

1 **METHOD FOR PREPARATION OF POLYOLEFINS**
2 **CONTAINING EXO-OLEFIN CHAIN ENDS**

3 This application claims the benefit of U.S. Provisional Application No.
4 60/603,410, filed August 20, 2004.

5 FIELD OF THE INVENTION

6 The present invention is directed to a method for preparation of polyolefins
7 containing exo-olefin chain ends. The method involves quenching a cationic
8 quasi-living polyolefin polymer system with one or more hindered secondary
9 or tertiary amines.

10 BACKGROUND OF THE INVENTION

11 Linear polyolefins made using a mono-functional initiator containing a single
12 "exo-olefin", "di-substituted" olefin, or "methyl vinylidene group," end group
13 are useful precursors for the preparation of polymers containing specific
14 functional end groups. Polymers made using multi-functional initiators would
15 have multiple exo-olefinic end groups. Polymers containing specific end
16 groups are useful as lubricating oil additives. One example of a functionalized
17 polymer containing hetero atoms is polyisobutenylsuccinic anhydride.
18 Functional end groups may also be desirable for making polymers with
19 potential for further reactions.

20 Conventional ionic polymerizations can be anionic or cationic. Anionic
21 polymerizations proceed, in the presence of a base, through carbanions and
22 favor monomers having electron withdrawing groups. Cationic
23 polymerizations proceed, in the presence of an acid, through a carbocation,
24 also called a carbenium ion, and favor monomers that have electron releasing
25 groups.

1 Similarly to the conventional polymerization systems, living polymerization
2 systems may be either anionic or cationic. The difference between
3 conventional polymerizations and living polymerizations is that an ideal living
4 polymerization proceeds in the absence of chain transfer and chain
5 termination. Living polymerization systems are of great commercial
6 importance because the degree of polymerization may be controlled by
7 controlling the feed ratio of monomer to initiator and sequential addition of
8 two or more different monomers affords the ability to produce block
9 copolymers. Polymerization continues until the monomer is exhausted, but
10 the polymers retain their ability to add additional monomers any time in the
11 future. A number of such systems are well known in the art.

12 A further development is the cationic quasi-living polymerization systems
13 using conventional monomers. Quasi-living polymerization requires certain
14 restrictive conditions, for example anhydrous reagents. Cationic quasi-living
15 polymerizations differ from truly living polymerizations in that, although the
16 rate of chain transfer approaches zero, chain termination is present but
17 reversible. One important example of a cationic quasi-living polymerization is
18 the cationic quasi-living polymerization of isobutylene.

19 Typically, cationic quasi-living polymerizations of isobutylene yield narrow
20 molecular weight distribution and one major polymer product containing the
21 2-chloro-2-methylpropyl end group, also referred to as the "tert-chloride" end
22 group. Under certain conditions minor amounts of olefinic isomers may also
23 be produced.

24 On the other hand, there are two major olefinic isomers produced during
25 conventional polymerization of isobutylene with BF_3 , for example, the highly
26 reactive exo-olefin isomer and the relatively unreactive 2-methyl-1-propenyl
27 isomer, also referred to as the "tri-substituted" isomer or "endo olefin" isomer.
28 Furthermore, conventional polymerizations of isobutylene yield polymers with
29 broad molecular weight distributions or polydispersity indices.

1 Exclusive production of the exo-olefin isomer has not been previously
2 achieved under conventional polymerization conditions for isobutylene.

3 There are two established methods for producing polyisobutylene containing
4 only the exo-olefin end group. One method involves chemical
5 dehydrohalogenation of tert-chloride terminated polyisobutylene using
6 potassium tert-butoxide in a post polymerization reaction (U.S. Patent
7 No. 4,342,849). The other method involves in situ quenching of quasi-living
8 isobutylene with methallyltrimethylsilane, which converts an active, living
9 carbenium ion to the exo-olefin end group. (M. Roth and H. Mayr,
10 Macromolecules, 29, 6104, 1996)

11 Polyisobutylene polymers containing more than one exo-olefin end group may
12 be prepared using the above methods by the use of a multi-functional initiator.

13 The preparation of polyolefins, including polyisobutylene polymers, is well
14 known in the art. A number of patents have discussed processes for making
15 polyisobutylene polymers containing exo-olefin end groups, but none using
16 quenching a cationic quasi-living polymerization system with a hindered
17 secondary or tertiary amine.

18 European Patent No. 341012 discloses a method for producing polymers with
19 narrow molecular weight distribution, where the ratio of the weight average
20 molecular weight, $M(w)$, to the number average molecular weight, $M(n)$,
21 approaches 1.

22 U.S. Patent No. 4,152,499 discloses isobutene polymers having a mean
23 degree of polymerization from 10 to 100 and where the proportion of
24 theoretically possible terminal double bonds is greater than in products
25 prepared using aluminum trichloride. The patent also discloses the method of
26 making the isobutene polymers using boron trifluoride as the initiator.

1 U.S. Patent No. 4,342,849 discloses the synthesis of polyisobutylene carrying
2 either unsaturation or hydroxyl groups at both ends, in the case of a linear
3 polymer, or at all ends in the case of a star polymer. The method involves the
4 steps of refluxing a solution of telechelic di-halogen polyisobutylene, adding a
5 solution strong base such as potassium t-butoxide and stirring to form the
6 telechelic di-olefin polyisobutylene.

7 U.S. Patent No. 4,393,199 discloses a method for carrying out cationic
8 polymerization with molecular weight control in which a pre-initiator and a
9 catalyst effective for cationic polymerization are mixed with a monomer. The
10 resulting living polymer is then treated as desired.

11 U.S. Patent No. 4,758,631 discloses a method of preparing allyl-terminated
12 polyisobutylene by allylation with allyltrimethylsilane of tertiary chloro-capped
13 polyisobutylene by electrophilic substitution. The synthesis begins with the
14 boron trichloride catalyzed mono- or oligo-tertiary chloride "inifer" initiated
15 polymerization of isobutylene, followed in the same reaction vessel by the
16 addition of hexane, allyltrimethylsilane and titanium tetrachloride.

17 U.S. Patent Nos. 4,910,321 and 5,122,572 disclose a catalyst composed of a
18 complex of an organic acid or its ester and a Lewis acid, preferably boron
19 trichloride that can add olefin monomers to increase the molecular weight of
20 the complex from as low as 200 to in excess of a million. The patents also
21 disclose polymers of different molecular weights having useful end groups
22 such as halogens and specifically chloride, allyl, acryl or methacryl, acetate or
23 formate.

24 U.S. Patent Nos. 4,929,683 and 5,066,730 disclose a catalyst composed of a
25 complex of an organic ether and a Lewis acid, preferably boron trichloride that
26 can add olefin monomers to increase the molecular weight of the complex
27 from as low as 200 to in excess of a million. The patents also disclose

1 polymers of different molecular weights having useful end groups such as
2 halogens and specifically chloride, allyl, acryl or methacryl, acetate or formate.

3 U.S. Patent No. 5,219,948 discloses a method for preparing elastomeric
4 polymers comprising alpha-olefins or conjugated alkadienes by cationic
5 polymerization in the presence of titanium tetrachloride and an electron pair
6 donor selected from pyridine or a non-hindered alkylpyridine. The polymers
7 have very narrow, mono-modal molecular weight distribution.

8 U.S. Patent No. 5,336,745 discloses a method for the direct synthesis of
9 polymeric materials functionalized with desirable nitrogen-containing
10 functional groups such as terminal azido, cyano, carbonylamino or
11 thiocarbonylamino groups. Polymerization and functionalization occur in a
12 substantially simultaneous manner.

13 U.S. Patent No. 5,428,111 discloses a process for the living polymerization of
14 aromatic, preferably styrenic monomers initiated from a living polyolefin,
15 particularly polyisobutylene, chain end for making block copolymers having
16 polyolefin mid-blocks and styrenic end-blocks.

17 U.S. Patent No. 5,448,000 discloses a one-pot method of preparing sulfonic
18 acid-terminated polyisobutylene by sulfonation with acetyl sulfate of a living
19 polyisobutylene in a single step. The method involves "inifer" initiated
20 carbocationic polymerization with Lewis acid to form the polymer followed by
21 the sulfonation.

22 U.S. Patent Nos. 5,637,647 and 5,677,386 disclose the capping of a living
23 polymer with one or more capping compounds comprising non-polymerizable
24 monomer selected from a group consisting of substituted or unsubstituted
25 diphenyl alkylene, methoxystyrene, trans-stilbene, 1-isopropenylnaphthalene
26 and 2,4-dimethyl styrene.

1 U.S. Patent Application No. 10/433,439, Publication No. 2004/0015029 A1,
2 discloses a process for the preparation of polyisobutylenes in which at least
3 60 percent of the polymer chains have at least one olefinically unsaturated
4 terminal group, by cationic polymerization of isobutene or isobutene-
5 containing monomer mixtures in the condensed phase and in the presence of
6 an initiator system.

7 U.S. Patent Application Serial No. 10/600,898, Publication No. 2004/0260033
8 A1, discloses the method for manufacturing and producing monodisperse
9 telechelic polymers through cationic polymerization of suitable monomer
10 under living polymerization conditions and quenching the polymerization with
11 an N-substituted pyrrole. The functionalized polymers containing N-
12 substituted pyrroles may be employed as fuel additives and/or lubricating oil
13 additives.

14 PCT International Application No. PCT/EP/05472, International Publication
15 No. WO99/09074, discloses a process for functionalizing polymers prepared
16 by cationic polymerization wherein a living carbocationic polymerization
17 system is reacted with one or more aromatic ring systems, and the use of
18 substituted or unsubstituted reaction products of said process in lubricating oil
19 or fuel compositions and additive concentrates, for example as dispersants,
20 detergents or antioxidant additives or VI improvers.

21 β -Proton elimination by Free Bases in the Living cationic Polymerization of
22 Isobutylene, by Young Cheol Bae and Rudolf Faust, *Macromolecules*,
23 Volume 30, 7341-7344 (1997). The authors investigated β -proton elimination
24 from quasi-living polyisobutylene, after observing *exo*-olefin formation in the
25 presence of 2,6-di-*tert*-butylpyridine (DTBP) of low purity. They ascribed
26 elimination to the presence of a sterically hindered cyclic imine base present
27 in the DTBP in a concentration of 6×10^{-6} moles per liter. They simulated this
28 impurity using 2-*tert*-butylpyridine (TBP) and discovered that the latter, when
29 added to the reactor at the start of the polymerization (i.e., in the presence of

1 monomer) resulted in about 65 percent elimination after 3 hours of reaction
2 time to produce exclusively *exo*-olefin. When the extent of elimination had
3 reached 20 percent or higher, significant coupling was observed from both ^1H
4 NMR and GPC analyses. Bae and Faust clearly considered that elimination
5 by sterically hindered bases, such as TBP, was undesirable and should be
6 avoided. The first paragraph of the paper was summarized as follows:
7 "Finally, strong bases may also eliminate β -protons, which should be
8 avoided." Later, they refer to the cyclic imine base impurity in DTBP as "the
9 culprit." Finally, they summarized the entire paper by saying that the
10 elimination process should be avoided for polymer preparation purposes,
11 although it might facilitate the measurement of kinetic rate constants: "While
12 β -proton elimination should be avoided for the synthesis of well-defined
13 macromolecules, if diffusion control of this process can be shown, it may
14 provide a novel method of establishing the concentration of active centers,
15 from which absolute propagation rate constants could be calculated."

16 SUMMARY OF THE INVENTION

17 The present invention is directed to a method for the preparation of polyolefins
18 containing *exo*-olefin chain ends. The method involves quenching a cationic
19 quasi-living polyolefin polymer system with one or more hindered secondary
20 or tertiary amines. The method also involves use of Lewis acid and an
21 electron donor, or a common ion salt or its precursor to form the cationic
22 quasi-living polyolefin polymer to which is added the quenching agent to form
23 the polymer product.

24 More specifically, the present invention is directed to a method for preparing a
25 polyolefin containing one or more *exo*-olefinic end groups on the polymer
26 chain, comprising quenching a cationic quasi-living polyolefin polymer system
27 with one or more hindered secondary or tertiary amines containing only
28 carbon, hydrogen, and nitrogen atoms, provided the hindered secondary or
29 tertiary amines are not:

- 1 (a) Triethylamine;
- 2 (b) Tri-n-butylamine;
- 3 (c) Trihexylamine;
- 4 (d) Triisooctylamine;
- 5 (e) 2-phenylpyridine;
- 6 (f) 2,3-cyclododecapyridine;
- 7 (g) Di-p-tolylamine;
- 8 (h) Quinaldine; and
- 9 (i) 1-pyrrolidino-1-cyclopentene.

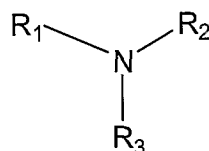
10 Preferably the quenching is carried out at a temperature in the range of from
11 about -130°C to about 10°C. More preferably the quenching is carried out at a
12 temperature of about -80°C to about 0°C, even more preferably the quenching
13 is carried out at a temperature of about -70°C to about -10°C, and most
14 preferably the quenching is carried out at a temperature in the range of from
15 about -60°C to about -20°C.

16 Preferably the polyolefin is polyisobutylene.

17 In a further embodiment of the present invention the polyolefin is prepared
18 in situ.

19 The hindered secondary or tertiary amine may be a linear secondary or
20 tertiary amine, a cyclic secondary or tertiary amine or an aromatic secondary
21 or tertiary amine.

22 In a preferred embodiment of the present invention the quenching agent is a
23 hindered secondary or tertiary amine having the general formula:

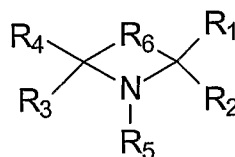


1

2 wherein R_1 , R_2 and R_3 are independently hydrogen, alkyl containing one
 3 carbon atom to about 20 carbon atoms, cycloalkyl of about 3 to about 7
 4 carbon atoms, aryl of about 6 to about 30 carbon atoms, alkaryl of about
 5 7 to about 30 carbon atoms, or aralkyl of about 7 to about 30 carbon
 6 atoms; or at least one of R_1 and R_2 , R_2 and R_3 and R_3 and R_1 , taken in
 7 pairs, independently form a fused aliphatic ring of from about 4 carbon
 8 atoms to about 8 carbon atoms;

9 provided that no more than one of R_1 , R_2 and R_3 is hydrogen, and
 10 provided that R_1 , R_2 , and R_3 are not all linear alkyl of about 3 carbons or
 11 less.

