**

3 **FIELD OF THE INVENTION**

This is a Division of Application No. 09/588,103, filed May 31, 2000, now allowed.

4 The present invention relates to the preparation of high viscosity
5 polyalphaolefins prepared using an ionic liquid catalyst.

6 **BACKGROUND OF THE INVENTION**

7 Alphaolefins may be oligomerized to prepare synthetic lubricating oil base
8 stocks which have desirable lubricating properties such as a low pour point
9 and a high viscosity index (VI). However, very high viscosity polyalphaolefins,
10 such as disclosed in U.S. Patent 4,827,064, are expensive to manufacture
11 using conventional oligomerization processes. U.S. Patent 5,304,615 teaches
12 the oligomerization of butene using an ionic liquid catalyst. European Patent
13 Application 97300875.8 describes a process for oligomerizing alphaolefins,
14 such as decene, using an ionic liquid catalyst to produce polyalphaolefins
15 having a viscosity up to about 20 centistokes (cSt) at 100°C. Unfortunately,
16 the process taught in this application has not been shown to be suitable for
17 making very high viscosity material, i.e., polyalphaolefins having a viscosity
18 above 22 cSt at 100°C.

19 Additionally, the prior art teaches the use of imidazolium, pyridinium, or
20 phosphonium as one component in the ionic liquid in addition to aluminum
21 halide or gallium halide. Ternary compositions with ammonium halides are
22 described in WO 95/21872 as being useful for olefinic oligomerization.

23 Applicants have found that it is possible to readily make polyalphaolefins
24 having very high viscosity using an ionic liquid catalyst by carrying out the
25 oligomerization reaction in the absence of organic solvents which have
26 hitherto been used as a diluent for the feed. Accordingly, Applicants have

1 been able to make polyalphaolefins from feeds comprised primarily of olefins,
2 such as decene and dodecene, having viscosities in excess of 22 cSt and
3 even in excess of 30 cSt. Polyalphaolefins made using the process of the
4 present invention also have been shown to display excellent viscosity index
5 (VI) values, low pour points, and low Noack volatility values.

6 As used in this disclosure, the words "comprises" or "comprising" is intended
7 as an open-ended transition meaning the inclusion of the named elements,
8 but not necessarily excluding other unnamed elements. The phrase "consists
9 essentially of" or "consisting essentially of" is intended to mean the exclusion
10 of other elements of any essential significance to the combination. The
11 phrase "consisting of" is intended as a transition meaning the exclusion of all
12 but the recited elements with the exception of only minor traces of impurities.

13 SUMMARY OF THE INVENTION

14 The present invention is directed to a process for producing a very high
15 viscosity polyalphaolefin product comprising contacting a feed consisting
16 essentially of at least one alphaolefin having from 4 to about 14 carbon atom
17 with an effective oligomerizing amount of an acidic ionic liquid oligomerization
18 catalyst, maintaining said feed and oligomerization catalyst under preselected
19 oligomerization conditions for a sufficient time to oligomerize the alphaolefin to
20 the polyalphaolefin product, and recovering the high viscosity polyalphaolefin
21 product. As noted above, it has been found that very high viscosity products
22 may be obtained using the process of the present invention by carrying out
23 the oligomerization reaction in the absence of organic diluent. Using the
24 process of the invention, polyalphaolefins having viscosities in excess of
25 22 cSt and even in excess of 30 cSt may be readily prepared. Especially
26 preferred in preparing the polyalphaolefin product are feeds comprising
27 decene or dodecene.

