

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

This application claims the benefit of U.S. Provisional Application No. 60/603,423, filed August 20, 2004.

FIELD OF THE INVENTION

The present invention is directed to a method for preparation of polyolefins containing exo-olefin chain ends. The method involves quenching a cationic quasi-living polyolefin polymer system with one or more nitrogen-containing five-membered aromatic ring compounds having at least two hydrocarbyl substituents attached to the ring.

BACKGROUND OF THE INVENTION

Linear polyolefins made using a mono-functional initiator containing a single "exo-olefin", "1,1-di-substituted" olefin, or "methylvinylidene," end group are useful precursors for the preparation of polymers containing specific functional end groups. Polymers made using multi-functional initiators would have multiple exo-olefinic end groups. Polymers containing specific end groups are useful as lubricating oil additives. One example of a functionalized polymer containing hetero atoms is polyisobutenylsuccinic anhydride. Functional end groups may also be desirable for making polymers with potential for further reactions.

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

Similarly to the conventional polymerization systems, living polymerization systems may be either anionic or cationic. The difference between

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

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

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

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

28 Exclusive production of the exo-olefin isomer has not been previously
29 achieved under conventional polymerization conditions.

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

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

11 The preparation of polyolefins, including polyisobutylene polymers, is well
12 known in the art. A number of patents have discussed processes for making
13 polyisobutylene polymers containing exo-olefin end groups, but none using
14 quenching a cationic quasi-living polymerization system with one or more
15 nitrogen-containing five-membered aromatic ring compounds.

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

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

25 U.S. Patent No. 4,342,849 discloses the synthesis of polyisobutylene carrying
26 either unsaturation or hydroxyl groups at both ends, in the case of a linear
27 polymer, or at all ends in the case of a star polymer. The method involves the
28 steps of refluxing a solution of telechelic di-halogen polyisobutylene, adding a

1 solution strong base such as potassium t-butoxide and stirring to form the
2 telechelic di-olefin polyisobutylene.

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

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

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

20 U.S. Patent Nos. 4,929,683 and 5,066,730 disclose a catalyst composed of a
21 complex of an organic ether and a Lewis acid, preferably boron trichloride that
22 can add olefin monomers to increase the molecular weight of the complex
23 from as low as 200 to in excess of a million. The patents also disclose
24 polymers of different molecular weights having useful end groups such as
25 halogens and specifically chloride, allyl, acryl or methacryl, acetate or formate.

26 U.S. Patent No. 5,219,948 discloses a method for preparing elastomeric
27 polymers comprising alpha-olefins or conjugated alkadienes by cationic
28 polymerization in the presence of titanium tetrachloride and an electron pair

1 donor selected from pyridine or a non-hindered alkylpyridine. The polymers
2 have very narrow, mono-modal molecular weight distribution.

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

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

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

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

22 U.S. Patent Application No. 10/433,439, Publication No. 2004/0015029 A1,
23 discloses a process for the preparation of polyisobutylenes in which at least
24 60 percent of the polymer chains have at least one olefinically unsaturated
25 terminal group, by cationic polymerization of isobutylene or isobutylene-
26 containing monomer mixtures in the condensed phase and in the presence of
27 an initiator system.

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

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

15 β -Proton elimination by Free Bases in the Living cationic Polymerization of
16 Isobutylene, by Young Cheol Bae and Rudolf Faust, Macromolecules,
17 Volume 30, 7341-7344 (1997). The authors investigated β -proton elimination
18 from quasi-living polyisobutylene, after observing *exo*-olefin formation in the
19 presence of 2,6-di-*tert*-butylpyridine (DTBP) of low purity. They ascribed
20 elimination to the presence of a sterically hindered cyclic imine base present
21 in the DTBP in a concentration of 6×10^{-6} moles per liter. They simulated this
22 impurity using 2-*tert*-butylpyridine (TBP) and discovered that the latter, when
23 added to the reactor at the start of the polymerization (i.e., in the presence of
24 monomer) resulted in about 65 percent elimination after 3 hours of reaction
25 time to produce exclusively *exo*-olefin. When the extent of elimination had
26 reached 20 percent or higher, significant coupling was observed from both ^1H
27 NMR and GPC analyses. Bae and Faust clearly considered that elimination
28 by sterically hindered bases such as TBP was undesirable and should be
29 avoided. The first paragraph of the paper was summarized as follows:
30 "Finally, strong bases may also eliminate β -protons, which should be

1 avoided." Later, they refer to the cyclic imine base impurity in DTBP as "the
2 culprit". Finally, they summarized the entire paper by saying that the
3 elimination process should be avoided for polymer preparation purposes,
4 although it might facilitate the measurement of kinetic rate constants: "While
5 β -proton elimination should be avoided for the synthesis of well-defined
6 macromolecules, if diffusion control of this process can be shown, it may
7 provide a novel method of establishing the concentration of active centers,
8 from which absolute propagation rate constants could be calculated."

9 SUMMARY OF THE INVENTION

10 The present invention is directed to a method for the preparation of polyolefins
11 containing exo-olefin chain ends. The method involves quenching a cationic
12 quasi-living polyolefin polymer system with one or more nitrogen-containing
13 five-membered aromatic ring compounds having at least two hydrocarbyl
14 substituents attached to the ring. The method also involves use of Lewis acid
15 and an electron donor, or a common ion salt or its precursor to form the
16 cationic quasi-living polyolefin polymer to which is added the quenching agent
17 to form the polymer product.