12 In the above method the hindered amine is a tertiary or secondary amine
 13 having the general formula:

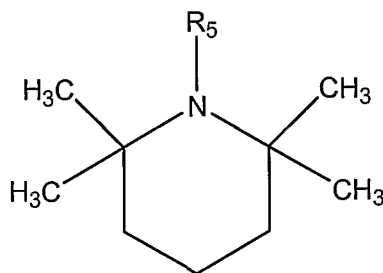


14

15 wherein R_6 is a divalent hydrocarbyl group of one carbon atom to about 4
 16 carbon atoms each of which may be substituted with an alkyl group
 17 having one carbon atom to about 6 carbon atoms, and R_1 , R_2 , R_3 , R_4 ,
 18 and R_5 are independently hydrogen, alkyl containing one carbon atom to
 19 about 20 carbon atoms, cycloalkyl of about 3 to about 8 carbon atoms,
 20 aryl of about 6 to about 30 carbon atoms, alkaryl of 7 to 30 carbon
 21 atoms, or aralkyl of 7 to 30 carbon atoms; provided if R_1 , R_2 , R_3 , and R_4
 22 are hydrogen, then R_5 is a branched alkyl from about 4 to about 20
 23 carbon atoms, aryl of about 6 to about 30 carbon atoms, or aralkyl of
 24 about 7 to about 30 carbon atoms, and provided if R_5 is hydrogen, then

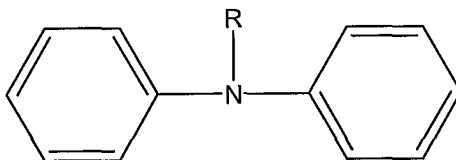
1 R_1 , R_2 , R_3 , and R_4 are not hydrogen, unless one of R_1 or R_2 and one of
2 R_3 or R_4 is a branched alkyl having from about 4 to about 20 carbon
3 atoms.

4 In a particularly preferred embodiment of the above method the hindered
5 amine is a secondary or tertiary amine of the formula:



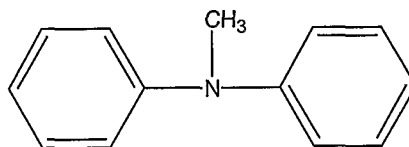
6
7 wherein R_5 is hydrogen or methyl.

8 In another preferred embodiment of the above method the hindered
9 secondary or tertiary amine has the general formula:

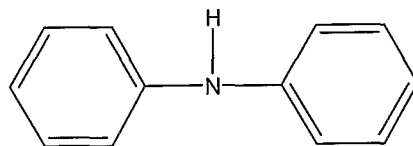


10
11 wherein R is hydrogen or alkyl containing one carbon atom to about 20
12 carbon atoms or an aromatic or an aliphatic ring having about 3 carbon
13 atoms to about 7 carbon atoms.

14 In a particularly preferred embodiment of the above method the hindered
15 amine is a tertiary amine of the formula:

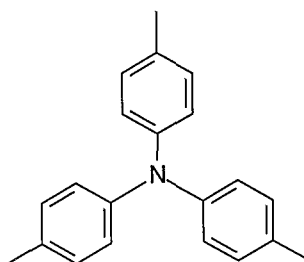


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17 In a further preferred embodiment of the above method the hindered amine is
18 a secondary amine of the formula:



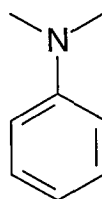
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- 2 In another preferred embodiment of the above method the hindered amine is
 3 a tertiary amine of the formula:



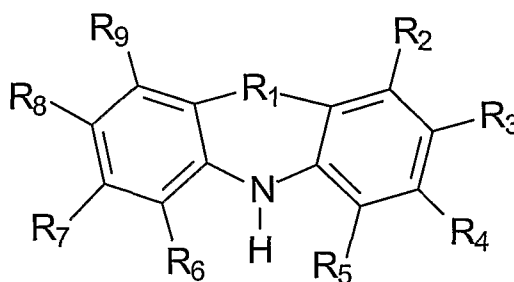
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- 5 In yet another preferred embodiment of the above method the hindered amine
 6 is a tertiary amine of the formula:



7

- 8
 9 The hindered secondary or tertiary amine in another embodiment of the
 10 method of the present invention has the general formula:



11

- 12 wherein R_1 is a divalent hydrocarbyl group of one carbon atom to about 4
 13 carbons and R_2 , R_3 , R_4 , R_7 , R_8 , and R_9 are independently hydrogen, alkyl
 14 containing one carbon atom to about 20 carbon atoms, cycloalkyl of

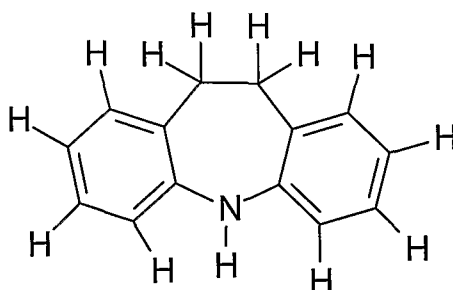
1 about 3 to about 8 carbon atoms, aryl of about 6 to about 30 carbon
 2 atoms, alkaryl of about 7 to about 30 carbon atoms, or aralkyl of about 7
 3 to about 30 carbon atoms, and one of R₅ and R₆ is hydrogen and the
 4 other is linear alkyl from one carbon atom to about 20 carbon atoms.

5

6 In a preferred embodiment of the above method where in one of R₅ and R₆ is
 7 hydrogen.

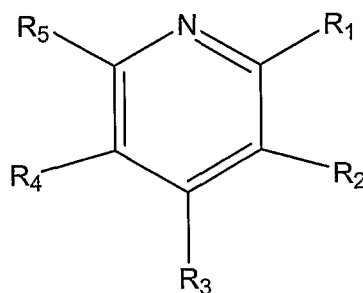
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9 In an embodiment of the above method the amine has the formula:



10

11 In yet another embodiment of the method of the present invention the
 12 hindered amine is a tertiary amine of the general formula:



13

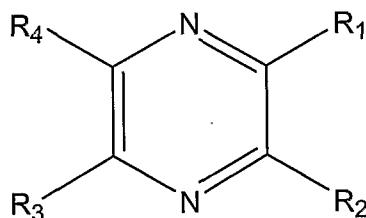
14 wherein one of R₁ and R₅ is hydrogen and the other is a branched alkyl
 15 of about 3 to about 20 carbon atoms, aryl of about 10 to about 30 carbon
 16 atoms, or aralkyl of about 11 to about 30 carbon atoms; R₂, R₃ and R₄
 17 are independently hydrogen, alkyl of one carbon atom to about 20
 18 carbon atoms, cycloalkyl of about 3 to about 7 carbon atoms, aryl of
 19 about 6 to about 30 carbon atoms, alkaryl of about 7 to about 30 carbon
 20 atoms, or aralkyl of about 7 to about 30 carbon atoms; or at least one of

1 R_1 and R_2 , R_2 and R_3 , R_3 and R_4 , and R_4 and R_5 , taken in pairs,
2 independently form a fused aromatic ring of from 5 carbon atoms to 7
3 carbon atoms or aliphatic ring of from about 4 carbon atoms to about 8
4 carbon atoms,

5 provided that if R_1 and R_2 form a fused aliphatic or aromatic ring, then R_5
6 is a branched alkyl of about 3 to about 20 carbon atoms, aryl of about
7 10 to about 30 carbon atoms, or aralkyl of about 11 to about 30 carbon
8 atoms, and provided that if R_4 and R_5 form a fused aliphatic or aromatic
9 ring, then R_1 is a branched alkyl of about 3 to about 20 carbon atoms,
10 aryl of about 10 to about 30 carbon atoms, or aralkyl of about 11 to about
11 30 carbon atoms.

12 In a further embodiment of the above method R_1 , R_2 , R_3 and R_4 are hydrogen
13 and R_5 is tert-butyl.

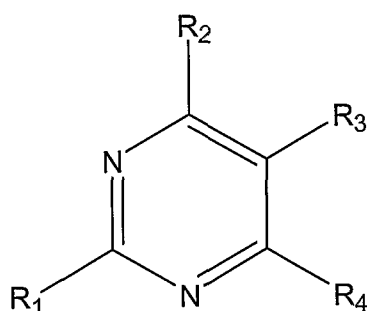
14 In another embodiment of the method of the present invention the hindered
15 amine is nitrogen containing hetero-aromatic ring having the following
16 formulas, (a), (b) and (c):



(a)

17
18 wherein in formula (a)
19 one of R_1 and R_4 is hydrogen and the other is alkyl of one carbon atom
20 to about 20 carbon atoms, cycloalkyl of about 3 to about 8 carbon atoms,
21 aryl of about 6 to about 30 carbon atoms, alkaryl of about 7 to about 30
22 carbon atoms, or aralkyl of about 7 to about 30 carbon atoms, one of R_2
23 and R_3 is hydrogen and the other is alkyl of one carbon atom to about 20
24 carbon atoms, cycloalkyl of about 3 to about 8 carbon atoms, aryl of

1 about 6 to about 30 carbon atoms, alkaryl of about 7 to about 30 carbon
2 atoms, or aralkyl of about 7 to about 30 carbon atoms; or at least one of
3 R_1 and R_2 and R_3 and R_4 , taken in pairs, independently form a fused
4 aromatic ring of from 5 carbon atoms to 7 carbon atoms or aliphatic ring
5 of from about 4 carbon atoms to about 8 carbon atoms;



(b)

6

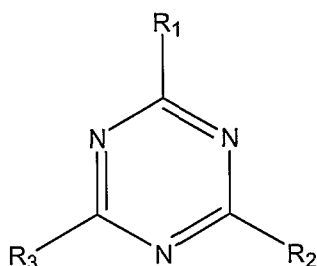
7 wherein in formula (b)

8 R_1 , R_2 and R_4 are independently hydrogen or alkyl of one carbon atom to
9 about 20 carbon atoms, cycloalkyl of about 3 to about 8 carbon atoms,
10 aryl of about 6 to about 30 carbon atoms, alkaryl of about 7 to about 30
11 carbon atoms, or aralkyl of about 7 to about 30 carbon atoms, R_3 is
12 hydrogen, alkyl of one carbon atom to about 20 carbon atoms, cycloalkyl
13 of about 3 to about 8 carbon atoms, aryl of about 6 to about 30 carbon
14 atoms, alkaryl of about 7 to about 30 carbon atoms, or aralkyl of about 7
15 to about 30 carbon atoms; or at least one of R_2 and R_3 or R_3 and R_4 ,
16 taken in pairs, independently form a fused aromatic ring of from 5 carbon
17 atoms to 7 carbon atoms or aliphatic ring of from about 4 carbon atoms
18 to about 8 carbon atoms,

19 provided that if R_1 is hydrogen then R_2 and R_4 are independently alkyl of
20 one carbon atom to about 20 carbon atoms, cycloalkyl of about 3 to
21 about 8 carbon atoms, aryl of about 6 to about 30 carbon atoms, alkaryl
22 of about 7 to about 30 carbon atoms, or aralkyl of about 7 to about
23 30 carbon atoms, and further provided that if R_2 or R_4 is hydrogen, then

1 R₁ is alkyl of one carbon atom to about 20 carbon atoms, cycloalkyl of
2 about 3 to about 8 carbon atoms, aryl of about 6 to about 30 carbon
3 atoms, alkaryl of about 7 to about 30 carbon atoms, or aralkyl of about
4 7 to about 30 carbon atoms;

5 and

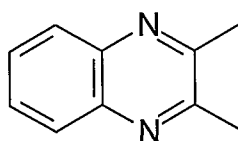


6 (c)

7 wherein in formula (c)

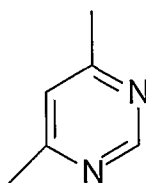
8 R₁, R₂ and R₃ are independently hydrogen or alkyl of one carbon to
9 about 20 carbon atoms, cycloalkyl of about 3 to about 8 carbon atoms,
10 aryl of about 6 to about 30 carbon atoms, alkaryl of about 7 to about
11 30 carbon atoms, or aralkyl of about 7 to about 30 carbon atoms.

12 In a preferred embodiment of the above method the hindered amine has the
13 formula:



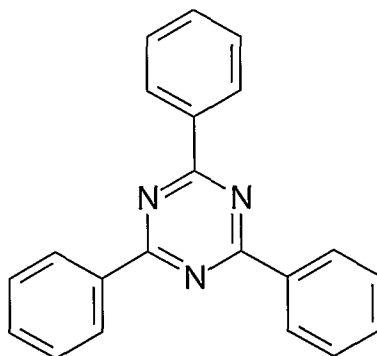
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15 In a further embodiment of the above method the hindered amine has the
16 formula:



17

- 1 In yet another preferred embodiment of the above method the hindered amine
2 has the formula:



- 3
- 4 In the method of the present invention the polyolefin is prepared by quenching
5 a quasi-living polyolefin polymer product containing terminal tert-chloride
6 chain ends or a mixture comprising terminal olefinic chain ends and terminal
7 tert-chloride chain ends with a hindered secondary or tertiary amine in the
8 presence of a Lewis acid.
- 9 In yet another embodiment of the present invention the polyolefin is prepared
10 by quenching a quasi-living polyolefin polymer product containing terminal
11 tert-chloride chain ends with a hindered secondary or tertiary amine in the
12 presence of a Lewis acid.
- 13 Preferably the Lewis acid is a halide of titanium or boron. More preferably the
14 Lewis acid is a titanium halide. Most preferably Lewis acid is titanium
15 tetrachloride. Preferably the concentration of the titanium tetrachloride
16 exceeds 2 times the combined concentrations of protic impurities, electron
17 donor, common ion salt or its precursor, and the quenching agent or
18 quenching agents.
- 19 The polyolefin product obtained using the method of the present invention has
20 exo-olefin chain ends in the range of one percent to 100 percent based on the
21 total chain ends. Preferably the polyolefin product has at least 3 percent exo-
22 olefin chain ends, more preferably at least 20 percent exo-olefin chain ends,
23 even more preferably at least 50 percent exo-olefin chain ends, still more

1 preferably at least 70 percent exo-olefin chain ends, and still more preferably
2 90 percent exo-olefin chain ends. Most preferably the polyolefin product has
3 at least 99 percent exo-olefin chain ends based on the total chain ends.

4 In the method of the present invention the quasi-living polyolefin polymer is
5 formed by contacting at least one cationically polymerizable monomer with an
6 initiator, in the presence of a Lewis acid under reaction conditions suitable for
7 quasi-living polymerization. Preferably the at least one cationically
8 polymerizable monomer comprises at least one of isobutylene, 2-methyl-1-
9 butene, 3-methyl-1-butene, 4-methyl-1-pentene, and beta-pinene. More
10 preferably the at least one cationically polymerizable monomer is isobutylene.

11 In the method of the present invention two or more different cationically
12 polymerizable monomers may be employed.

13 In the method of the present invention the initiator may be mono-functional or
14 multi-functional. Preferably the initiator is mono-functional or di-functional.
15 More preferably the initiator is mono-functional.