1 The acidic ionic liquid oligomerization catalyst usually will be comprised of at
2 least two components, and in most instances it will be a binary catalyst, i.e., it
3 will consist of only two components. The first component is a compound
4 selected from the group consisting of aluminum halide, alkyl aluminum halide,
5 gallium halide, and alkyl gallium halide. Preferred compounds for use as the
6 first component of the oligomerization catalyst are an aluminum halide or an
7 alkyl aluminum halide, such as, for example, aluminum trichloride. The
8 second component is quaternary ammonium, quaternary phosphonium, or
9 tertiary sulfonium, such as, for example, a liquid salt selected from one or
10 more of hydrocarbyl substituted ammonium halides, hydrocarbyl substituted
11 imidazolium halide, hydrocarbyl substituted pyridinium halide, alkylene
12 substituted pyridinium dihalide, or hydrocarbyl substituted phosphonium
13 halide. Particularly preferred as the second component are alkyl substituted
14 ammonium halides, such as trimethylamine hydrochloride or alkyl substituted
15 imidazolium halides, such as 1-ethyl-3-methyl-imidazolium chloride. The mole
16 ratio of the two components will usually fall within the range of from about 1:1
17 to about 5:1 of said first component to said second component, and more
18 preferably the mole ratio will be in the range of from about 1:1 to about 2:1.

19 The use of a binary catalyst composition consisting essentially of
20 trimethylamine hydrochloride and aluminum trichloride is particularly
21 advantageous for carrying out the process of the present invention due to the
22 ease of preparation, the ready commercial availability of the components, and
23 the relatively low cost.

24 The amount of catalyst present to promote the oligomerization of the
25 α -olefin should be not less than an effective oligomerizing amount, that is
26 to say, the minimum amount of the catalyst necessary to oligomerize the
27 α -olefin to the desired product. This may vary to some degree depending
28 on the composition of the catalyst, the ratio of the two components of the
29 catalyst to one another, the feed, the oligomerization conditions chosen, and
30 the like. However, a determination of the effective catalytic amount should be

1 well within the ability of one skilled in the art with no more than routine testing
2 necessary to establish the amount needed to carry out the invention.

3 The present invention is also directed to the unique polyalphaolefin product
4 prepared using the present invention. This product is characterized by a
5 viscosity of not less than 22 cSt at 100°C, and more preferably will have a
6 viscosity of at least 30 cSt at 100°C. In addition, the polyalphaolefin product
7 will display a low pour point, preferably less than -30°C, and low volatility,
8 preferably with a Noack number of 3 or less. Preferably, the product will have
9 a dimer content of less than 2 weight percent.

10 DETAILED DESCRIPTION OF THE INVENTION

11 As noted above, it is essential that the oligomerization reaction be conducted
12 in the absence of any organic diluent. In carrying out the process of the
13 present invention, the alphaolefin feed may be added to the catalytic mixture
14 or the catalyst may be added to the alphaolefin feed. In either case, the feed
15 and the product formed during the oligomerization will form a separate phase
16 from the ionic liquid which allows the two phases to be readily separated. In
17 order to facilitate mixing of the catalyst and the feed, it is desirable to either
18 stir the oligomerization mixture or bubble the alphaolefin feed through the
19 ionic liquid catalyst. Following completion of the oligomerization reaction, the
20 mixing should be halted, and the product and residual feed should be allowed
21 to form a distinct layer apart from the catalyst phase. In previous processes,
22 the feed and product phase usually also contained an organic diluent, such as
23 hexane. Applicants have discovered the presence of the organic diluent of
24 the previous processes interferes with the oligomerization reaction and
25 prevents the formation of the desired very high viscosity polyalphaolefin
26 product.

27 The feed will consist essentially of one or more alphaolefins having from 4 to
28 about 14 carbon atoms in the molecule, generally from about 8 to about

1 12 carbon atoms. Especially preferred are feeds containing 1-decene and
2 1-dodecene. While the feed may consist of a mixture of different alphaolefins,
3 it is essential that the feed not contain any organic diluent. As explained
4 above and as further illustrated in the examples below, it has been found that
5 the presence of an organic diluent interferes with the oligomerization reaction
6 and prevents the formation of the desired very high viscosity polyalphaolefin
7 product. This differs from the prior processes which included an organic
8 diluent, such as hexane or heptane, as part of the organic phase of the
9 reaction mixture.

10 The acidic ionic liquid oligomerization catalyst is comprised of two
11 components which form a complex. The first component of the catalyst which
12 will usually comprise a compound selected from the group consisting of
13 aluminum halide, alkyl aluminum halide, gallium halide, and alkyl gallium
14 halide. Especially preferred for the first component are aluminum halide or
15 alkyl aluminum halide. Aluminum trichloride has been used successfully as
16 the first component for preparing the oligomerization catalyst used in
17 practicing the present invention.