18 More specifically, the present invention is directed to a method for preparing a
19 polyolefin containing one or more exo-olefinic end groups on the polymer
20 chain, comprising quenching a cationic quasi-living polyolefin polymer system
21 with one or more nitrogen-containing five-membered aromatic ring
22 compounds selected from pyrroles and imidazoles having at least two
23 hydrocarbyl substituents attached to the aromatic ring, provided the nitrogen
24 containing five-membered aromatic ring is not:

- 25 (a) 2,4-dimethylpyrrole;
26 (b) 1,2,5-trimethylpyrrole;
27 (c) 2-phenylindole;
28 (d) 2-methylbenzimidazole;

- 1 (e) 1,2-dimethylimidazole;
2 (f) 2-phenylimidazole; and
3 (g) 2,4,5-triphenylimidazole.

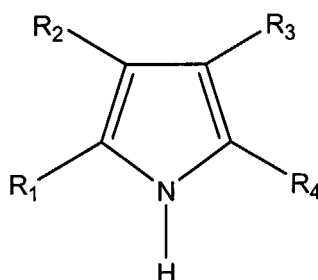
4 Preferably the quenching is carried out at a temperature in the range of from
5 about -130°C to about 10°C. More preferably the quenching is carried out at
6 a temperature from about -80°C to about 0°C, and even more preferably from
7 about -72°C to about -10°C. Most preferably the quenching is carried out at a
8 temperature in the range of from about -60°C to about -20°C.

9 Preferably the polyolefin is polyisobutylene.

10 In a preferred embodiment of the present invention the polyolefin is prepared
11 in situ.

12 The nitrogen-containing five-membered aromatic ring employed in an
13 embodiment of the present invention is a substituted pyrrole.

14 The substituted pyrrole employed in the method of the present invention has
15 the general formula:

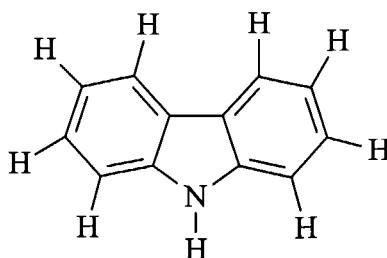


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17 wherein:

- 18 (a) R₁ and R₄ are independently alkyl containing one carbon atom to
19 about 20 carbon atoms, R₂ and R₃ are independently hydrogen or
20 alkyl containing one carbon atom to about 20 carbon atoms,
21 cycloalkyl of about 3 to about 7 carbon atoms, aryl of about 6 to

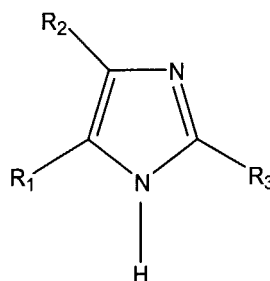
- 1 about 30 carbon atoms, alkaryl of about 7 to about 30 carbon
2 atoms, or aralkyl of about 7 to about 30 carbon atoms; or
- 3 (b) R₁ and R₂ form a fused aromatic ring of from 6 carbon atoms to 10
4 carbon atoms or an aliphatic ring of from 4 carbon atoms to about
5 8 carbon atoms, R₄ is alkyl containing one carbon atom to about
6 20 carbon atoms, and R₃ is hydrogen or alkyl containing one
7 carbon atom to about 20 carbon atoms, cycloalkyl of about 3 to
8 about 7 carbon atoms, aryl of about 6 to about 30 carbon atoms,
9 alkaryl of about 7 to about 30 carbon atoms, or aralkyl of about 7
10 to about 30 carbon atoms; or
- 11 (c) R₂ and R₃ form a fused aromatic ring of from 6 carbon atoms to
12 10 carbon atoms or an aliphatic ring of from 4 carbon atoms to
13 about 8 carbon atoms, and R₁ and R₄ are independently alkyl
14 containing one carbon atom to about 20 carbon atoms; or
- 15 (d) both R₁ and R₂, and R₃ and R₄, taken in pairs, independently form
16 a fused aromatic ring of from 6 carbon atoms to 10 carbon atoms
17 or an aliphatic ring of from 4 carbon atoms to about 8 carbon
18 atoms.
- 19 Preferably in the above method R₁ and R₄ are methyl and R₂ and R₃ are
20 hydrogen.
- 21 In another preferred embodiment of the above method R₁, R₂, R₃ and R₄ are
22 methyl.
- 23 In another preferred embodiment R₁ and R₂ are methyl and R₃ and R₄ form a
24 fused benzo ring.
- 25 In a preferred embodiment the substituted-pyrrole has the following formula:



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2 The nitrogen-containing five-membered aromatic ring employed in another
3 embodiment of the present invention is a substituted imidazole.

4 The substituted imidazole in the method of the present invention has the
5 general formula:



6

7 wherein R₃ is branched alkyl containing from about 4 carbon atoms to about
8 20 carbon atoms, and wherein

9 (a) R₁ and R₂ are independently hydrogen, alkyl of one carbon atom
10 to about 20 carbon atoms, cycloalkyl of about 3 to about 7
11 carbon atoms, aryl of about 6 to about 30 carbon atoms, alkaryl
12 of about 7 to about 30 carbon atoms, or aralkyl of about
13 7 to about 30 carbon atoms; or

14 (b) R₁ and R₂ form a fused aromatic ring of from 6 carbon atoms to
15 10 carbon atoms or an aliphatic ring of from 4 carbon atoms to 8
16 carbon atoms.

17

1 In another preferred embodiment of the above method R₁ is methyl, R₂ is
2 hydrogen and R₃ is tert-butyl.

3 Preferably the alkyl group on the nitrogen-containing five-membered aromatic
4 ring in the method of the present invention has from about one carbon atom to
5 about 20 carbon atoms. More preferably the alkyl group on the
6 alkyl-substituted nitrogen-containing five-membered aromatic ring has from
7 about one carbon atom to about 12 carbon atoms. Most preferably the alkyl
8 group on the alkyl-substituted nitrogen-containing five-membered aromatic
9 ring has from about one carbon atom to about 4 carbon atoms.