16 In the method of the present invention the mono-functional initiator comprises
17 at least one of 2-chloro-2-phenylpropane; 2-acetyl-2-phenylpropane; 2-
18 propionyl-2-phenylpropane, 2-methoxy-2-phenylpropane, 2-ethoxy-2-
19 phenylpropane, 2-chloro-2,4,4-trimethylpentane, 2-acetoxy-2,4,4,-
20 trimethylpentane, 2-propionoxy-2,4,4-trimethylpentane, 2-methoxy-2,4,4-
21 trimethylpentane, and 2-ethoxy-2,4,4-trimethylpentane.

22

23 In the method of the present invention the di-functional initiators include
24 1,3-di(2-chloro-2-propyl)-5-tert-butylbenzene,
25 1,4-di(2-chloro-2-propyl)benzene, 1,4-di(2-acetoxy-2-propyl)benzene,
26 1,3-di(2-acetoxy-2-propyl)-5-tert-butylbenzene,
27 1,3-di(2-methoxy-2-propyl)-5-tert-butylbenzene and
28 1,4-di(2-methoxy-2-propyl)benzene.

1 In the method of the present invention an example of a multi-functional
2 initiator is 1,3,5-tri(2-chloro-2-propyl)-benzene.

3 In the method of the present invention the molecular weight distribution,
4 M_w/M_n , of the polyolefin polymer is present in the range of about
5 1.01 to about 3.0. Preferably the molecular weight distribution, M_w/M_n , of the
6 polyolefin polymer is present in the range of about 1.1 to about 2.0. More
7 preferably the molecular weight distribution, M_w/M_n , of the polyolefin polymer
8 is less than 1.5.

9 The present invention is also directed to a further method for preparing a
10 polyolefin containing one or more exo-olefinic end groups on the polymer
11 chain, comprising quenching a cationic quasi-living polyolefin polymer system
12 with one or more hindered secondary or tertiary amines containing only
13 carbon, hydrogen and nitrogen atoms, wherein the hindered secondary or
14 tertiary amine compounds are pre-reacted with a Lewis acid, and provided the
15 hindered secondary or tertiary amines are not:

- 16 (a) Triethylamine;
- 17 (b) Tri-n-butylamine;
- 18 (c) Trihexylamine;
- 19 (d) Triisooctylamine;
- 20 (e) 2-phenylpyridine;
- 21 (f) 2,3-cyclododecapyridine;
- 22 (g) Di-p-tolylamine;
- 23 (h) Quinaldine; and
- 24 (i) 1-pyrrolidino-1-cyclopentene.

25 In a preferred embodiment of the above method the Lewis acid is titanium
26 tetrachloride.

1 In a yet more preferred embodiment of the above method the Lewis acid is
2 titanium tetrachloride and the hindered amine is 1,2,2,6,6-
3 pentamethylpiperidine.

4 In another preferred embodiment of the above method the Lewis acid is
5 titanium tetrachloride and the hindered amine is 2,2,6,6-tetramethylpiperidine.

6 DETAILED DESCRIPTION OF THE INVENTION

7 Definitions

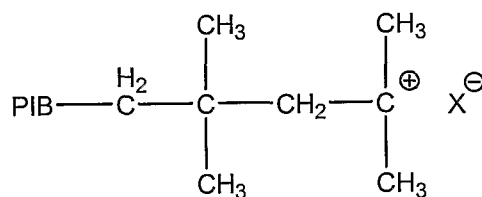
8 As used herein, the following terms have the following meanings unless
9 expressly stated to the contrary:

10 The term "alkyl" as used herein refers to straight chain and branched chain
11 saturated aliphatic groups typically having from one carbon atom to about 20
12 carbons atoms. Some examples of straight chain and branched chain
13 saturated aliphatic groups are methyl, ethyl, propyl, butyl, isopropyl, isobutyl,
14 sec-butyl, tert-butyl, and the like.

15 The term "aromatic or aliphatic fused ring" as used herein refers to the ring
16 formed by two adjacent carbon atoms on a ring and the formed ring is fused
17 to the ring.

18 The term "branched alkyl" as used herein refers to an alkyl group in which the
19 carbon atom representing the point of attachment of the group to the rest of
20 the molecule is either a tertiary or quaternary carbon atom. The term "tertiary
21 carbon" as used herein refers to a carbon atom that is attached to three other
22 carbon atoms. The term "quaternary carbon" as used herein refers to a
23 carbon atom that is attached to 4 other carbon atoms.

24 The terms "carbenium ion" or "carbocation" as used herein refer to a positively
25 charged carbon atom bearing three sp^2 -bonded substituents and an empty
26 p orbital.



PIB Carbenium Ion

1

2 The term "chain transfer" as used herein refers to the cessation of growth of
 3 one polymerization chain with the possible initiation of another polymerization
 4 chain.

5 The term "common ion salt" as used herein refers to an ionic salt that is
 6 optionally added to a quasi-living cationic polymerization mixture to prevent
 7 dissociation of the propagating carbenium ion and counter-ion pairs. The
 8 anion of the common ion salt is identical to the counter-ions of the
 9 propagating chain ends. The cation of the common ion salt is typically a fatty
 10 quaternary ammonium cation, such as tetra-n-butyl ammonium ion, which
 11 confers solubility in the organic media.

12 The term "common ion salt precursor" as used herein refers to an ionic salt,
 13 optionally added to a quasi-living cationic polymerization mixture, which
 14 generates counter-anions that are identical to those of the propagating chain
 15 ends, via in situ reaction with the Lewis acid. An example is
 16 tetra-n-butylammonium chloride.

17 The term "controlled molecular weight distribution" as used herein refers to
 18 polyolefin polymers having a desired molecular weight distribution. The
 19 molecular weight distribution or polydispersity index (PDI) herein is calculated
 20 by dividing the average molecular weight of the polymer chains by the number
 21 average molecular weight, M_w/M_n .

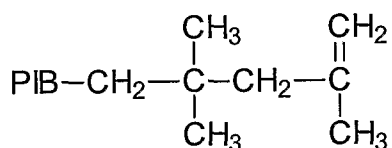
22 The term "coupled product" as used herein refers to the product of addition of
 23 a PIB terminal carbenium ion to a PIB exo-olefin chain end. Coupled product
 24 has a number average molecular weight that is approximately twice that of the
 25 main polymer product.

1 The term "coupling" as used herein refers to the addition of a polyisobutylene
2 terminal carbenium ion to a polyisobutylene exo-olefin chain end.

3 The term "conventional polymerization" as used herein refers to
4 polymerization wherein the chain-reaction polymerization involving olefins
5 proceeds with ions as chain carrying particles, either anions or cations.
6 Polymerization proceeds through the steps of chain initiation, chain
7 propogation, chain transfer and chain termination.

8 The term "di-EAS product" as used herein refers to the product which results
9 when two separate polyisobutylene terminal carbenium ions react to form a
10 covalent bond with a single quenching agent molecule. Di-EAS product
11 contains in its structure a residue from the quenching agent.

12 The terms "di-substituted olefin" or "exo-olefin" or "methyl vinylidene" as used
13 herein refer to an olefin polymer chain containing an exo-olefin chain end as
14 shown below.



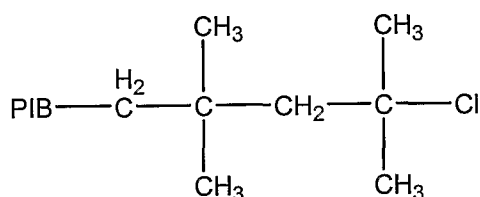
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16 The term "di-valent hydrocarbyl" as used herein refers to a hydrocarbyl group
17 which possesses two points of attachment to the rest of the molecule.

18 The term "EAS product" as used herein refers to the product which results
19 when one polyisobutylene terminal carbenium ion reacts to form a covalent
20 bond with a single quenching agent molecule. EAS product contains in its
21 structure a residue from the quenching agent.

22 The term "electron donor" as used herein refers to a basic and/or nucleophilic
23 substance added to the polymerization reaction that is either fully complexed
24 with the Lewis acid or fully non-complexed with the Lewis acid. The

- 1 concentration of electron donor exceeds the concentration of the protic
2 impurities, for example water.
- 3 The term "electrophilic aromatic substitution or EAS" as used herein refers to
4 the process by which the EAS product is produced.
- 5 The term "gem-dimethyl carbons" as used herein refers to the two methyl
6 carbons alpha to the carbenium ion or the chloride bonded carbon of the
7 polyolefin polymer chain end as depicted in the structure below.



PIB tert-Chloride

- 8
- 9 The term "hydrocarbyl" refers to an organic radical primarily composed of
10 carbon and hydrogen which may be aliphatic, alicyclic, aromatic or
11 combinations thereof, e.g., aralkyl or alkaryl. Such hydrocarbyl groups may
12 also contain aliphatic unsaturation, i.e., olefinic or acetylenic unsaturation, and
13 may contain minor amounts of heteroatoms, such as oxygen or nitrogen, or
14 halogens, such as chlorine.
- 15 The term "initiator" as used herein refers to the chemical moiety that starts the
16 polymerization and satisfies the valence at the head of the polymer chain, or
17 the molecule that provides that moiety. When a mono-functional initiator is
18 used, the chain end (CE) concentration equals the initiator concentration. For
19 a multi-functional initiator, when the functionality of the initiator equals x, then
20 the chain end concentration equals x times initiator concentration.
- 21 The term "hindered secondary or tertiary amine " as used herein refers to a
22 compound that is appropriately substituted such that it is sufficiently sterically
23 hindered to be not fully complexed with the Lewis acid, yet sufficiently

1 sterically hindered to allow its reaction with the carbenium ion. Preferably the
2 hindered amine is a tertiary amine.

3 The term "Lewis acid" as used herein refers to a compound that can accept a
4 pair of electrons to form a covalent bond.

5 The term "living polymerization" as used herein refers to the polymerizations
6 that proceed in the absence of measurable chain transfer and chain
7 termination.

8 The term "quasi-living polymerization" as used herein refers to living
9 polymerizations wherein reversible chain terminations is operable, but
10 irreversible chain termination and chain transfer approaches zero.

11 The term "quenching agent" as used herein refers to a chemical compound
12 which is added to the polymerization reactions to react with the growing chain
13 end.

14 The term "polyolefin" as used herein refers to a polymer produced by the
15 addition polymerization of one or more olefins, such as ethylene, propylene,
16 styrene, isobutylene, etc.

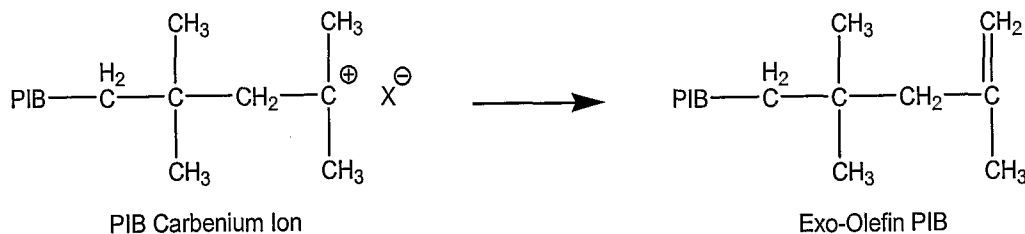
17 The term "protic impurity" as used herein refers to impurities within the
18 polymerization reaction mixture that contain acidic hydrogen atoms in their
19 structure, for example, water.

20 The term "regiospecific" as used herein refers to chemical reactions that give
21 exclusively or nearly exclusively one of several possible isomeric products.

22 The term "termination" as used herein refers to the chemical reaction that
23 terminates polymerization process or the quenching reaction by destruction of
24 the Lewis acid.

25 The term "terminator" as used herein refers to the chemical compound that
26 terminates polymerization process or the quenching reaction, but may not

- 1 simultaneously initiate a new polymer chain. A number of alcohols may be
 2 used as terminators.
- 3 The term "tert-chloride" refers to the 2-chloro-2-methylpropyl end group on a
 4 polyolefin polymer chain.
- 5 Unless otherwise specified, all percentages are in weight percent.
- 6 It has been determined that sufficiently hindered secondary or tertiary amines,
 7 such as 1,2,2,6,6-pentamethyl piperidine and N-methyldiphenylamine, used
 8 as quenching agents in the preparation of polyolefin polymers of the present
 9 invention are capable of quantitatively converting polyolefin polymer endo-
 10 olefin chain ends and tert-chloride chain ends to the exo-olefin chain ends.
 11 Without being bound by any theory it is believed that these quenching agents
 12 selectively catalyze the elimination of a proton exclusively from the gem-
 13 dimethyl carbon of the polyisobutylene chain end as shown below.



14

- 15 The quenching agents used in the present invention are able to quantitatively
 16 convert polyolefin polymer containing endo-olefin chain ends and tert-chloride
 17 chain ends to the exo-olefin chain ends independently of whether a
 18 mono-functional initiator is used or a multi-functional. Furthermore, the rate of
 19 conversion is the same for mono-functional and di-functional initiators. A 100
 20 percent conversion was observed within 15 minutes after addition of the
 21 mono-functional initiator, 2-chloro-2,4,4-trimethyl pentane.

1 General Procedure for Preparation of Polyolefin Polymers
2 Containing a High Percentage of Exo-olefin
3 End Groups on the Chain

4 A typical procedure for the preparation of polyolefin polymers of the present
5 invention is given below:

6 The method of the present invention may be conducted as a batch process, a
7 continuous process, a semi-batch process or by any process known by
8 persons skilled in the art.

9 The polymerization reaction is carried out under inert gas and in a
10 substantially anhydrous environment. The reactor is charged with the
11 following reactants:

- 12 1. a diluent,
- 13 2. an initiator,
- 14 3. an electron donor or common ion salt or its precursor,
- 15 4. one or more monomers, and
- 16 5. a Lewis acid, which typically comprises a halide of titanium or boron;

17 The reaction mixture is equilibrated at the desired temperature, ranging from
18 above -130°C to about 10°C. The method of the present invention may be
19 carried out at any desired pressure, atmospheric, sub-atmospheric or
20 super-atmospheric pressure.

21 The progress of the polymerization reaction is monitored in situ by
22 determination of the amount of monomer remaining in the reaction mixture.
23 After high conversion of the monomer is observed, an aliquot is removed for
24 determination of the pre-quench chain end composition before addition of the
25 quenching agent. The polymerization reaction in the aliquot is terminated with
26 an appropriate alcohol equilibrated at the desired temperature.

1 6. A hindered secondary or tertiary amine is added to the reaction mixture
2 to quench the polymerization reaction.