18 The second component making up the catalyst is an ionic liquid which is
19 primarily salt or mixture of salts which melts below room temperature. Ionic
20 liquids may be characterized by the general formula $Q^+ A^-$, wherein Q^+ is
21 quaternary ammonium, quaternary phosphonium, or quaternary sulfonium,
22 and A^- is a negatively charged ion such as Cl^- , Br^- , OCl_4^- , NO_3^- , BF_4^- , BCl_4^- ,
23 PF_6^- , SbF_6^- , $AlCl_4^-$, ArF_6^- , TaF_6^- , $CuCl_2^-$, $FeCl_3^-$, $SO_3CF_3^-$, $SO_3C_7H_7^-$, and
24 3-sulfurtrioxyphenyl. Preferred for use as the second component are those
25 quaternary ammonium halides containing one or more alkyl moieties having
26 from 1 to about 9 carbon atoms, such as, for example, trimethylamine
27 hydrochloride, or hydrocarbyl substituted imidazolium halides, such as, for
28 example, 1-ethyl-3-methyl-imidazolium chloride.

1 The presence of the first component should give the ionic liquid a Lewis (or
2 Franklin) acidic character. Generally, the greater the mole ratio of the first
3 component to the second component, the greater the acidity of the ionic liquid
4 mixture. When aluminum trichloride and trimethylamine hydrochloride are
5 used as the first and second components, respectively, of the acidic ionic
6 liquid oligomerization catalyst, they preferably will be present in a mole ratio of
7 from about 1:1 to about 2:1.

8 The oligomerization reaction takes place over a wide temperature range, but
9 preferably is carried out at about ambient temperature or slightly below. The
10 oligomerization reaction is somewhat exothermic and it may be desirable to
11 control the reaction temperature with an aqueous quench. Preferably, the
12 temperature of the reaction mixture will be maintained below about 50°C and
13 most preferably will be maintained below about 30°C.

14 Following completion of the oligomerization reaction, the organic layer
15 containing the α -olefin product and residual olefin feed is separated from
16 the ionic liquid phase. The unreacted olefin and dimers may be removed from
17 the product by conventional means, such as by distillation, and recycled back
18 for further conversion. Likewise, the acidic ionic liquid catalyst that remains
19 after recovery of the organic phase may be recycled to the oligomerization
20 zone.

21 Following recovery of the poly α -olefin product, it is generally desirable to
22 hydrogenate the unsaturated double bonds which remain in the product
23 mixture. This is readily accomplished by conventional means well known to
24 those skilled in the art. The hydrogenation of the unsaturated bonds is usually
25 carried out with hydrogen in the presence of a hydrogenation catalyst such as,
26 for example, catalyst containing nickel, palladium, platinum, cobalt or the like.

27 The present invention may be further illustrated by the following example
28 which is not intended to be a limitation on the process.

1

EXAMPLE 1

2 A catalyst mixture was prepared using a 2 to 1 ratio of aluminum trichloride to
3 trimethylamine hydrochloride. The catalyst (39.2 g) was placed in a 1 liter
4 round bottom flask to which 401.2 g of 1-decene was added dropwise. The
5 initial temperature of the oligomerization mixture was 0°C which was allowed
6 to raise to 22°C. An inert atmosphere was maintained by a nitrogen sweep
7 gas/bubbler. The reaction was allowed to proceed for 1 hour and was
8 quenched with aqueous potassium hydroxide. The product was water
9 washed and hydrogenated using a nickel catalyst. The residual monomer and
10 dimer were removed by distillation. The distilled oligomer was found to
11 display the following properties:

12	100°C Kinematic Viscosity	31.6 cSt
13	40°C Kinematic Viscosity	283 cSt
14	Viscosity Index	152
15	Pour Point	-39°C
16	Noack Volatility	1.68%