10 In the above method of the present invention the polyolefin is prepared by
11 quenching a quasi-living polyolefin polymer product containing tert-chloride
12 chain ends or a mixture comprising terminal olefinic chain ends and terminal
13 tert-chloride chain ends with the nitrogen-containing five-membered aromatic
14 ring in the presence of a Lewis acid.

15 In yet another embodiment of the present invention the polyolefin is prepared
16 by quenching a quasi-living polyolefin polymer product containing a terminal
17 tert-chloride chain end with the nitrogen-containing five-membered aromatic
18 ring in the presence of a Lewis acid.

19 Preferably the Lewis acid is a halide of titanium or boron. More preferably the
20 Lewis acid is a titanium halide. Most preferably the Lewis acid is titanium
21 tetrachloride. Preferred concentrations of the titanium tetrachloride exceed
22 2 times the combined concentrations of protic impurities, electron donor,
23 common ion salt or its precursor, and the quenching agent or quenching
24 agents.

25 The polyolefin product obtained using the method of the present invention has
26 exo-olefin chain ends in the range of one percent to 100 percent based on the
27 total chain ends. Preferably the polyolefin product has at least 3 percent exo-
28 olefin chain ends, more preferably at least 20 percent exo-olefin chain ends,
29 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-acetoxy-2-phenylpropane; 2-
18 propionyloxy-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-propionyloxy-2,4,4-trimethylpentane, 2-methoxy-2,4,4-
21 trimethylpentane, and 2-ethoxy-2,4,4-trimethylpentane.

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

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

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

6 The present invention is also directed to a further method for preparing a
7 polyolefin containing one or more exo-olefinic end groups on the polymer
8 chain, comprising quenching a cationic quasi-living polyolefin polymer system
9 with one or more nitrogen-containing five-membered aromatic ring
10 compounds selected from pyrroles and imidazoles having at least two
11 hydrocarbyl substituents attached to the aromatic ring, wherein the nitrogen-
12 containing five-membered aromatic ring compounds are pre-reacted with a
13 Lewis acid, and provided the nitrogen containing five-membered aromatic ring
14 is not:

- 15 (a) 2,4-dimethylpyrrole;
- 16 (b) 1,2,5-trimethylpyrrole;
- 17 (c) 2-phenylindole;
- 18 (d) 2-methylbenzimidazole;
- 19 (e) 1,2-dimethylimidazole;
- 20 (f) 2-phenylimidazole; and
- 21 (g) 2,4,5-triphenylimidazole.

22 In a preferred embodiment of the above method the Lewis acid is $TiCl_4$.

23 In a further preferred embodiment of the above method nitrogen-containing
24 five-membered aromatic ring compound is 2,5-dimethylpyrrole.

1 In another preferred embodiment of the above method nitrogen-containing
2 five-membered aromatic ring compound is 2,3-dimethylindole.

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4 DETAILED DESCRIPTION OF THE INVENTION

5 Definitions

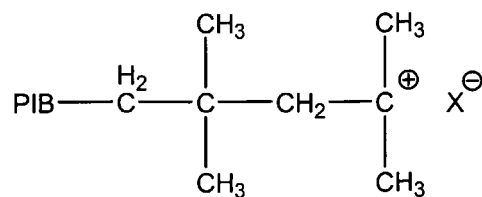
6 As used herein, the following terms have the following meanings unless
7 expressly stated to the contrary:

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

13 The term "aromatic or aliphatic fused ring" as used herein refers to the ring
14 formed by two adjacent carbon atoms on the pyrrole or imidazole ring, and the
15 ring thus formed is fused to the pyrrole or imidazole ring. An example of a
16 fused aromatic ring is a benzo group fused to the pyrrole ring or imidazole
17 ring. A fused aliphatic ring may be any cyclic ring structure fused to the
18 pyrrole ring or imidazole ring.

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

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



PIB Carbenium Ion

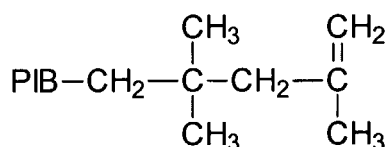
- 1
- 2 The term "chain transfer" as used herein refers to the cessation of growth of
 3 one polymerization chain with the possible initiation of another polymerization
 4 chain.
- 5 The term "common ion salt" as used herein refers to an ionic salt that is
 6 optionally added to a quasi-living cationic 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.



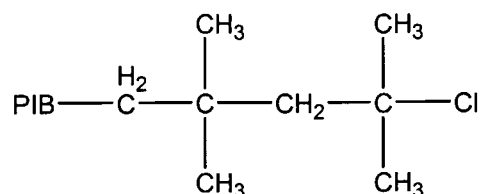
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16 The term "EAS product" as used herein refers to the product which results
17 when one polyisobutylene terminal carbenium ion reacts to form a covalent
18 bond with a single quenching agent molecule. EAS product contains in its
19 structure a residue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

20 The term "electron donor" as used herein refers to a basic and/or nucleophilic
21 substance added to the polymerization reaction that is either fully complexed
22 with the Lewis acid or fully non-complexed with the Lewis acid. The
23 concentration of electron donor exceeds the concentration of the protic
24 impurities, for example water.

1 The term "electrophilic aromatic substitution or EAS" as used herein refers to
2 the process by which the EAS product is produced.

3 The term "gem-dimethyl carbons" as used herein refers to the two methyl
4 carbons alpha to the carbenium ion or the chloride bonded carbon of the
5 polyolefin polymer chain end as depicted in the structure below.



6 PIB tert-Chloride

7 The term "hydrocarbyl" refers to an organic radical primarily composed of
8 carbon and hydrogen which may be aliphatic, alicyclic, aromatic or
9 combinations thereof, e.g., aralkyl or alkaryl. Such hydrocarbyl groups may
10 also contain aliphatic unsaturation, i.e., olefinic or acetylenic unsaturation, and
11 may contain minor amounts of heteroatoms, such as oxygen or nitrogen, or
12 halogens, such as chlorine.