3 Although, the concentration of the reactants may be varied to obtain the
4 desired product, it has been found that certain ratios of the reactants are
5 important for obtaining high exo-olefin chain end yield. The ratios are
6 described below:

7 The molar ratio of monomer to initiator is in the range from about 3:1 to about
8 20,000:1. Preferably the molar ratio of monomer to initiator is in the range of
9 about 5:1 to about 2,000:1. More preferably the molar ratio of monomer to
10 initiator is about 10:1 to 150:1. The mole ratio of monomer to initiator controls
11 the final molecular weight of the polyolefin.

12 The molar ratio of Lewis acid to chain ends is in the range from about
13 0.1:1 to about 2,500:1. Preferably the molar ratio of Lewis acid to chain ends
14 is in the range of about 2:1 to about 200:1. More preferably the molar ratio of
15 Lewis acid to chain ends is about 2:1 to 15:1.

16 The molar ratio of Lewis acid to electron donor is in the range from about
17 1.1:1 to about 10,000:1. Preferably the molar ratio of Lewis acid to electron
18 donor is in the range of about 2:1 to about 100:1. More preferably the molar
19 ratio of Lewis acid to electron donor is about 4:1 to 30:1.

20 The molar ratio of Lewis acid to quenching agent is in the range from about
21 1.1:1 to about 2,500:1. Preferably the molar ratio of Lewis acid to quenching
22 agent is in the range of about 2:1 to about 100:1. More preferably the molar
23 ratio of Lewis acid to quenching agent is about 2:1 to 15:1.

24 The molar ratio of quenching agent to chain ends is in the range from about
25 0.25:1 to about 20:1. Preferably the molar ratio of quenching agent to chain
26 end is in the range of about 0.5:1 to about 5:1. More preferably the molar
27 ratio of quenching agent to chain end is about 0.5:1 to 4:1.

1 Additional aliquots are removed from the reaction mixture at various time
2 intervals after addition of the quenching agent to determine the concentration
3 of the exo-olefin chain ends on the polyolefin polymers. The polymerization
4 reaction is terminated in all the aliquot samples and the remaining reaction
5 mixture with an appropriate alcohol equilibrated at the desired temperature.

6 The concentration of the exo-olefin chain ends, along with the concentration
7 of the endo-olefin and tert-chloride chain ends, is quantified using ^1H NMR.
8 GPC spectra are also obtained to qualitatively determine the amount of
9 coupled product.

10 Compounds suitable for use in the preparation of the polyolefin polymers of
11 the present invention are given below:

12 Diluents

13 Diluents influence the ionization equilibria and rates of exchange of growing
14 species through their polarity, which can be estimated from their dielectric
15 constants. Typically, solvents having low dielectric constants are preferred
16 since ion pairs are less dissociated. Suitable solvents include, but are not
17 limited to, low-boiling alkanes and alkyl mono or polyhalides with reasonably
18 low freezing points to be used at the preferred polymerization temperature.
19 Illustrative solvents include alkanes (generally C_2 to C_{10} alkanes, including
20 normal alkanes such as propane, normal butane, normal pentane, normal
21 hexane, normal heptane, normal octane, normal nonane and normal decane,
22 and branched alkanes including isobutane, isopentane, isohexane,
23 3-methylpentane, 2,2-dimethylbutane, 2,3-dimethylbutane and the like),
24 alkenes and alkenyl halides (such as vinyl chloride), carbon disulfide,
25 chloroform, ethylchloride, N-butyl chloride, methylene chloride, methyl
26 chloride, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, sulfur dioxide, acetic
27 anhydride, carbon tetrachloride, acetonitrile, neopentane, benzene, toluene,
28 methylcyclohexane, chlorobenzene, 1,1-dichloroethane, 1,1-dichloroethene,
29 1,2-dichloroethene, n-propyl chloride, iso-propyl chloride,

1 1,2-dichloropropane, or 1,3-dichloropropane, nitro-alkanes (such as
2 nitropropane) to name a few of the representative liquid diluents or solvents
3 useful in cationic polymerizations. Mixed solvents (for example combinations
4 of those listed above) can also be used.

5 Initiators

6 Initiator compounds for living and quasi-living carbocationic polymerization are
7 well known in the art. Initiators may be mono-functional or multi-functional
8 depending on the desired product. Mono-functional and di-functional initiators
9 are employed when the desired polymer is to be linear. For making star
10 polymers the initiator should have more than two reactive moieties. The
11 contemplated initiator compounds can be represented by the general formula
12 $(X'-CR_aR_b)_nR_c$ wherein R_a , R_b and R_c are independently comprises at least
13 one of alkyl, aromatic, alkyl aromatic groups, and can be the same or
14 different, and X' is an acetate, etherate, hydroxyl group, or a halogen. R_c has
15 a valance of n , and n is an integer of one to 4. Preferably R_a , R_b , and R_c are
16 hydrocarbon groups containing one carbon atom to about 20 carbon atoms,
17 preferably one carbon atom to about 8 carbons atoms. Preferably X' is a
18 halogen and more preferably chloride. In some instances it is preferable to
19 select the structure of R_a , R_b and R_c to mimic the growing species or
20 monomer, e.g. a 1-phenylethyl derivative for polystyrene or 2,4,4-trimethyl
21 pentyl derivative for polyisobutene. Suitable compounds, include for example,
22 cumyl, dicumyl and tricumyl halides, particularly the chlorides, i.e., 2-chloro-2-
23 phenylpropane, i.e., cumyl chloride; 1,4-di(2-chloro-2-propyl)benzene, i.e.,
24 di(cumylchloride); 1,3,5-tri(2-chloro-2-propyl)benzene, i.e., tri(cumylchloride);
25 2,4,4-trimethyl-2-chloropentane; 2-acetoxy-2-phenylpropane, i.e., cumyl
26 acetate; 2-propionoxy-2-phenyl propane, i.e., cumyl propionate;
27 2-methoxy-2-phenylpropane, i.e., cumylmethyl ether;
28 1,4-di(2-methoxy-2-propyl)benzene, i.e., di(cumylmethyl ether);
29 1,3,5-tri(2-methoxy-2-propyl)benzene, i.e., tri(cumylmethyl ether), and similar
30 compounds. Other suitable examples can be found in U.S. Patent

1 No. 4,946,899. Particularly preferred examples are 2-chloro-2,4,4-trimethyl
2 pentane (TMPCl), 1,3,5 tri(2-chloro-2-propyl)benzene, and
3 1,3-di(2-chloro-2-propyl)-5-tert-butylbenzene (bDCC),
4 1,3-di(2-acetoxy-2-propyl)-5-tert-butylbenzene,
5 1,3-di(2-methoxy-2-propyl)-5-tert-butylbenzene and
6 1,4-di(2-methoxy-2-propyl)benzene.

7 The concentration of the chain ends in the total reaction mixture may be in the
8 range from about 0.0001 moles per liter to about 2.0 moles per liter.
9 Preferably the concentration of the chain ends is in the range from about
10 0.001 moles per liter to about 1.0 moles per liter. More preferably the
11 concentration of the chain ends is in the range from about 0.005 moles
12 per liter to about 0.5 moles per liter.

13 Electron Donors

14 Electron Donors have been shown to convert traditional polymerization
15 systems into living and/or quasi-living cationic polymerizations systems. The
16 electron donor used in the present invention is not specifically limited to any
17 particular compound or class of compounds. Examples include pyridines and
18 alkyl amines, aprotic amides, sulfoxides, esters, metal compounds having an
19 oxygen atom bonded to a metal atom, and others. Pyridine compounds
20 include 2,6-di-*tert*-butylpyridine, 2,6-dimethylpyridine, 2,4-dimethylpyridine,
21 2,4,6-trimethylpyridine, 2-methylpyridine and pyridine. N,N-dimethylaniline
22 and N,N-dimethyltoluidine may also be employed. Amide compounds include
23 N,N-dimethylformamide, N,N-dimethylacetamide and N,N-diethylacetamide.
24 An example of a sulfoxide compound is dimethyl sulfoxide. Diethyl ether is an
25 example of an ether compound, and methyl acetate and ethyl acetate are
26 examples of ester compounds. Phosphate compounds such as trimethyl
27 phosphate, tributyl phosphate, triamide hexamethylphosphate may also be
28 employed. Oxygen-containing metal compounds such as tetraisopropyl
29 titanate are also useful as electron donors.

1 The concentration of the electron donors in the total reaction mixture may be
2 in the range from about 0.001 moles per liter to about 0.1 moles per liter.
3 Preferably the concentration of the electron donors is in the range from about
4 0.001 moles per liter to about 0.05 moles per liter. More preferably the
5 concentration of the electron donors is in the range from about
6 0.002 moles per liter to about 0.02 moles per liter.

7 Common Ion Salts and Common Ion Salt Precursors

8 Common ion salts or salt precursors may be optionally added to the reaction
9 mixture in addition to or replacement of the electron donor. Typically, these
10 salts are used to increase the ionic strength, suppress free ions, and
11 beneficially interact with ligand exchange. Particularly preferred are common
12 ion salt precursors, for example tetra-n-butylammonium chloride ($n\text{-Bu}_4\text{NCl}$).

13 The concentration of the common ion salts or salt precursors in the total
14 reaction mixture may be in the range from about 0.0005 moles per liter to
15 about 0.05 moles per liter. Preferably the concentration of the common ion
16 salts or salt precursors is in the range from about 0.0005 moles per liter to
17 about 0.025 moles per liter. More preferably the concentration of the common
18 ion salt or salt precursors is in the range from about 0.001 moles per liter to
19 about 0.007 moles per liter.

20 Monomers

21 Suitable monomers for use in the method of the present invention are
22 hydrocarbon monomers, i.e., compounds containing only hydrogen and
23 carbon atoms, especially olefins and diolefins, and normally those having from
24 2 to about 20 carbon atoms, but preferably from about 4 to about 8 carbon
25 atoms. The process can be employed for the polymerization of such
26 monomers to produce polymers of different, but uniform molecular weights,
27 for example, from about 300 to in excess of a million g/mol. Such polymers
28 can be low molecular weight liquid or viscous polymers having a molecular
29 weight of from about 200 to 10,000 g/mol, or solid waxy to plastic, or

1 elastomeric materials having molecular weights of from about a 100,000 to
2 1,000,000 g/mol, or more. Suitable monomers include such compounds as
3 isobutylene, styrene, beta pinene, isoprene, butadiene, substituted
4 compounds of the preceding types, and others. Particularly preferred
5 monomers are isobutylene, 2-methyl-butene, 3-methyl-1-butene, 4-methyl-1-
6 pentene, and beta-pinene. An even more preferred monomer is isobutylene.
7 Mixtures of monomers may be used.

8 The concentration of the monomers in the total reaction mixture may be in the
9 range from about 0.01 moles per liter to about 5.0 moles per liter. Preferably
10 the concentration of the monomers is in the range from about
11 0.1 moles per liter to about 2.0 moles per liter. More preferably the
12 concentration of the monomers is in the range from about 0.3 moles per liter
13 to about 1.0 mole per liter. Most preferably the concentration of the
14 monomers is 0.5 moles per liter.

15 Lewis Acids

16 Lewis acids that are suitable as catalysts for purposes of the invention
17 include, but are not limited to, titanium and boron halides, particularly titanium
18 tetrachloride and boron trichloride. Use of the titanium halides and particularly
19 titanium tetrachloride is preferred. The strength of the Lewis acid and its
20 concentration should be adjusted for the particular monomer. Additionally, the
21 strength of these Lewis acids can be adjusted using nucleophilic additives. In
22 some instances these Lewis acids are also referred to as co-initiators.

23

24 The amount of the Lewis acid present in the initiator system may vary.
25 However, it is desirable that the concentration of Lewis acid is sufficient to
26 achieve an appropriate rate of polymerization and quenching. The Lewis acid
27 concentration should not be so high as to precipitate the formed polymer.

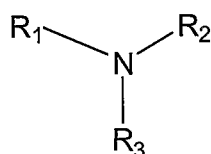
28 The concentration of the Lewis acid in the total reaction mixture may be in the
29 range from about 0.001 moles per liter to about 3.0 moles per liter. Preferably

1 the concentration of the Lewis acid is in the range from about 0.005 moles
2 per liter to about 1.5 moles per liter. More preferably the concentration of the
3 Lewis acid is in the range from about 0.05 moles per liter to about
4 1.0 mole per liter.

5 Quenching agents

6 Quenching agents contemplated for use in preparation of the polyolefin in the
7 present invention are hindered secondary or tertiary amine compounds, such
8 as 2-tertbutyl pyridine, n-tributylamine, 1,2,2,6,6-pentamethyl piperidine and
9 N-methyldiphenylamine.

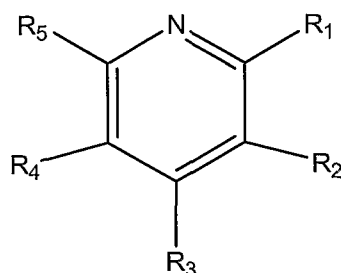
10 The hindered secondary or tertiary amine employed as a quenching agent in
11 the present invention has the general formula:



12
13 wherein R_1 , R_2 and R_3 are independently hydrogen, alkyl containing one
14 carbon atom to about 20 carbon atoms, cycloalkyl of about 3 to about 7
15 carbon atoms, aryl of about 6 to about 30 carbon atoms, alkaryl of about
16 7 to about 30 carbon atoms, or aralkyl of about 7 to about 30 carbon
17 atoms; or at least one of R_1 and R_2 , R_2 and R_3 and R_3 and R_1 , taken in
18 pairs, independently form a fused aliphatic ring of from about 4 carbon
19 atoms to about 8 carbon atoms;

20 provided that no more than one of R_1 , R_2 and R_3 is hydrogen, and
21 provided that R_1 , R_2 , and R_3 are not all linear alkyl of about 3 carbons or
22 less.