17

EXAMPLE 2

18 The general procedure was the same as in Example 1, above, except for the
19 addition of 185 grams of heptane diluent which was mixed with 400 grams of
20 decene. Catalyst was prepared in a 2 to 1 molar ratio of aluminum trichloride
21 to trimethylamine hydrochloride and 40.1 grams were added to the reaction in
22 a dropwise manner. The initial reaction temperature was -6°C. The product
23 was water washed and hydrogenated using a nickel catalyst. The residual
24 monomer and dimer were removed by distillation to less than 1%. The
25 distilled oligomer was found to display the following properties:

26	100°C Kinematic Viscosity	15.0 cSt
27	40°C Kinematic Viscosity	109 cSt

1	Viscosity Index	143
2	Pour Point	−45°C

3 It should be noted that the kinematic viscosity of the oligomer of Example 2
4 was significantly less at both 100°C and 40°C than that for the oligomer of
5 Example 1. The viscosity index of the product of Example 2 was also lower.

1 WHAT IS CLAIMED IS:

- 2 1. A process for producing a very high viscosity polyalphaolefin product
3 comprising contacting a feed consisting essentially of at least one
4 alphaolefin having from 4 to about 14 carbon atom with an effective
5 oligomerizing amount of an acidic ionic liquid oligomerization catalyst,
6 maintaining said feed and oligomerization catalyst under preselected
7 oligomerization conditions for a sufficient time to oligomerize the
8 alphaolefin to the polyalphaolefin product, and recovering the high
9 viscosity polyalphaolefin product.
- 10 2. The process of claim 1 wherein the feed comprises 1-decene.
- 11 3. The process of claim 1 wherein the feed comprises 1-dodecene.
- 12 4. The process of claim 1 wherein the acidic ionic oligomerization catalyst
13 comprises a first component and a second component, said first
14 component comprising a compound selected from the group consisting
15 of aluminum halide, alkyl aluminum halide, gallium halide, and alkyl
16 gallium halide, and said second component is an ionic liquid
17 comprising a liquid salt containing quaternary ammonium, quaternary
18 phosphonium, or quaternary sulfonium.
- 19 5. The process of claim 4 wherein said first component is aluminum
20 halide or alkyl aluminum halide.
- 21 6. The process of claim 5 wherein said first component is aluminum
22 trichloride.
- 23 7. The process of claim 4 wherein said second component is selected
24 from one or more of hydrocarbyl substituted ammonium halide,
25 hydrocarbyl substituted imidazolium halide, hydrocarbyl substituted

- 1 pyridinium halide, alkylene substituted pyridinium dihalide, or
2 hydrocarbyl substituted phosphonium halide.
- 3 8. The process of claim 7 wherein the second component is an alkyl
4 substituted ammonium halide containing one or more alkyl moieties
5 having from 1 to about 9 carbon atoms.
- 6 9. The process of claim 8 wherein the second component comprises at
7 least trimethyl amine hydrochloride.
- 8 10. The process of claim 7 wherein the second component is an alkyl
9 substituted imidazolium halide.
- 10 11. The process of claim 10 wherein the second component comprises at
11 least 1-ethyl-3-methyl-imidazolium chloride.
- 12 12. The process of claim 4 wherein the ratio of first component to the
13 second component of the oligomerization catalyst is within the range of
14 from about 1:1 to about 5:1.
- 15 13. The process of claim 5 wherein the ratio of the first component to the
16 second component is within the range of from about 1:1 to about 2:1.
- 17 14. The process of claim 1 including the additional step of hydrogenating
18 the unsaturated double bonds present in the polyalphaolefin product.
- 19 15. The process of claim 1 wherein the dimer in the product is reduced to
20 less than 2 weight percent.
- 21 16. A polyalphaolefin product having a viscosity of not less than
22 22 centistokes at 100°C made using the process of claim 1.