13 The term "initiator" as used herein refers to the chemical moiety that starts the
14 polymerization and satisfies the valence at the head of the polymer chain, or
15 the molecule that provides that moiety. When a mono-functional initiator is
16 used, the chain end (CE) concentration equals the initiator concentration. For
17 a multi-functional initiator, when the functionality of the initiator equals x, then
18 the chain end concentration equals x times initiator concentration.

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

21 The term "living polymerization" as used herein refers to the polymerizations
22 that proceed in the absence of measurable chain transfer and chain
23 termination.

1 The term "nitrogen-containing five-membered aromatic ring" as used herein
2 refers to pyrroles and imidazoles containing at least one nitrogen atom in the
3 aromatic ring and a maximum of 2 nitrogen atoms in the aromatic ring, and
4 having from about 2 alkyl groups to about 4 alkyl groups containing from
5 about one carbon atom to about 20 carbon atoms attached to the ring. Some
6 examples of nitrogen-containing five-membered aromatic ring compounds
7 contemplated for use in the present invention are substituted-pyrroles.

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.

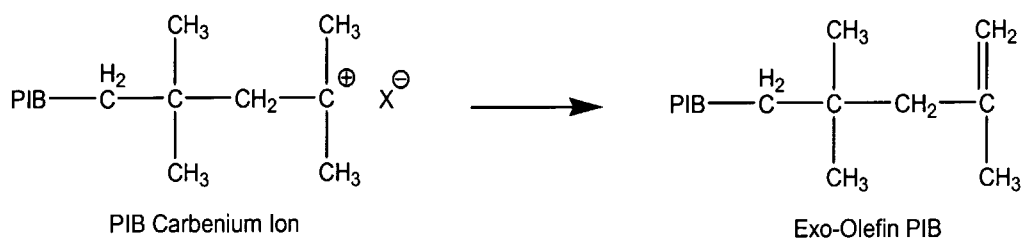
22 The term "termination" as used herein refers to the chemical reaction that
23 terminates polymerization process or the quenching reaction by destruction of
24 the Lewis acid.

25 The term "terminator" as used herein refers to the chemical compound that
26 terminates polymerization process or the quenching reaction, but may not
27 simultaneously initiate a new polymer chain. A number of alcohols may be
28 used as terminators.

1 The term "tert-chloride" refers to the 2-chloro-2-methylpropyl end group on a
2 polyolefin polymer chain.

3 Unless otherwise specified, all percentages are in weight percent.

4 It has been determined that the nitrogen-containing five-membered aromatic
5 ring compounds, such as substituted-pyrroles and substituted-imidazoles,
6 used as quenching agents in the preparation of polyolefin polymers of the
7 present invention are capable of quantitatively converting polyolefin polymer
8 endo-olefin chain ends and tert-chloride chain ends to the exo-olefin chain
9 ends. Without being bound by any theory it is believed that these quenching
10 agents selectively catalyze the elimination of a proton exclusively from the
11 gem-dimethyl carbon of the polyisobutylene chain end as shown below.



13 This result was unexpected since the quenching agents with very similar
14 structures are known in the prior art to quench quasi-living cationic
15 polymerizations by an electrophilic aromatic substitution (EAS) mechanism as
16 disclosed in U.S. Patent Application No. 10/600,898. Compounds which
17 provide the highest EAS yields are typically substituted with electron donating
18 groups located at strategic positions on the ring. It is believed that these
19 substituents provide stabilization for the Friedel-Craft intermediates formed
20 when, for example, polyisobutylene carbenium ions react with olefins in the
21 ring.

22 The quenching agents used in the present invention are able to quantitatively
23 convert polyolefin polymer containing olefinic chain ends and tert-chloride
24 chain ends to the exo-olefin chain ends independently of whether a
25 mono-functional initiator is used or a multi-functional. Furthermore, the rate of

1 conversion is the same for mono-functional and di-functional initiators. A 100
2 percent conversion was observed within 15 minutes after addition of
3 quenching agent to quasi-living cationic polyisobutylene chains initiated with
4 the mono-functional initiator, 2-chloro-2,4,4-trimethyl pentane. Similar
5 results were obtained with the di-functional initiator
6 1,3-di(2-chloro-2-propyl)-5-tert-butylbenzene.

7 Temperature dependence was observed for the preparation of the
8 polyisobutylene polymers containing a high concentration of exo-olefin chain
9 ends based on the total chain ends. It has been found that raising the
10 reaction temperature increases the yield of exo-olefin by suppressing
11 coupling. The data indicate that essentially quantitative conversion to exo-
12 olefin was achieved within 15 minutes at -60°C and -50°C with no coupling.
13 However, some coupling was observed at -70°C in the ¹H NMR and GPC
14 spectra. Coupling is seen as a peak centered at 4.82 just up-field from the
15 exo-olefin peak at 4.85 parts per million peak in the ¹H NMR spectrum and
16 also in the GPC spectrum, represented by a low elution volume shoulder on
17 the main peak.

18 In the method of the present invention, it is critical that certain principles be
19 observed when designing the conditions for quasi-living polymerization and
20 subsequent quenching. Without being bound by any theory, it is believed that
21 the desired elimination reaction is always in competition with the production of
22 coupled product through reaction of the carbenium ion with already-formed
23 exo-olefin. Therefore conditions must be sought that favor elimination and
24 disfavor coupling.