23 In a preferred embodiment of the above method the hindered secondary or
24 tertiary amine has the general formula:



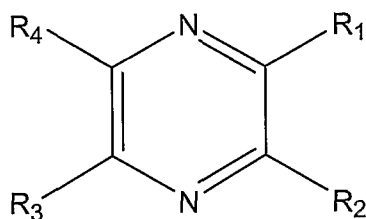
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2 wherein one of R_1 and R_5 is hydrogen and the other is a branched alkyl
 3 of about 3 to about 20 carbon atoms, aryl of about 10 to about 30 carbon
 4 atoms, or aralkyl of about 11 to about 30 carbon atoms; R_2 , R_3 and R_4
 5 are independently hydrogen, alkyl of one carbon atom to about 20
 6 carbon atoms, cycloalkyl of about 3 to about 7 carbon atoms, aryl of
 7 about 6 to about 30 carbon atoms, alkaryl of about 7 to about 30 carbon
 8 atoms, or aralkyl of about 7 to about 30 carbon atoms; or at least one of
 9 R_1 and R_2 , R_2 and R_3 , R_3 and R_4 , and R_4 and R_5 , taken in pairs,
 10 independently form a fused aromatic ring of from 5 carbon atoms to 7
 11 carbon atoms or aliphatic ring of from about 4 carbon atoms to about 8
 12 carbon atoms,

13 provided that if R_1 and R_2 form a fused aliphatic or aromatic ring, then R_5
 14 is a branched alkyl of about 3 to about 20 carbon atoms, aryl of about
 15 10 to about 30 carbon atoms, or aralkyl of about 11 to about 30 carbon
 16 atoms, and provided that if R_4 and R_5 form a fused aliphatic or aromatic
 17 ring, then R_1 is a branched alkyl of about 3 to about 20 carbon atoms,
 18 aryl of about 10 to about 30 carbon atoms, or aralkyl of about 11 to about
 19 30 carbon atoms.

20 In a preferred embodiment in the above method R_1 is hydrogen and R_5 is tert-
 21 butyl and R_2 , R_3 and R_4 are hydrogen.

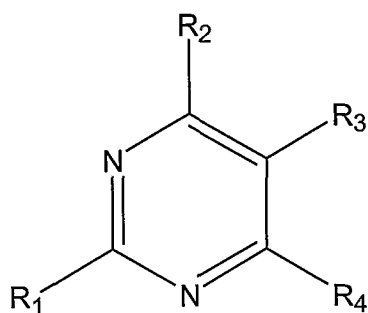
22 The hindered amine employed in the method of the present invention may be
 23 a nitrogen containing hetero-aromatic ring having the following formulas, (a),
 24 (b) and (c):



(a)

wherein in formula (a)

one of R₁ and R₄ is hydrogen and the other is alkyl of one carbon atom to about 20 carbon atoms, cycloalkyl of about 3 to about 8 carbon atoms, aryl of about 6 to about 30 carbon atoms, alkaryl of about 7 to about 30 carbon atoms, or aralkyl of about 7 to about 30 carbon atoms, one of R₂ and R₃ is hydrogen and the other is alkyl of one carbon atom to about 20 carbon atoms, cycloalkyl of about 3 to about 8 carbon atoms, aryl of about 6 to about 30 carbon atoms, alkaryl of about 7 to about 30 carbon atoms, or aralkyl of about 7 to about 30 carbon atoms; or at least one of R₁ and R₂ and R₃ and R₄, taken in pairs, independently form a fused aromatic ring of from 5 carbon atoms to 7 carbon atoms or aliphatic ring of from about 4 carbon atoms to about 8 carbon atoms;



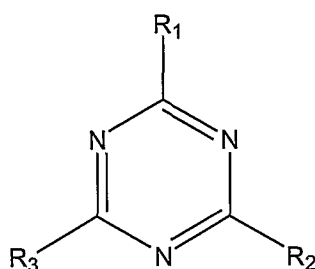
(b)

wherein in formula (b)

1 R₁, R₂ and R₄ are independently hydrogen or alkyl of one carbon atom to
2 about 20 carbon atoms, cycloalkyl of about 3 to about 8 carbon atoms,
3 aryl of about 6 to about 30 carbon atoms, alkaryl of about 7 to about 30
4 carbon atoms, or aralkyl of about 7 to about 30 carbon atoms, R₃ is
5 hydrogen, alkyl of one carbon atom to about 20 carbon atoms, cycloalkyl
6 of about 3 to about 8 carbon atoms, aryl of about 6 to about 30 carbon
7 atoms, alkaryl of about 7 to about 30 carbon atoms, or aralkyl of about 7
8 to about 30 carbon atoms; or at least one of R₂ and R₃ or R₃ and R₄,
9 taken in pairs, independently form a fused aromatic ring of from 5 carbon
10 atoms to 7 carbon atoms or aliphatic ring of from about 4 carbon atoms
11 to about 8 carbon atoms,

12 provided that if R₁ is hydrogen then R₂ and R₄ are independently alkyl of
13 one carbon atom to about 20 carbon atoms, cycloalkyl of about 3 to
14 about 8 carbon atoms, aryl of about 6 to about 30 carbon atoms, alkaryl
15 of about 7 to about 30 carbon atoms, or aralkyl of about 7 to about
16 30 carbon atoms, and further provided that if R₂ or R₄ is hydrogen, then
17 R₁ is alkyl of one carbon atom to about 20 carbon atoms, cycloalkyl of
18 about 3 to about 8 carbon atoms, aryl of about 6 to about 30 carbon
19 atoms, alkaryl of about 7 to about 30 carbon atoms, or aralkyl of about
20 7 to about 30 carbon atoms;

21 and



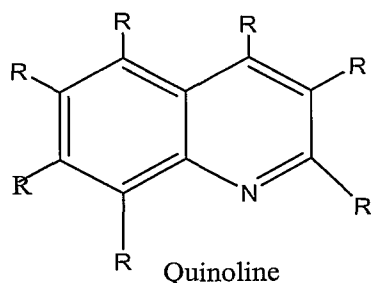
(c)

22 wherein in formula (c)

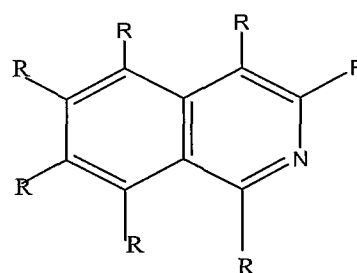
23 R₁, R₂ and R₃ are independently hydrogen or alkyl of one carbon to
24

about 20 carbon atoms, cycloalkyl of about 3 to about 8 carbon atoms,
aryl of about 6 to about 30 carbon atoms, alkaryl of about 7 to about
30 carbon atoms, or aralkyl of about 7 to about 30 carbon atoms.

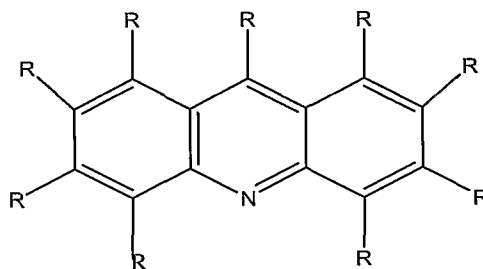
5 Structures of other hindered secondary or tertiary amines that may be
6 employed in the method of the present invention are given below. The given
7 structures are only intended as examples and in no way limit the scope of the
8 present invention.



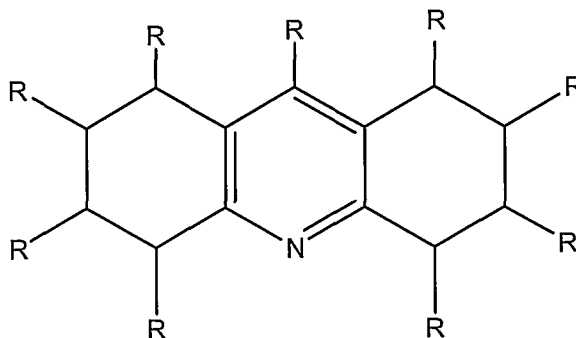
Quinoline



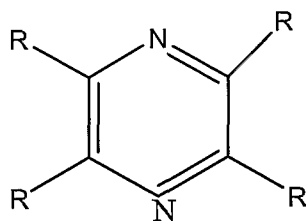
Isoquinoline



Acridine

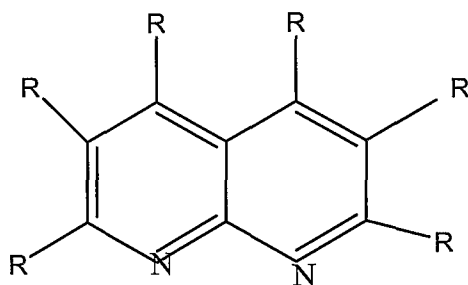


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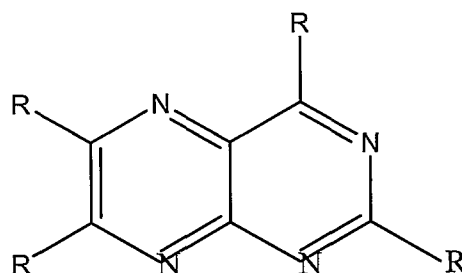
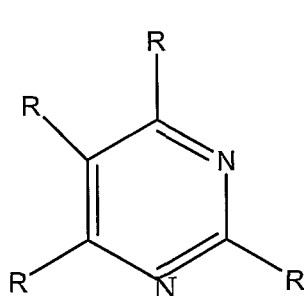


2

Pyrazine



3



4

Pyrimidine

Pteridine

5 Structures of other hindered secondary or tertiary that may be employed in
6 the method of the present invention may be obtained by substitution of the
7 nitrogen atoms with phosphorus atoms. The given structures are only
8 intended as examples and in no way limit the scope of the present invention.

9 The concentration of the quenching agent in the total reaction mixture may be
10 in the range from about 0.0001 moles per liter to about 2.0 moles per liter.
11 Preferably the concentration of the quenching agent is in the range from about
12 0.001 moles per liter to about 1.0 moles per liter. More preferably the

1 concentration of the quenching agent is in the range from about
2 0.005 moles per liter to about 0.5 moles per liter.

3 Terminators

4 Any soluble alcohol may be used to terminate the polymerization reaction in
5 the present invention. Preferred are mono-alcohols containing from about
6 one carbon atom to about 8 carbon atoms.

7 EXAMPLES

8 Example 1

9 Preparation of Polyisobutylene Using a Mono-functional 10 Initiator and 1,2,2,6,6-pentamethyl piperidine

11 A four-neck 250 milliliter round-bottom flask, equipped with an overhead
12 mechanical stirrer and platinum resistance thermometer, was fitted to the end
13 of a ATR-FTIR probe which is connected an FTIR spectrometer via a light
14 conduit as described in R. F. Storey; Q. A. Thomas, Macromolecules, 2003,
15 36, 5065-5071. This assembly was immersed into a heptane bath at -60°C
16 under dry nitrogen gas in a substantially inert atmosphere MBraun glovebox.
17 An air background spectrum was acquired and subtracted from all
18 subsequently collected spectra. The flask was then charged with the
19 following reactants:

20 113 milliliters hexane equilibrated at -60°C,

21 75.7 milliliters methylchloride equilibrated at -60°C,

22 0.477 milliliters 2-chloro-2,4,4-trimethylpentane equilibrated at room
23 temperature,

24 0.233 milliliters 2,6-dimethylpyridine equilibrated at room temperature.

1 The contents of the round-bottom flask were equilibrated and
2 Fourier Transform Infrared spectroscopy (FTIR) data were continuously
3 acquired for roughly 10 minutes to establish a reference absorbance at 887
4 cm^{-1} prior to addition of 8.2 milliliters isobutylene equilibrated at -60°C .

5 With continued stirring, next 1.82 milliliters titanium tetrachloride was charged
6 to the flask. The reaction was allowed to proceed to high conversion,
7 approximately 95 percent as determined by in situ Fourier Transform Infrared
8 spectroscopy monitoring of the 887 cm^{-1} peak of isobutylene. The procedure
9 used for the Fourier Transform Infrared spectroscopy monitoring is given
10 below. A pre-quench aliquot, approximately 5-10 milliliter, was removed from
11 the flask using a glass pipette and charged into a scintillation vial containing
12 4 milliliters anhydrous methanol equilibrated at -60°C to terminate the
13 polymerization reaction. The aliquot was used to determine a baseline for the
14 quenching reaction with the 1,2,2,6,6-pentamethyl piperidine and to provide a
15 reference for structural and molecular weight characterization in the absence
16 of quenching agent.

17 The polymerization reaction in the round-bottom flask was quenched by the
18 addition of 0.71 milliliters 1,2,2,6,6-pentamethyl piperidine at an isobutylene
19 conversion of 99 percent. Post-quench aliquots, approximately 5-10 milliliters,
20 were terminated at various time intervals after the addition of the
21 1,2,2,6,6-pentamethyl piperidine by being placed in scintillation vials
22 containing 4 milliliters anhydrous methanol equilibrated at -60°C .

23 The round-bottom flask was next charged with an appropriate amount
24 methanol equilibrated at -60°C to terminate the remaining polymerization
25 reaction mixture at 90 minutes after the addition of 1,2,2,6,6-pentamethyl
26 piperidine.

27 The aliquot samples and the final terminated reaction mixture were allowed to
28 warm to room temperature, which allowed the volatile components to
29 evaporate. To each aliquot sample 1-2 milliliter hexane was added and the

1 polymer was precipitated in methanol. Polyisobutylene was recovered in
2 each aliquot sample and agitated in using a vortex mixture with fresh
3 methanol to remove any remaining contaminants, and the methanol was
4 decanted. Polyisobutylene samples recovered in each aliquot were placed in
5 a vacuum oven at room temperature for at least 24 hours to remove any
6 remaining solvents.

7 The diluent used in Examples 1-5 and Comparative Examples A-E was a
8 mixture of hexane and methyl chloride in a volume ratio of 60:40.

9 Polyisobutylene samples were analyzed using ^1H Nuclear Magnetic
10 Resonance Spectroscopy (^1H NMR) and Gel Permeation Chromatography
11 (GPC) as described below.

12 Procedure for Fourier Transform Infrared
13 Spectroscopy Monitoring of Isobutylene

14 The polymerization reaction was followed by Fourier Transform Infrared
15 spectroscopy monitoring of isobutylene peak at 887 cm^{-1} . This procedure is
16 described in R. F. Storey; Q. A. Thomas, Macromolecules, 36, 5065-5071,
17 2003.

18 Procedure for Collecting ^1H NMR Data

19 ^1H NMR spectra were collected using a Bruker AC-300 (300MHz)
20 spectrophotometer using samples concentrations of 3 percent to 5 percent
21 (weight/weight) in CDCl_3 . ^1H NMR spectra were used for analysis of the end
22 groups. Fractions of exo-olefin, endo-olefin, tert-chloride and coupled olefin
23 chain ends were obtained using ^1H NMR integration as described in the
24 following section.

25

26

1 Procedure for Collecting GPC Data

2 GPC data were used to determine number average molecular weight (M_n),
3 weight average molecular weight (M_w) and Polydispersity index (PDI),
4 i.e. M_w/M_n . GPC was also used to qualitatively detect olefin coupled product.

Procedure for Calculating the Fractional Amounts
of Chain Ends on the Polyisobutylene Product

The fractions of exo-olefin, endo-olefin, and tert-chloride chain ends, and EAS, di-EAS, and coupled products in the polyisobutylene samples were quantified using ^1H NMR integration. It was assumed that these six species represent 100 percent of the chain ends. In some instances, EAS, di-EAS, and coupled products were deemed to be absent by qualitative inspection of the ^1H NMR spectrum, and for di-EAS and coupled products, by confirming the absence of a shoulder on the low elution volume side of the main polymer peak in the GPC chromatogram. Two procedures are given below. The "General Procedure" was used when coupled product was detected; the "Special Procedure" was used when coupled product was deemed to be absent.