- 1 17. The product of claim 16 having a viscosity of not less than
2 30 centistokes at 100°C.
- 3 18. The product of claim 17 wherein the product contains less than
4 2 weight percent of dimer.
- 5 19. A process for producing a very high viscosity polyalphaolefin product
6 which is characterized by a viscosity of at least 22 centistokes at
7 100°C, said process comprising contacting a feed consisting
8 essentially of at least one alphaolefin having from 4 to about 14 carbon
9 atom⁷ with an effective oligomerizing amount of a acidic binary ionic
10 liquid oligomerization catalyst having a first component consisting of an
11 aluminum halide or an alkyl aluminum halide and a second component
12 consisting of a quaternary ammonium selected from selected from a
13 quaternary ammonium halide containing one or more alkyl moieties
14 having from 1 to about 9 carbon atoms or a hydrocarbyl substituted
15 imidazolium halide; maintaining said feed and oligomerization catalyst
16 under preselected oligomerization conditions for a sufficient time to
17 oligomerize the alphaolefin to the polyalphaolefin product; and
18 recovering the high viscosity polyalphaolefin product.
- 19 20. The process of claim 19 wherein the acidic binary ionic liquid
20 oligomerization catalyst comprises a first component of aluminum
21 trichloride and a second component of trimethylamine hydrochloride.
- 22 21. The process of claim 19 wherein the acidic binary ionic liquid
23 oligomerization catalyst comprises a first component of aluminum
24 trichloride and a second component of 1-ethyl-3-methyl-imidazolium
25 chloride.

- 1 22. The process according to claims 20 or 21 wherein the mole ratio of
2 aluminum trichloride to the second component is within the range of
3 from about 1:1 and 2:1.

1 23. A high viscosity polyalphaolefin composition comprising a product resulting
2 from the oligomerization under oligomerization conditions of a feed stock containing at least
3 1-decene or 1-dodecene in the presence of an oligomerization catalyst comprising an ionic
4 liquid comprising a first component and a second component wherein said first component is
5 a compound selected from the group consisting of aluminum halide, alkyl aluminum halide,
6 gallium halide, and alkyl gallium halide and wherein said second component is selected from
7 the group consisting of quaternary ammonium, quaternary phosphonium, and tertiary
8 sulfurium, and wherein said product has a viscosity in excess of 22 ct at 100°C.

9 24. A high viscosity polyalphaolefin composition of claim 23 wherein said
10 product has a dimer content of less than 2 weight percent.

11 25. A high viscosity polyalphaolefin composition of claim 23 wherein said
12 product has a viscosity of at least 30 ct at 100°C.

13 26. A high viscosity polyalphaolefin composition of claim 23 wherein said
14 product has a pour point of less than -30°C.

15 27. A high viscosity polyalphaolefin composition of claim 23 wherein said
16 product has a viscosity of not less than 22 cst at 100°C.

17 28. A process comprising:
18 contacting under reaction conditions a feed comprising an alpha olefin having four
19 carbon atoms with an acidic ionic liquid oligomerization catalyst formed by combining
20 aluminum halide and trimethylamine hydrochloride to thereby form a reaction product
21 comprising a polyalphaolefin product.

22 29. A process as defined in claim 28 wherein the mole ratio of aluminum halide to
23 trimethylamine hydrochloride combined to form said acidic ionic liquid oligomerization
24 catalyst is within the range of from about 1:1 to about 5:1.

1 30. A process as defined in claim 29 wherein the contacting step is conducted in
2 the absence of an organic diluent.

3 31. A process as defined in claim 30 wherein the contacting step is carried out at a
4 temperature below about 50°C.

5 32. A process for producing a polyalphaolefin product, said process comprises:
6 mixing an alpha olefin feed comprising at least 1-decene or 1-dodecene with an
7 effective oligomerizing amount of an acidic ionic liquid oligomerization catalyst comprising
8 a first component and a second component wherein said first component is a compound
9 selected from the group consisting of aluminum halide, alkyl aluminum halide, gallium
10 halide, and alkyl gallium halide and wherein said second component is selected from the
11 group consisting of quaternary ammonium, quaternary phosphonium, and tertiary sulfonium to
12 produce a reaction product comprising polyalphaolefin.

13 33. A process as recited in claim 32, further comprising:
14 forming an organic phase comprising said reaction product and an ionic liquid phase
15 comprising said acidic ionic liquid oligomerization catalyst.

16 34. A process as recited in claim 33, further comprising:
17 separating said organic phase into a first product comprising unreacted alpha olefin or
18 dimer of alpha olefin and a polyalphaolefin product comprising oligomer of alpha olefin.

19 35. A process as recited in claim 34, further comprising:
20 hydrogenating said polyalphaolefin product.