25 Higher reaction temperature has been found to favor elimination and disfavor
26 coupling. In quasi-living cationic polymerization of isobutylene, an equilibrium
27 exists between active, carbenium ions and dormant, tert-chloride chain ends.
28 When the temperature of the system is raised, this equilibrium increasingly
29 favors the dormant chain ends, but this should decrease the rates of
30 elimination and coupling to an equal extent. However, higher temperature

1 also should displace the equilibrium for the complex between quenching
2 agent and Lewis acid toward un-complexed quenching agent, which is
3 believed to be the agent that causes elimination. Raising the temperature thus
4 provides a competitive advantage to the desired reaction. Temperature
5 cannot be increased without limit, however, because the exo-olefin product
6 begins to be contaminated with small fractions of endo olefin.

7 Chain-end concentration and its relationship to quenching agent concentration
8 and Lewis acid concentration are also critical. Higher chain-end
9 concentrations, which become necessary when low molecular weights are
10 targeted, preferentially favor olefin coupling since that process is second order
11 in polymer chains. Therefore, to maintain the desired dominance of the rate
12 of elimination, quenching agent concentration and/or temperature must be
13 raised. Both of these changes, however, have the undesirable effect of
14 reducing the concentration of carbenium ions and thus retarding the
15 conversion of chain ends to exo-olefin. Increasing quenching agent
16 concentration diminishes the concentration of Lewis acid through the
17 formation of a complex between quenching agent and Lewis acid, and this
18 strongly diminishes carbenium ion concentration since the latter varies
19 approximately with the square of the Lewis acid concentration. Therefore,
20 recipes targeting low molecular weight must be formulated with higher
21 quenching agent concentrations and higher Lewis acid concentrations and
22 preferably run at higher temperatures. A expedient way to reduce coupling at
23 any target molecular weight is to dilute all reactants with additional diluent.

24 It has been found that in the presence of sufficient concentrations of a basic
25 electron donor, complete conversion to exo-olefin chain ends can be attained
26 when the quenching agent concentration is but a fraction of the quasi-living
27 chain end concentration. This suggests that under these conditions, the
28 quenching agent removes a proton from the carbenium ion and subsequently
29 transfers the proton to the electron donor, that is, the quenching agent acts
30 only as a catalyst for elimination, and the electron donor serves as proton

1 acceptor. The use of a less-than-stoichiometric concentration (relative to
2 chain ends) of quenching agent could confer economic advantages in
3 practicing the method the present invention. On the other hand, in the
4 absence of a basic electron donor, for example, when the latter is replaced by
5 a common ion salt or its precursor, it has been found that complete
6 conversion of the chain ends to exo-olefin requires a stoichiometric or higher
7 concentration of quenching agent. Under these conditions the quenching
8 agent serves both as catalyst and proton acceptor.

9 General Procedure for Preparation of Polyolefin Polymers
10 Containing Exo-olefin End Groups on the Chain

11 A typical procedure for the preparation of polyolefin polymers of the present
12 invention is given below:

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

16 The polymerization reaction is carried out under inert gas and in a
17 substantially anhydrous environment. The reactor is charged with the
18 following reactants:

- 19 1. a diluent,
- 20 2. an initiator,
- 21 3. an electron donor or common ion salt, or its precursor,
- 22 4. one or more monomers, and
- 23 5. a Lewis acid, which typically comprises a halide of titanium or boron;

24 The reaction mixture is equilibrated at the desired temperature, ranging from
25 about -130°C to about 10°C. The method of the present invention may be

1 carried out at any desired pressure, atmospheric, sub-atmospheric or
2 super-atmospheric pressure.

3 The progress of the polymerization reaction is monitored in situ by
4 determination of the amount of monomer remaining in the reaction mixture.
5 After high conversion of the monomer is observed, an aliquot is removed for
6 determination of the pre-quench chain end composition before addition of the
7 quenching agent. The polymerization reaction in the aliquot is terminated with
8 an appropriate alcohol equilibrated at the desired temperature.

9 6. One or more nitrogen-containing five-membered ring quenching agents
10 is added to the reaction mixture to quench the polymerization reaction.

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

15 The molar ratio of monomer to initiator is in the range from about 3:1 to about
16 20,000:1. Preferably the molar ratio of monomer to initiator is in the range of
17 about 5:1 to about 2,000:1. More preferably the molar ratio of monomer to
18 initiator is about 10:1 to 150:1. The mole ratio of monomer to initiator controls
19 the final molecular weight of the polyolefin.

20 The molar ratio of Lewis acid to chain ends is in the range from about 0.1:1 to
21 about 2,500:1. Preferably the molar ratio of Lewis acid to chain ends is in the
22 range of about 2:1 to about 200:1. More preferably the molar ratio of
23 Lewis acid to chain ends is about 2:1 to 15:1.

24 The molar ratio of Lewis acid to electron donor is in the range from about
25 1.1:1 to about 10,000:1. Preferably the molar ratio of Lewis acid to electron
26 donor is in the range of about 2:1 to about 100:1. More preferably the molar
27 ratio of Lewis acid to electron donor is about 4:1 to 30:1.

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

5 The molar ratio of quenching agent to chain ends is in the range from about
6 0.25:1 to about 20:1. Preferably the molar ratio of quenching agent to chain
7 end is in the range of about 0.5:1 to about 5:1. More preferably the molar ratio
8 of quenching agent to chain end is about 0.5:1 to 4:1.

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

14 The concentration of the exo-olefin chain ends, along with the concentration
15 of the endo-olefin and tert-chloride chain ends, is quantified using ^1H NMR.
16 GPC spectra are also obtained to qualitatively determine the amount of the
17 EAS product, the di-EAS product and the coupled product.