18 General Procedure

19 The fractional molar amount of each type of chain end was obtained using an
20 equation analogous to the equation given below for determining the fractional
21 amount of *exo*-olefin.

$$22 \quad F(\text{exo}) = (A_{\text{exo}}) / (A_{\text{exo}} + A_{\text{endo}} + A_{\text{tert-Cl}} + A_{\text{EAS}} + 2A_{\text{di-EAS}} + 2A_{\text{coupled}}) \quad (1)$$

23 where A_{endo} is the area of the single olefinic resonance at 5.15ppm, A_{exo} is the
24 area of the exo-olefinic resonance 4.63ppm, and $A_{\text{tert-Cl}}$ was calculated as
25 follows:

$$A_{\text{tert-Cl}} = (A_{1.65-1.72}/6) - A_{\text{endo}} \quad (2)$$

1 where $A_{1.65-1.72}$ is the integrated area of the convoluted peaks associated with
 2 the gem-dimethyl protons of the endo-olefin and the tert-chloride chain ends.
 3 The integrated area of EAS or di-EAS product, when present, was evaluated
 4 on a situation-by-situation basis; the integration was determined based on a
 5 peak that is not convoluted by other peaks, and the area was normalized
 6 based on the number of protons that have that characteristic peak. It will be
 7 noted that a co-efficient of 2 appears in equation (1) for both di-EAS and
 8 coupled product, to account for the fact that creation of either of these
 9 products consumes 2 polyisobutylene chains. $A_{coupled}$ was calculated as
 10 follows:

$$11 \quad A_{coupled} = (A_{5.0-4.75} - A_{4.5-4.75})/2 \quad (3)$$

12 where $A_{5.0-4.75}$ is the integrated area of the convoluted peaks associated with
 13 one of the exo-olefin protons and the two identical protons of the coupled
 14 product, and where $A_{4.5-4.75}$ is the integrated area of the peak associated with
 15 the other exo-olefin proton.

16 Special Procedure

17 In the qualitative absence of coupled product, the fractional molar amount of
 18 each type of chain end was obtained using an equation analogous to the
 19 equation given below for determining the fractional amount of exo-olefin,

$$20 \quad F(\text{exo}) = (A_{\text{exo}}) / (A_{\text{exo}} + A_{\text{endo}} + A_{\text{tert-Cl}} + A_{\text{EAS}} + 2A_{\text{di-EAS}}) \quad (1)$$

21 where A_{endo} is the area of the single olefinic resonance at 5.15ppm, A_{exo}
 22 is the average area of the two exo-olefinic resonances at 4.63 and
 23 4.85 parts per million, and $A_{\text{tert-Cl}}$, A_{EAS} , and $A_{\text{di-EAS}}$ were calculated in the
 24 same manner as described in the "General Procedure."

25 Table I below summarizes the reactant quantities used in Examples 1-15 and
 26 Comparative Examples A-E.

1 Table II below summarizes the molar quantities of the reactants used in
2 Examples 1-15 and Comparative Examples A-E.

3 Table III below summarizes the exo-olefin content of the polyisobutylene
4 samples prepared in Examples 1-15 and Comparative Examples A-E. The
5 data are given as mole percent of the total end groups.

6 Table IV below summarizes complete chain end compositions of
7 polyisobutylene samples prepared in Examples 1-15 and Comparative
8 Examples A-E.

9 The following abbreviations are used for the reactants in Tables I, II, III, and
10 IV below:

11 TMPCI is an abbreviation of 2-chloro-2,4,4-trimethylpentane.

12 12266PMPip is an abbreviation of 1,2,2,6,6-pentamethylpiperidine.

13 NMDPA is an abbreviation of N-methyldiphenylamine.

14 2tBP is an abbreviation of 2-tert-butylpyridine.

15 TPA is an abbreviation of triphenylamine (mixture of isomers).

16 DPA is an abbreviation of diphenylamine.

17 TTA is an abbreviation of tri-p-tolylamine.

18 DMA is an abbreviation of N,N-dimethylaniline.

19 BET is an abbreviation of N-benzyl-N-ethyl-m-toluidine.

20 2,3DMQ is an abbreviation of 2,3-dimethylquinoxaline.

21 DDA is an abbreviation of 10,11-dihydro-5H-dibenz[b,f]azepine.

22 4,6DMP is an abbreviation of 4,6-dimethylpyrimidine.

23 246TT is an abbreviation of 2,4,6-triphenyl-1,3,5-triazine.

24 THA is an abbreviation of tri-n-hexylamine.

25 2PP is an abbreviation of 2-phenylpyridine.

- 1 DTA is an abbreviation of di-p-tolylamine.
- 2 TnBA is an abbreviation of tri-n-butylamine.
- 3 2266TMPip is an abbreviation for 2,2,6,6-tetramethylpiperadine.
- 4 NNDIPPA is an abbreviation of N,N-diisopropyl-3-pentylamine
- 5 12266TMPip/TiCl₄ is an abbreviation for the mixture of 1,2,2,6,6-
- 6 pentamethylpiperadine and titanium tetrachloride.
- 7

Table I

Example	Initiator	Initiator (g)	2,6-Dimethylpyridine (g)	Isobutylene (g)	Titanium Tetrachloride (g)	Quenching Agent	Quenching Agent (g)	Total Reaction Volume (L)	Total Diluent Volume (L)	Temperature (°C)
1	TMPCI	0.4163	0.2143	5.6110	3.1489	12266PMPip	0.6087	0.200	0.189	-60
2	TMPCI	0.4163	0.2143	5.6110	3.1489	NMDPA	0.7183	0.200	0.189	-60
3	TMPCI	0.4163	0.2143	5.6110	3.1489	2tBP	0.5300	0.200	0.189	-60
4	TMPCI	0.417	0.212	5.611	3.149	2266TMPip	0.792	0.201	0.19	-60
5	TMPCI	0.417	0.214	5.611	3.149 ^a	12266PMPip/ TiCl ₄	0.871 ^b	0.201	0.19 ^c	-60
6	TMPCI	0.0416	0.0214	1.1222	0.3149	TPA	0.1270	0.020	0.018	-60
7	TMPCI	0.0416	0.0214	1.1222	0.3149	DPA	0.0948	0.020	0.018	-60
8	TMPCI	0.0416	0.0214	1.1222	0.3149	TTA	0.1610	0.020	0.018	-60
9	TMPCI	0.0416	0.0214	1.1222	0.3149	DMA	0.0679	0.020	0.018	-60
10	TMPCI	0.0416	0.0214	1.1222	0.3149	BET	0.1260	0.020	0.018	-60
11	TMPCI	0.0416	0.0214	1.1222	0.3149	2,3DMQ	0.0860	0.020	0.018	-60
12	TMPCI	0.0416	0.0214	1.1222	0.3149	DDA	0.1090	0.020	0.018	-60
13	TMPCI	0.0416	0.0214	1.1222	0.3149	4,6DMP	0.0610	0.020	0.018	-60
14	TMPCI	0.0416	0.0214	1.1222	0.3149	246TT	0.1730	0.020	0.018	-60
15	TMPCI	0.417	0.214	5.611	3.149	NNDIPPA	0.961	0.202	0.19	-60
A	TMPCI	0.0416	0.0214	1.1222	0.3149	THA	0.1510	0.020	0.018	-60

B	TMPCl	0.0416	0.0214	1.1222	0.3149	2PP	0.0870	0.020	0.018	-60
C	TMPCl	0.0416	0.0214	1.1222	0.3149	Quinaldine	0.0800	0.020	0.018	-60
D	TMPCl	0.0416	0.0214	1.1222	0.3149	DTA	0.1100	0.020	0.018	-60
E	TMPCl	0.0416	0.0214	1.1222	0.3149	TnBA	0.1040	0.020	0.018	-60

1

2 ^a 2.087 grams (66.3%) of the total TiCl₄ was used to catalyze the polymerization of isobutylene; 1.062 grams (33.7%) was

3 pre-reacted with the 12266PMPip.

4 ^b 12266PMPip was pre-reacted with 1.062 grams of TiCl₄ and 0.0475 liters diluent for 33 minutes prior to its addition to the
5 polymerization reactor.

6 ^c 0.1425 liters (75%) of the total diluent was diluted to dilute the polymerization of isobutylene; 0.475 liters (25%) was used
7 to dilute the 12266PMPip/ TiCl₄ pre-reaction.

8

9

10

11

Table II

Example	Initiator	Initiator (M)	2,6-Dimethylpyridine (M)	Isobutylene (M)	Titanium Tetrachloride (M)	Quenching Agent	Quenching Agent (M)	Total Reaction Volume (L)	Total Diluent Volume (L)	Temperature (°C)
1	TMPCl	0.014	0.010	0.500	0.083	12266PMPip	0.0196	0.200	0.189	-60
2	TMPCl	0.014	0.010	0.500	0.083	NMDPA	0.0196	0.200	0.189	-60
3	TMPCl	0.014	0.010	0.500	0.083	2tBP	0.0196	0.200	0.189	-60
4	TMPCl	0.014	0.010	0.500	0.083	2266TMPip	0.028	0.201	0.19	-60
5	TMPCl	0.018 ^a (0.014)	0.013 ^a (0.010)	0.655 ^a (0.500)	0.072 ^a (0.083)	12266PMPip/ TiCl ₄	0.028 ^b	0.201 ^c	0.19 ^c	-60
6	TMPCl	0.014	0.010	1.0	0.083	TPA	0.028	0.020	0.018	-60
7	TMPCl	0.014	0.010	1.0	0.083	DPA	0.028	0.020	0.018	-60
8	TMPCl	0.014	0.010	1.0	0.083	TTA	0.028	0.020	0.018	-60
9	TMPCl	0.014	0.010	1.0	0.083	DMA	0.028	0.020	0.018	-60
10	TMPCl	0.014	0.010	1.0	0.083	BET	0.028	0.020	0.018	-60
11	TMPCl	0.014	0.010	1.0	0.083	2,3DMQ	0.028	0.020	0.018	-60
12	TMPCl	0.014	0.010	1.0	0.083	DDA	0.028	0.020	0.018	-60
13	TMPCl	0.014	0.010	1.0	0.083	4,6DMP	0.028	0.020	0.018	-60
14	TMPCl	0.014	0.010	1.0	0.083	246TT	0.028	0.020	0.018	-60
15	TMPCl	0.014	0.010	0.5	0.083	NNDIPPA	0.028	0.202	0.19	-60
A	TMPCl	0.014	0.010	1.0	0.083	THA	0.028	0.020	0.018	-60
B	TMPCl	0.014	0.010	1.0	0.083	2PP	0.028	0.020	0.018	-60

C	TMPCl	0.014	0.010	1.0	0.083	Quinaldine	0.028	0.020	0.018	-60
D	TMPCl	0.014	0.010	1.0	0.083	DTA	0.028	0.020	0.018	-60
E	TMPCl	0.014	0.010	1.0	0.083	TnBA	0.028	0.020	0.018	-60

1

- 2 ^a Concentration during IB polymerization; number in parenthesis is final concentration after polymerization reaction and
- 3 quencher/TiCl₄ pre-reaction were combined.
- 4
- 5 ^b Final concentration after polymerization reaction and quencher/TiCl₄ pre-reaction were combined.
- 6
- 7 ^c Final volume after polymerization reaction and quencher/TiCl₄ pre-reaction were combined.
- 8

9

1 Example 2

2 Preparation of Polyisobutylene Using a Mono-functional
3 Initiator and N-methyldiphenylamine

4 Polyisobutylene was prepared as described in Example 1 and using the
5 conditions listed in table 1. Example 2 conditions are identical to Example 1
6 conditions except that the quenching agent was N-methyldiphenylamine in
7 stead of 1,2,2,6,6-pentamethylpiperidine.

8 The polyisobutylene samples were collected and analyzed as described
9 above for the Example 1 polyisobutylene samples.

10 Table III below summarizes the data obtained at various times intervals after
11 the addition of the quenching agents. The actual time for collecting the
12 aliquots samples, in minutes, was within a few minutes, 1-5 minutes, of the
13 time given in Table III.

14 Example 3

15 Preparation of Polyisobutylene Using a Mono-functional
16 Initiator and 2-Tert-butylpyridine

17 Polyisobutylene was prepared as described in Example 1 and using the
18 conditions listed in table 1. Example 3 conditions are identical to Example 1
19 conditions except that the quenching agent was 2-tert-butylpyridine instead of
20 1,2,2,6,6-pentamethyl piperidine.

21 The polyisobutylene samples were collected and analyzed as described
22 above for the Example 1 polyisobutylene samples.

23

24

25

1 Example 4

2 Preparation of Polyisobutylene Using a Mono-functional

3 Initiator and 2,2,6,6-tetramethylpiperidine

4 Polyisobutylene was prepared as described in Example 1 and using the
5 conditions listed in table 1. Example 4 conditions are similar to example 1
6 conditions except that the quencher was 2,2,6,6-tetramethylpiperidine, and it
7 was used at a concentration two times that of the chain end concentration.

8
9 The polyisobutylene samples were collected and analyzed as described
10 above for the Example 1 polyisobutylene samples.

11 Table III below summarizes the data obtained at various times intervals after
12 the addition of the quenching agents.

13 Example 5

14
15 Preparation of Polyisobutylene Using a Mono-functional Initiator and

16 1,2,2,6,6-pentamethylpiperidine – Pre-reaction of 1,2,2,6,6-
17 pentamethylpiperidine with Titanium Tetrachloride Prior to Quenching

18
19 The reactor configuration, ATR-FTIR probe and conduit, FTIR spectrometer
20 and spectroscopic method and analysis, constant-temperature heptane bath,
21 and glovebox were the same as described in Example 1. A 250-milliliter
22 reactor flask was charged with the following reactants:

23
24 85.5 milliliters hexane equilibrated at -60°C,
25 57 milliliters methyl chloride equilibrated at -60°C,
26 0.23 milliliters 2,6-dimethyl pyridine equilibrated at room temperature, and
27 0.48 milliliters 2-chloro-2,4,4-trimethyl pentane equilibrated at room
28 temperature.

29

1 A reference absorbance at 887 cm^{-1} was established and then 8.18 milliliters
2 isobutylene equilibrated at -60°C was charged to the 250-milliliter reactor
3 flask.

4 A separate 2-neck 500-milliliter flask was charged with the following reactants:

5 28.5 milliliters hexane equilibrated at -60°C ,
6 19 milliliters methyl chloride equilibrated at -60°C , and
7 1.02 milliliters 1,2,2,6,6-pentamethylpiperidine equilibrated at room
8 temperature.

9 Both flasks were equilibrated in the -60°C heptane bath.

10 Next, 1.2 milliliters titanium tetrachloride was charged to the 250- milliliter
11 reactor flask. Then, 0.62 milliliters titanium tetrachloride was charged to the
12 500- milliliter flask.

13 After a polymerization time of 33 minutes, a pre-quench aliquot (5-10 milliliter)
14 was removed from the contents of the 250- milliliter reactor flask and
15 terminated with 10-15 milliliters per-chilled methanol, and then the
16 polymerization was quenched by pouring the contents of the 500- milliliter
17 flask into the 250- milliliter reactor flask. Aliquots were removed at 1, 3, 5, 8,
18 15, and 30 minutes and terminated with pre-chilled methanol. The balance of
19 the reactor contents was terminated at 60 minutes using pre-chilled methanol.

20 The polyisobutylene samples were collected and analyzed as described
21 above for the Example 1 polyisobutylene samples.

22 Example 6

23 Preparation of Polyisobutylene Using a Mono-functional 24 Initiator and Tripentylamine Composed of Mixed Isomers (TPA)

25 A four-neck 250 milliliter round-bottom flask was equipped with an overhead
26 mechanical stirrer and platinum resistance thermometer. This assembly was
27 immersed into a heptane bath at -60°C under dry nitrogen gas in a

1 substantially inert atmosphere glovebox. The flask was then charged with the
2 following reactants:

3 108 milliliters hexane equilibrated at -60°C,

4 72 milliliters methyl chloride equilibrated at -60°C,

5 0.48 milliliters 2-chloro-2,4,4-trimethyl pentane equilibrated at room
6 temperature,

7 0.23 milliliters 2,6-dimethyl pyridine equilibrated at room temperature,

8 16.4 milliliters of isobutylene equilibrated at -60°C.

9 The contents of the round-bottom flask were equilibrated at -60°C.

10 With continued stirring, next 1.82 milliliters titanium tetrachloride was charged
11 to the flask. The reaction was allowed to proceed 12 minutes and then 20
12 milliliters of the polymerization solution was charged to 4 separate 60 milliliter
13 test tubes, equipped with threaded caps.

14 The polymerization was allowed to continue in each test tube for 4 additional
15 minutes (16 total reaction minutes) at which point 1 of the 4 tubes was
16 terminated with 5 milliliters of methanol to provide a comparative example
17 prior to addition of quenching agents . The remaining 3 solutions were
18 allowed to proceed 8 minutes with intermittent shaking (24 total reaction
19 minutes), at which time 0.1270 grams triphenylamine (a mixture of isomers)
20 was added to one of the test tubes containing a reactive polymerization. After
21 addition of TPA, 1 of the remaining polymerizations was terminated with 5
22 milliliters of methanol to provide another comparative example. The TPA
23 quenching reaction was allowed to proceed 15 minutes at which time 5
24 milliliters of methanol was charged in order to terminate the reaction. The
25 final non quenched polymerization test tube was then terminated with 5
26 milliliters of methanol to provide a final comparative example. Non-quencher
27 containing reactions were used to provide a comparative baseline for the

1 quenching reactions and to provide references for structural and molecular
2 weight characterization in the absence of a quenching agent.

3 The molar quantities of the reactants in the final reaction mixture are given
4 below in Table II and the exo-olefin results for various time intervals are
5 summarized in Table III.

6 Examples 7-14

7 Preparation of Polyisobutylene Using a Mono-functional 8 Initiator and Various Quenching Agents

9 Polyisobutylene was prepared according to the procedure described in
10 example 6 above but using various quenching agents other than TPA. The
11 following quenching agents (examples 7-14) were evaluated and yielded exo-
12 olefin PIB: diphenylamine (DPA), tri-p-tolylamine (TTA), N,N-dimethylaniline
13 (DMA), N-benzyl-N-ethyl-m-toluidine (BET), 2,3-dimethylquinoxaline
14 (23DMQ), 10,11-dihydro-5H-dibenz[b,f]azepine (DDA), 4,6-dimethylpyrimidine
15 (46DMP), and 2,4,6-triphenyl-1,3,5-triazine (246TT).

16 The reactant quantities for examples 7-14 are listed in Table 1. The molar
17 quantities of the reactants in the final reaction mixture are given below in
18 Table II and the exo-olefin results for various time intervals are summarized in
19 Table III.

20 Example 15

21 Preparation of Polyisobutylene Using a Mono-functional 22 Initiator and N,N-diisopropyl-3-pentylamine

23 Polyisobutylene was prepared according to the procedure of Example 1 using
24 the conditions listed in Table 1. Example 15 conditions are identical to
25 Example 4 conditions except that the quencher was N,N-diisopropyl-3-
26 pentylamine.

27

1 The polyisobutylene samples were collected and analyzed as described
2 above for the Example 1 polyisobutylene samples.

3 Table III below summarizes the data obtained at various times intervals after
4 the addition of the quenching agents.

5 Comparative Examples A-E

6 Preparation of Polyisobutylene Using a Mono-functional
7 Initiator and Various Quenching Agents

8 Polyisobutylene was prepared according to the procedure described in
9 example 6 above but using various quenching agents other than TPA. The
10 comparative examples represent secondary and tertiary amines which did not
11 yield exo-olefin PIB above that of the PIB generated in the control aliquot.

12 The reactant quantities for examples A-E are listed in Table 1. The molar
13 quantities of the reactants in the final reaction mixture are given below in
14 Table II and the exo-olefin results for various time intervals are summarized in
15 Table III.

1

Table III

Example	Quenching Agent	Quench Time (minutes after the addition of the quenching agent)							
		~0	~15	~30	~45	~50 - 60	~75	~90	~180
		Exo-olefin (% of total chain ends)							
1	1,2,2,6,6-pentamethyl piperidine	1	79	81	90	87	93	91	N/A
2	N-methyl diphenylamine	0	85	86	84	85	84	84	84
3	2-tertbutyl pyridine	3	62	65	69	66	67	68	N/A
4	2,2,6,6- tetramethylpiperidine	3	96	96	N/A	96	N/A	N/A	N/A
5	12266PMPip/TiCl ₄	11	76	76	N/A	76	N/A	N/A	N/A
6	TPA	7	N/A	N/A	22	N/A	N/A	N/A	N/A
7	DPA	7	50	N/A	N/A	N/A	N/A	N/A	N/A
8	TTA	7	70	N/A	N/A	N/A	N/A	N/A	N/A
9	DMA	7	61	N/A	N/A	N/A	N/A	N/A	N/A
10	BET	7	63	N/A	N/A	N/A	N/A	N/A	N/A
11	2,3DMQ	7	94	N/A	N/A	N/A	N/A	N/A	N/A
12	DDA	7	99	N/A	N/A	N/A	N/A	N/A	N/A
13	4,6DMP	7	69	N/A	N/A	N/A	N/A	N/A	N/A
14	246TT	7	67	N/A	N/A	N/A	N/A	N/A	N/A
15	N,N-diisopropyl-3- pentaylamine	0	N/A	10	N/A	N/A	N/A	N/A	N/A
A	THA	7	7	N/A	N/A	N/A	N/A	N/A	N/A
B	2PP	7	7	N/A	N/A	N/A	N/A	N/A	N/A
C	Quinaldine	7	7	N/A	N/A	N/A	N/A	N/A	N/A
D	DTA	7	7	N/A	N/A	N/A	N/A	N/A	N/A
E	TnBA	7	7	N/A	N/A	N/A	N/A	N/A	N/A

2

Table IV

Composition of Chain Ends after 90 minutes of Quenching^b

	Quenching Agent	Exo-Olefin Chain End (%)	Endo-Olefin Chain End (%)	Tert-Cl Chain End (%)	EAS Chain End (%)	di-EAS Chain End (%)	Coupled Product (%)	Reaction Temperature (°C)
Examples	1 1,2,2,6,6,- pentamethylpiperidine	91	0	3	0	0	6	-60
	2 N-methyldiphenylamine	84	0	0	15	N/A	1	-60
	3 2-tert-butylpyridine	68	0	0	0	0	32	-60
	4 2,2,6,6-tetramethylpiperidine	96	0	<2	0	0	<2	-60
	5 12266PMPip/TiCl ₄ ^c	76	<1	20	0	0	<3	-60
	6 TPA ^d	22	<2	75	0	0	0	-60
	7 DPA ^e	50	<1	46	0	0	<3	-60
	8 TTA ^e	70	<1	23	0	0	7	-60
	9 DMA ^d	61	<1	38	0	0	0	-60
	10 BET ^e	63	<1	36	0	0	<1	-60
	11 2,3DMQ ^e	94	<2	<1	N/A	N/A	<2	-60
	12 DDA ^e	99	<1	<1	0	0	<1	-60

13	4,6DMP ^e	69	<1	24	0	0	6	-60
14	246TT ^e	67	<1	32	N/A	N/A	<1	-60
15	N,N-diisopropyl-3-pentylamine ^a	17	0	82	0	0	1	-60
A	THA ^d	8	<1	89	0	0	<2	-60
B	2PP ^e	8	<1	89	0	0	<2	-60
C	Quinaldine ^e	8	<1	89	0	0	<2	-60
D	DTA ^e	8	<1	89	0	0	<2	-60
E	TnBA ^d	8	<1	89	0	0	<2	-60

1
2

3 N/A The di-EAS chain end data for N-methyldiphenylamine is not available.

4 ^a quenching time was 180 minutes.5 ^b quenching time was 90 minutes.6 ^c quenching time was 60 minutes.7 ^d quenching time was 45 minutes.8 ^e quenching time was 15 minutes.

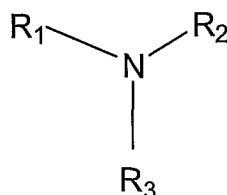
13

1 WHAT IS CLAIMED IS:

- 2 1. A method for preparing a polyolefin containing one or more exo-olefinic
3 end groups on the polymer chain, comprising quenching a cationic
4 quasi-living polyolefin polymer system with one or more hindered
5 secondary or tertiary amines containing only carbon, hydrogen, and
6 nitrogen atoms, provided the hindered secondary or tertiary amines are
7 not:
- 8 (a) Triethylamine;
 - 9 (b) Tri-n-butylamine;
 - 10 (c) Trihexylamine;
 - 11 (d) Triisooctylamine;
 - 12 (e) 2-phenylpyridine;
 - 13 (f) 2,3-cyclododecapyridine;
 - 14 (g) Di-p-tolylamine;
 - 15 (h) Quinaldine; and
 - 16 (i) 1-pyrrolidino-1-cyclopentene.
- 17 2. The method of claim 1, wherein the quenching of the cationic
18 quasi-living polyolefin polymer system is at a temperature in the range
19 of about -130°C to about 10°C.
- 20 3. The method of claim 2, wherein the quenching is carried out at a
21 temperature in the range of about -80°C to about 0°C.
- 22 4. The method of claim 3, wherein the quenching is carried out at a
23 temperature in the range of about -70°C to about -10°C.
- 24 5. The method of claim 4, wherein the quenching is carried out at a
25 temperature in the range of from about -60°C to about -20°C.
- 26 6. The method of claim 1, wherein the polyolefin is prepared in situ.

1 7. The method of claim 1, wherein the polyolefin is polyisobutylene.

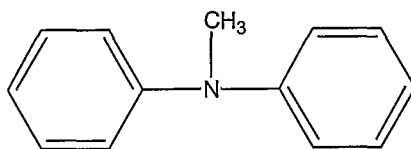
2 8. The method of claim 1, wherein the hindered secondary or tertiary
3 amine has the general formula:



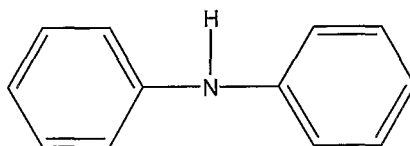
4
5 wherein R_1 , R_2 and R_3 are independently hydrogen, alkyl
6 containing one carbon atom to about 20 carbon atoms, cycloalkyl
7 of about 3 to about 7 carbon atoms, aryl of about 6 to about 30
8 carbon atoms, alkaryl of about 7 to about 30 carbon atoms, or
9 aralkyl of about 7 to about 30 carbon atoms; or at least one of R_1
10 and R_2 , R_2 and R_3 and R_3 and R_1 , taken in pairs, independently
11 form a fused aliphatic ring of from about 4 carbon atoms to about
12 8 carbon atoms;

13 provided that no more than one of R_1 , R_2 and R_3 is hydrogen, and
14 provided that R_1 , R_2 , and R_3 are not all linear alkyl of about 3
15 carbons or less.

16 9. The method of claim 8, wherein the hindered amine is a tertiary amine
17 of the formula:

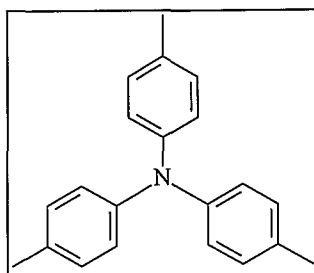


18
19 10. The method of claim 8, wherein the hindered amine is a secondary
20 amine of the formula:



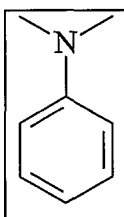
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- 2 11. The method of claim 8, wherein the hindered amine is a tertiary amine
3 of the formula:



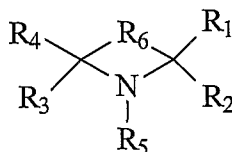
4

- 5 12. The method of claim 8, wherein the hindered amine is a tertiary amine
6 of the formula:



7

- 8 13. The method of claim 1 wherein the hindered amine is a tertiary or
9 secondary amine having the general formula:

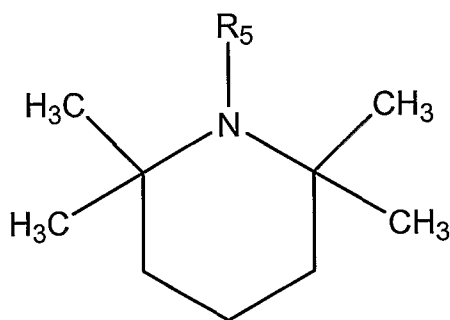


10

- 11 wherein R₆ is a divalent hydrocarbyl group of one carbon atom to
12 about 4 carbon atoms, each of which may be substituted with an
13 alkyl group having one carbon atom to about 6 carbon atoms, and
14 R₁, R₂, R₃, R₄, and R₅ are independently hydrogen, alkyl
15 containing one carbon atom to about 20 carbon atoms, cycloalkyl
16 of about 3 to about 8 carbon atoms, aryl of about 6 to about 30

1 carbon atoms, alkaryl of about 7 to about 30 carbon atoms, or
 2 aralkyl of about 7 to about 30 carbons; provided if R₁, R₂, R₃, and
 3 R₄ are hydrogen, then R₅ is a branched alkyl having from about 4
 4 to about 20 carbon atoms, aryl of about 6 to about 30 carbon
 5 atoms, or aralkyl of about 7 to about 30 carbon atoms, and
 6 provided if R₅ is hydrogen, then R₁, R₂, R₃, and R₄ cannot be
 7 hydrogen unless either R₁ or R₂ and either R₃ or R₄ is a branched
 8 alkyl from about 4 to about 20 carbon atoms.