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

20 Diluents

21 Diluents influence the ionization equilibria and rates of exchange of growing
22 species through their polarity, which can be estimated from their dielectric
23 constants. Typically, solvents having low dielectric constants are preferred
24 since ion pairs are less dissociated. Suitable solvents include, but are not
25 limited to, low-boiling alkanes and alkyl mono or polyhalides with reasonably
26 low freezing points to be used at the preferred polymerization temperature.
27 Illustrative solvents include alkanes (generally C_2 to C_{10} alkanes, including
28 normal alkanes such as propane, normal butane, normal pentane, normal

1 hexane, normal heptane, normal octane, normal nonane and normal decane,
2 and branched alkanes including isobutane, isopentane, isohexane,
3 3-methylpentane, 2,2-dimethylbutane, 2,3-dimethylbutane and the like),
4 alkenes and alkenyl halides (such as vinyl chloride), carbon disulfide,
5 chloroform, ethylchloride, N-butyl chloride, methylene chloride,
6 methyl chloride, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, sulfur dioxide,
7 acetic anhydride, carbon tetrachloride, acetonitrile, neopentane, benzene,
8 toluene, methylcyclohexane, chlorobenzene, 1,1-dichloroethane,
9 1,1-dichloroethene, 1,2-dichloroethene, n-propyl chloride, iso-propyl chloride,
10 1,2-dichloropropane, or 1,3-dichloropropane, nitro-alkanes (such as
11 nitropropane) to name a few of the representative liquid diluents or solvents
12 useful in cationic polymerizations. Mixed solvents (for example combinations
13 of those listed above) can also be used.

14 Initiators

15 Initiator compounds for living and quasi-living carbocationic polymerization are
16 well known in the art. Initiators may be mono-functional or multi-functional
17 depending on the desired product. Mono-functional and di-functional initiators
18 are employed when the desired polymer is to be linear. For making star
19 polymers the initiator should have more than two reactive moieties. The
20 contemplated initiator compounds can be represented by the general formula
21 $(X'-CR_aR_b)_nR_c$ wherein R_a , R_b and R_c are independently comprises at least
22 one of alkyl, aromatic, alkyl aromatic groups, and can be the same or
23 different, and X' is an acetate, etherate, hydroxyl group, or a halogen. R_c has
24 a valence of n , and n is an integer of one to 4. Preferably R_a , R_b and R_c are
25 hydrocarbon groups containing one carbon atom to about 20 carbon atoms,
26 preferably one carbon atom to about 8 carbon atoms atoms. Preferably X' is a
27 halogen and more preferably chloride. In some instances it is preferable to
28 select the structure of R_a , R_b and R_c to mimic the growing species or
29 monomer, e.g. a 1-phenylethyl derivative for polystyrene or 2,4,4-trimethyl
30 pentyl derivative for polyisobutylene. Suitable compounds, include for

1 example, cumyl, dicumyl and tricumyl halides, particularly the chlorides, i.e.,
2 2-chloro-2-phenylpropane, i.e., cumyl chloride; 1,4-di(2-chloro-2-
3 propyl)benzene, i.e., di(cumylchloride); 1,3,5-tri(2-chloro-2-propyl)benzene,
4 i.e., tri(cumylchloride); 2,4,4-trimethyl-2-chloropentane; 2-acetyl-2-
5 phenylpropane, i.e., cumyl acetate; 2-propionyl-2-phenyl propane, i.e., cumyl
6 propionate; 2-methoxy-2-phenylpropane, i.e., cumylmethyl ether;
7 1,4-di(2-methoxy-2-propyl)benzene, i.e., di(cumylmethyl ether);
8 1,3,5-tri(2-methoxy-2-propyl)benzene, i.e., tri(cumylmethyl ether), and similar
9 compounds. Other suitable examples can be found in U.S. Patent
10 No. 4,946,899. Particularly preferred examples are 2-chloro-2,4,4-trimethyl
11 pentane (TMPCI), 1,3-di(2-chloro-2-propyl)benzene,
12 1,3,5 tri(2-chloro-2-propyl)benzene, and
13 1,3,-di(2-chloro-2-propyl)-5-tert-butylbenzene (bDCC).

14 The concentration of the chain ends in the total reaction mixture may be in the
15 range from about 0.0001 moles per liter to about 2.0 moles per liter.
16 Preferably the concentration of the chain ends is in the range from about
17 0.001 moles per liter to about 1.0 moles per liter. More preferably the
18 concentration of the chain ends is in the range from about 0.005 moles
19 per liter to about 0.5 moles per liter.

20 Electron Donors

21 Electron donors have been shown to convert traditional polymerization
22 systems into living and/or quasi-living cationic polymerizations systems. The
23 electron donor used in the present invention is not specifically limited to any
24 particular compound or class of compounds. Examples include pyridines and
25 alkyl amines, aprotic amides, sulfoxides, esters, metal compounds having an
26 oxygen atom bonded to a metal atom, and others. Pyridine compounds
27 include 2,6-di-*tert*-butylpyridine, 2,6-dimethylpyridine, 2,4-dimethylpyridine,
28 2,4,6-trimethylpyridine, 2-methylpyridine and pyridine. N,N-dimethylaniline
29 and N,N-dimethyltoluidine may be also employed. Amide compounds include
30 N,N-dimethylformamide, N,N-dimethylacetamide and N,N-diethylacetamide.

1 An example of a sulfoxide compound is dimethyl sulfoxide. Diethyl ether is an
2 example of an ether compound, and methyl acetate and ethyl acetate are
3 examples of ester compounds. Phosphate compounds such as trimethyl
4 phosphate, tributyl phosphate, triamide hexamethylphosphate may also be
5 employed. Oxygen-containing metal compounds such as tetraisopropyl
6 titanate are also useful as electron donors.

7 The concentration of the electron donors in the total reaction mixture may be
8 in the range from about 0.001 moles per liter to about 0.1 moles per liter.
9 Preferably the concentration of the electron donors is in the range from about
10 0.001 moles per liter to about 0.05 moles per liter. More preferably the
11 concentration of the electron donors is in the range from about 0.002 moles
12 per liter to about 0.02 moles per liter.