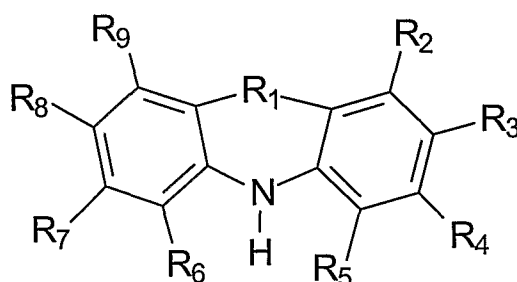
9
 10 14. The method of claim 13, wherein the hindered amine is a secondary or
 11 tertiary amine of the formula:



12

13 wherein R₅ is hydrogen or methyl.

14
 15 15. The method of claim 8 wherein the hindered secondary or tertiary amine
 16 has the general formula:



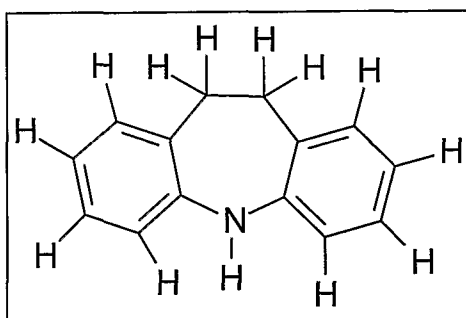
17

18 wherein R₁ is a divalent hydrocarbonyl group of one carbon atom to
 19 about 4 carbons and R₂, R₃, R₄, R₇, R₈, and R₉ are independently
 20 hydrogen, alkyl containing one carbon atom to about 20 carbon

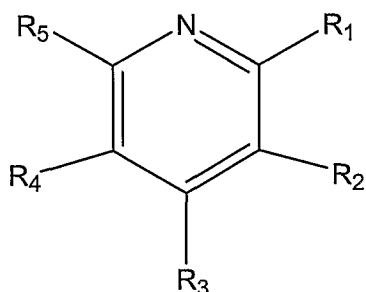
atoms, cycloalkyl of about 3 to about 8 carbon atoms, aryl of about 6 to about 30 carbon atoms, alkaryl of about 7 to about 30 carbon atoms, or aralkyl of about 7 to about 30 carbons, and one of R_5 and R_6 is hydrogen and the other is linear alkyl from one carbon atom to about 20 carbon atoms.

16. The method of claim 15, wherein one of R_5 and R_6 is hydrogen.

17. The method of claim 15, wherein the amine has the formula:



18. The method of claim 1, wherein the hindered amine is a tertiary amine of the general formula:



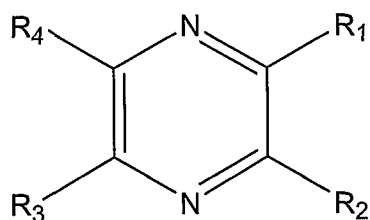
wherein one of R_1 and R_5 is hydrogen and the other is a branched alkyl of about 3 to about 20 carbon atoms, aryl of about 10 to about 30 carbon atoms, or aralkyl of about 11 to about 30 carbon atoms; R_2 , R_3 and R_4 are independently hydrogen, alkyl of one carbon atom to about 20 carbon atoms, cycloalkyl of about 3 to about 7 carbon atoms, aryl of about 6 to about 30 carbon atoms, alkaryl of about 7 to about 30 carbon atoms, or aralkyl of about 7 to about 30 carbon atoms; or at least one of R_1 and R_2 , R_2 and R_3 ,

1 R₃ and R₄, and R₄ and R₅, taken in pairs, independently form a
 2 fused aromatic ring of from 5 carbon atoms to 7 carbon atoms or
 3 aliphatic ring of from about 4 carbon atoms to about 8 carbon
 4 atoms,

5 provided that if R₁ and R₂ form a fused aliphatic or aromatic ring,
 6 then R₅ is a branched alkyl of about 3 to about 20 carbon atoms,
 7 aryl of about 10 to about 30 carbon atoms, or aralkyl of about
 8 11 to about 30 carbon atoms, and provided that if R₄ and R₅ form
 9 a fused aliphatic or aromatic ring, then R₁ is a branched alkyl of
 10 about 3 to about 20 carbon atoms, aryl of about 10 to about 30
 11 carbon atoms, or aralkyl of about 11 to about 30 carbon atoms.

12 19. The method of claim 18, wherein R₁ is hydrogen and R₅ is tert-butyl
 13 and R₂, R₃ and R₄ are hydrogen.

14 20. The method of claim 1, wherein the hindered amine is a nitrogen
 15 containing hetero-aromatic having the following formulas, (a), (b) and
 16 (c):

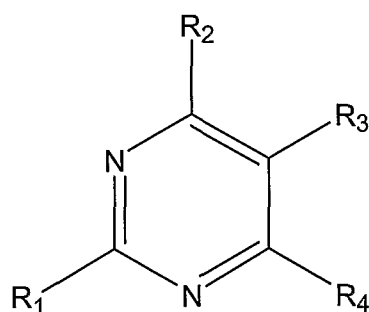


(a)

18 wherein in formula (a)

19 one of R₁ and R₄ is hydrogen and the other is alkyl of one carbon
 20 atom to about 20 carbon atoms, cycloalkyl of about 3 to about 8
 21 carbon atoms, aryl of about 6 to about 30 carbon atoms, alkaryl of
 22 about 7 to about 30 carbon atoms, or aralkyl of about 7 to about
 23 30 carbon atoms, one of R₂ and R₃ is hydrogen and the other is
 24 alkyl of one carbon atom to about 20 carbon atoms, cycloalkyl of

1 about 3 to about 8 carbon atoms, aryl of about 6 to about
2 30 carbon atoms, alkaryl of about 7 to about 30 carbon atoms, or
3 aralkyl of about 7 to about 30 carbon atoms; or at least one of R₁
4 and R₂ and R₃ and R₄, taken in pairs, independently form a fused
5 aromatic ring of from 5 carbon atoms to 7 carbon atoms or
6 aliphatic ring of from about 4 carbon atoms to about 8 carbon
7 atoms;



(b)

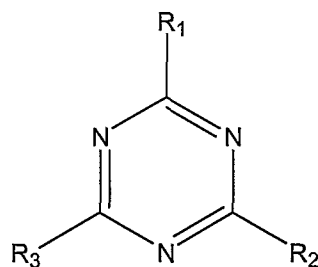
8
9 wherein in formula (b)

10 R₁, R₂ and R₄ are independently hydrogen or alkyl of one carbon
11 atom to about 20 carbon atoms, cycloalkyl of about 3 to about 8
12 carbon atoms, aryl of about 6 to about 30 carbon atoms, alkaryl of
13 about 7 to about 30 carbon atoms, or aralkyl of about 7 to about
14 30 carbon atoms, R₃ is hydrogen, alkyl of one carbon atom to
15 about 20 carbon atoms, cycloalkyl of about 3 to about 8 carbon
16 atoms, aryl of about 6 to about 30 carbon atoms, alkaryl of about
17 7 to about 30 carbon atoms, or aralkyl of about 7 to about 30
18 carbon atoms; or at least one of R₂ and R₃ or R₃ and R₄, taken in
19 pairs, independently form a fused aromatic ring of from 5 carbon
20 atoms to 7 carbon atoms or aliphatic ring of from about 4 carbon
21 atoms to about 8 carbon atoms,

22 provided that if R₁ is hydrogen then R₂ and R₄ are independently
23 alkyl of one carbon atom to about 20 carbon atoms, cycloalkyl of

about 3 to about 8 carbon atoms, aryl of about 6 to about 30 carbon atoms, alkaryl of about 7 to about 30 carbon atoms, or aralkyl of about 7 to about 30 carbon atoms, and further provided that if R_2 or R_4 is hydrogen, then R_1 is alkyl of one carbon atom to about 20 carbon atoms, cycloalkyl of about 3 to about 8 carbon atoms, aryl of about 6 to about 30 carbon atoms, alkaryl of about 7 to about 30 carbon atoms, or aralkyl of about 7 to about 30 carbon atoms;

and

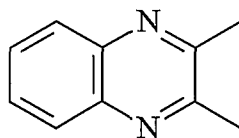


(c)

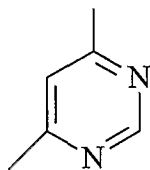
wherein in formula (c)

R_1 , R_2 and R_3 are independently hydrogen or alkyl of one carbon to about 20 carbon atoms, cycloalkyl of about 3 to about 8 carbon atoms, aryl of about 6 to about 30 carbon atoms, alkaryl of about 7 to about 30 carbon atoms, or aralkyl of about 7 to about 30 carbon atoms.

21. The method of Claim 1, where the hindered amine has the formula:

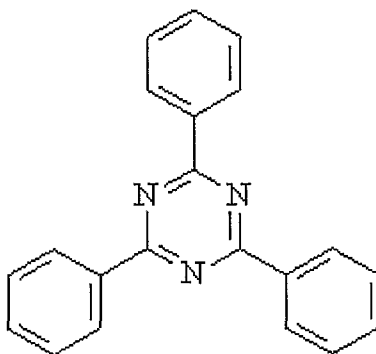


22. The method of Claim 20, where the hindered amine has the formula:



1

2 23. The method of Claim 20, where the hindered amine has the formula:



3

4 24. The method of claim 1, wherein the polyolefin is prepared by
5 quenching a quasi-living polyolefin polymer product containing terminal
6 tert-chloride chain ends or a mixture of terminal tert-chloride chain ends
7 and terminal olefinic chain ends in the presence of a Lewis acid.

8 25. The method of claim 24, wherein the quasi-living polyolefin polymer
9 product contains terminal tert-chloride chain ends.

10 26. The method of claim 24, wherein the Lewis acid is a titanium or boron
11 halide.

12 27. The method of claim 26, wherein the Lewis acid is a titanium halide.

13 28. The method of claim 26, wherein the Lewis acid is titanium
14 tetrachloride.

15 29. The method of claim 1, wherein the quasi-living polyolefin polymer is
16 formed by contacting at least one cationically polymerizable monomer
17 with an initiator, in the presence of a Lewis acid under reaction
18 conditions suitable for quasi-living polymerization.

- 1 30. The method of claim 29, wherein the at least one cationically
2 polymerizable monomer comprises at least one of isobutylene, 2-
3 methyl-1-butene, 3-methyl-1-butene, 4-methyl-1-pentene, and beta-
4 pinene.
- 5 31. The method of claim 30, wherein the at least one cationically
6 polymerizable monomer is isobutylene.
- 7 32. The method of claim 31, wherein two or more different cationically
8 polymerizable monomers are employed.
- 9 33. The method of claim 29, wherein the initiator is multi-functional.
- 10 34. The method of claim 33, wherein the initiator is di-functional.
- 11 35. The method of claim 34, wherein the di-functional initiator comprises at
12 least one of 1,3-di(2-chloro-2-propyl)-5-tert-butylbenzene,
13 1,4-di(2-chloro-2-propyl)benzene and
14 1,4-di(2-acetoxy-2-propyl)benzene,
15 1,3-di(2-acetoxy-2-propyl)-5-tert-butylbenzene,
16 1,3-di(2-methoxy-2-propyl)-5-tert-butylbenzene and
17 1,4-di(2-methoxy-2-propyl)benzene.
- 18 36. The method of claim 29, wherein the initiator is mono-functional.
- 19 37. The method of claim 36, wherein the mono-functional initiator comprises
20 at least one of 2-chloro-2-phenylpropane; 2-acetoxy-2-phenylpropane;
21 2-propionoxy-2-phenylpropane, 2-methoxy-2-phenylpropane, 2-ethoxy-
22 2-phenylpropane, 2-chloro-2,4,4-trimethylpentane, 2-acetoxy-2,4,4,-
23 trimethylpentane, 2-propionoxy-2,4,4-trimethylpentane,
24 2-methoxy-2,4,4-trimethylpentane, and 2-ethoxy-2,4,4-trimethylpentane.
- 25 38. The method of claim 1, wherein the molecular weight distribution,
26 M_w/M_n , of the polyolefin polymer is present in the range of about
27 1.01 to about 3.0.

- 1 39. The method of claim 38, wherein the molecular weight distribution,
2 M_w/M_n , of the polyolefin polymer is present in the range of about
3 1.1 to about 2.0.
- 4 40. The method of claim 39, wherein the molecular weight distribution,
5 M_w/M_n , of the polyolefin polymer is less than 1.5.
- 6 41. A method for preparing a polyolefin containing one or more exo-olefinic
7 end groups on the polymer chain, comprising quenching a cationic
8 quasi-living polyolefin polymer system with one or more hindered
9 secondary or tertiary amines containing only carbon, hydrogen, and
10 nitrogen atoms, wherein the hindered secondary or tertiary amine
11 compounds are pre-reacted with a Lewis acid, and provided the
12 hindered secondary or tertiary amines are not:
- 13 (a) Triethylamine;
- 14 (b) Tri-n-butylamine;
- 15 (c) Trihexylamine;
- 16 (d) Triisooctylamine;
- 17 (e) 2-phenylpyridine;
- 18 (f) 2,3-cyclododecapyridine;
- 19 (g) Di-p-tolylamine;
- 20 (h) Quinaldine; and
- 21 (i) 1-pyrrolidino-1-cyclopentene.
- 22 42. The above method of claim 41, wherein the Lewis acid is titanium
23 tetrachloride.

- 1 43. The above method of claim 41, wherein the hindered amine is 1,2,2,6,6-
2 pentamethylpiperidine.
- 3 44. The method of claim 41, wherein the Lewis acid is titanium tetrachloride
4 and the hindered secondary or tertiary amine is 2,2,6,6-
5 tetramethylpiperidine.
- 6 45. The method of claim 1, wherein the polyolefin has at least 20 percent
7 exo-olefin end groups.
- 8 46. The method of claim 1, wherein the polyolefin has at least 50 percent
9 exo-olefin end groups.
- 10 47. The method of claim 1, wherein the product has at least 70 percent exo-
11 olefin end groups.