13 Common Ion Salts and Common Ion Salt Precursors

14 Common ion salts or salt precursors may be optionally added to the reaction
15 mixture in addition to or replacement of the electron donor. Typically, these
16 salts are used to increase the ionic strength, suppress free ions, and
17 beneficially interact with ligand exchange. Particularly preferred are common
18 ion salt precursors, for example tetra-*n*-butylammonium chloride (*n*-Bu₄NCl).

19 The concentration of the common ion salts or salt precursors in the total
20 reaction mixture may be in the range from about 0.0005 moles per liter to
21 about 0.05 moles per liter. Preferably the concentration of the common ion
22 salts or salt precursors is in the range from about 0.0005 moles per liter to
23 about 0.025 moles per liter. More preferably the concentration of the common
24 ion salt or salt precursors is in the range from about 0.001 moles per liter to
25 about 0.007 moles per liter.

26 Monomers

27 Suitable monomers for use in the method of the present invention are
28 hydrocarbon monomers, i.e., compounds containing only hydrogen and

1 carbon atoms, especially olefins and diolefins, and normally those having from
2 about 2 to about 20, but preferably from about 4 to about 8 carbon atoms. The
3 process can be employed for the polymerization of such monomers to
4 produce polymers of different, but uniform molecular weights, for example,
5 from about 300 to in excess of a million g/mol. Such polymers can be low
6 molecular weight liquid or viscous polymers having a molecular weight of from
7 about 200 to 10,000 g/mol, or solid waxy to plastic, or elastomeric materials
8 having molecular weights of from about a 100,000 to 1,000,000 g/mol, or
9 more. Suitable monomers include such compounds as isobutylene, styrene,
10 beta pinene, isoprene, butadiene, substituted compounds of the preceding
11 types, and others. Particularly preferred monomers are isobutylene,
12 2-methyl-butene, 3-methyl-1-butene, 4-methyl-1-pentene, and beta-pinene.
13 An even more preferred monomer is isobutylene. Mixtures of monomers may
14 be used.

15 The concentration of the monomers in the total reaction mixture may be in the
16 range from about 0.01 moles per liter to about 5.0 moles per liter. Preferably
17 the concentration of the monomers is in the range from about 0.1 moles
18 per liter to about 2.0 moles per liter. More preferably the concentration of the
19 monomers is in the range from about 0.3 moles per liter to about 1.0 moles
20 per liter. Most preferably the concentration of the monomers is 0.5 moles
21 per liter.

22 Lewis Acids

23 Lewis acids that are suitable as catalysts for purposes of the invention
24 include, but are not limited to, titanium and boron halides, particularly titanium
25 tetrachloride and boron trichloride. Use of the titanium halides and particularly
26 titanium tetrachloride is preferred. The strength of the Lewis acid and its
27 concentration should be adjusted for the particular monomer. Additionally, the
28 strength of these Lewis acids can be adjusted using nucleophilic additives. In
29 some instances these Lewis acids are also referred to as co-initiators.

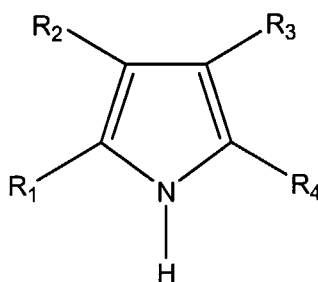
1 The amount of the Lewis acid present in the initiator system may vary.
2 However, it is desirable that the concentration of Lewis acid is sufficient to
3 achieve an appropriate rate of polymerization and quenching. The Lewis acid
4 concentration should not be so high as to precipitate the formed polymer.

5 The concentration of the Lewis acid in the total reaction mixture may be in the
6 range from about 0.001 moles per liter to about 3.0 moles per liter. Preferably
7 the concentration of the Lewis acid is in the range from about 0.005 moles
8 per liter to about 1.5 moles per liter. More preferably the concentration of the
9 Lewis acid is in the range from about 0.05 moles per liter to about 1.0 moles
10 per liter.

11 Quenching Agents

12 Quenching agents contemplated for use in preparation of the polyolefin in the
13 present invention are nitrogen-containing five membered aromatic ring
14 compounds such as substituted-pyrroles and substituted-imidazole.

15 The substituted-pyrrole employed in the method of the present invention has
16 the general formula:

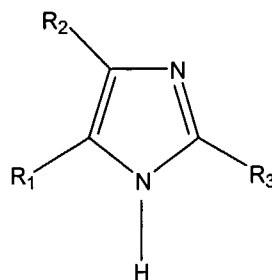


17

18 wherein:

19 (a) R_1 and R_4 are independently alkyl containing one carbon atom to
20 about 20 carbon atoms, R_2 and R_3 are independently hydrogen or
21 alkyl containing one carbon atom to about 20 carbon atoms,
22 cycloalkyl of about 3 to about 7 carbon atoms, aryl of about 6 to

- 1 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
- 3 (b) R_1 and R_2 form a fused aromatic ring of from 6 carbon atoms to 10
4 carbon atoms or an aliphatic ring of from 4 carbon atoms to about
5 8 carbon atoms, R_4 is alkyl containing one carbon atom to about
6 20 carbon atoms, and R_3 is hydrogen or alkyl containing one
7 carbon atom to about 20 carbon atoms, cycloalkyl of about 3 to
8 about 7 carbon atoms, aryl of about 6 to about 30 carbon atoms,
9 alkaryl of about 7 to about 30 carbon atoms, or aralkyl of about 7
10 to about 30 carbon atoms; or
- 11 (c) R_2 and R_3 form a fused aromatic ring of from 6 carbon atoms to 10
12 carbon atoms or an aliphatic ring of from 4 carbon atoms to about
13 8 carbon atoms, and R_1 and R_4 are independently alkyl containing
14 one carbon atom to about 20 carbon atoms; or
- 15 (d) both R_1 and R_2 , and R_3 and R_4 , taken in pairs, independently form
16 a fused aromatic ring of from 6 carbon atoms to 10 carbon atoms
17 or an aliphatic ring of from 4 carbon atoms to about 8 carbon
18 atoms.
- 19 The nitrogen-containing five-membered aromatic ring employed in another
20 embodiment of the present invention is a substituted imidazole.
- 21 The substituted imidazole in the method of the present invention has the
22 general formula:



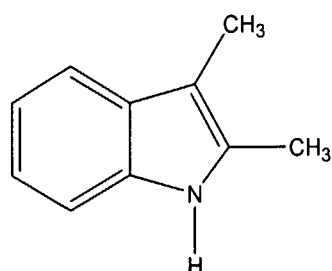
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1 wherein R_3 is branched alkyl containing from about 4 carbon atoms to about
2 20 carbon atoms, and wherein

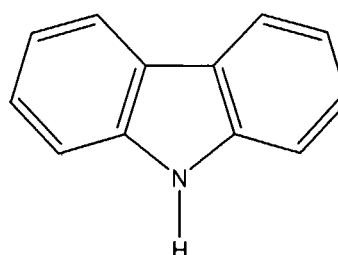
3 (a) R_1 and R_2 are independently hydrogen, alkyl of one carbon atom
4 to about 20 carbon atoms, cycloalkyl of about 3 to about 7
5 carbon atoms, aryl of about 6 to about 30 carbon atoms, alkaryl
6 of about 7 to about 30 carbon atoms, or aralkyl of about
7 7 to about 30 carbon atoms; or

8 (b) R_1 and R_2 form a fused aromatic ring of from 6 carbon atoms to
9 10 carbon atoms or an aliphatic ring of from 4 carbon atoms to 8
10 carbon atoms.

11 Structures of other nitrogen-containing five-membered aromatic ring
12 compounds that may be employed in the method of the present invention are
13 given below. The given structures are only intended as examples and in no
14 way limit the scope of the present invention.



15 2,3-dimethylindole



Carbazole

16 The concentration of the quenching agent in the total reaction mixture may be
17 in the range from about 0.0001 moles per liter to about 2.0 moles per liter.
18 Preferably the concentration of the quenching agent is in the range from about
19 0.001 moles per liter to about 1.0 moles per liter. More preferably the
20 concentration of the quenching agent is in the range from about 0.005 moles
21 per liter to about 0.5 moles per liter.

22 Terminators

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

4 EXAMPLES

5 Example 1

6 Preparation of Polyisobutylene Using a Mono-functional 7 Initiator and 2,5-dimethylpyrrole

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

17 85 milliliters hexane equilibrated at -60°C,

18 57 milliliters methyl chloride equilibrated at -60°C,

19 0.357 milliliters 2-chloro-2,4,4-trimethylpentane equilibrated at room
20 temperature, and

21 0.175 milliliters 2,6-dimethylpyridine equilibrated at room temperature.

22 The contents of the round-bottom flask were equilibrated and
23 Fourier Transform Infrared spectroscopy (FTIR) data were continuously
24 acquired for roughly 10 minutes to establish a reference absorbance at 887
25 cm^{-1} prior to addition of 6.1 milliliters isobutylene equilibrated at -60°C.

1 With continued stirring, next 1.37 milliliters titanium tetrachloride was charged
2 to the flask. The reaction was allowed to proceed to high conversion,
3 approximately 95 percent, as determined by in situ FTIR monitoring of the 887
4 cm^{-1} peak of isobutylene. The procedure used for the Fourier Transform
5 Infrared spectroscopy monitoring is given below. A pre-quench aliquot,
6 approximately 5-10 milliliter, was removed from the flask using a glass pipette
7 and charged into a scintillation vial containing 4 milliliters anhydrous methanol
8 equilibrated at -60°C to terminate the polymerization reaction. The aliquot
9 was used to determine a baseline for the quenching reaction with 2,5-
10 dimethylpyrrole and to provide a reference for structural and molecular weight
11 characterization in the absence of a quenching agent.

12 The polymerization reaction in the round-bottom flask was quenched by the
13 addition of 0.3 milliliters 2,5-dimethylpyrrole at an isobutylene conversion of
14 99 percent. Post-quench aliquots, approximately 5-10 milliliters, were
15 terminated at various time intervals after the addition of the 2,5-
16 dimethylpyrrole by being placed in scintillation vials containing 4 milliliters
17 anhydrous methanol equilibrated at -60°C .

18 The round-bottom flask was next charged with an appropriate amount
19 methanol equilibrated at -60°C to terminate the remaining polymerization
20 reaction mixture at 91.9 minutes after the addition of the 2,5-dimethylpyrrole.

21 The aliquot samples and the final terminated reaction mixture were allowed to
22 warm to room temperature, which allowed the volatile components to
23 evaporate. To each aliquot sample 1-2 milliliter hexane was added and the
24 polymer was precipitated in methanol. Polyisobutylene was recovered in
25 each aliquot sample and agitated using a vortex mixer with fresh methanol to
26 remove any remaining contaminants and the methanol was decanted.
27 Polyisobutylene samples recovered in each aliquot were placed in a vacuum
28 oven at room temperature for at least 24 hours to remove any remaining
29 solvents.

1 Table I below summarizes the reactant quantities used in Examples 1-20 and
2 Comparative Examples A-D.

3 Table II below summarizes the molarity of the reactants used in Examples 1-
4 20 and Comparative Examples A-D.

5 The following abbreviations are used for the reactants in Tables I and II
6 below:

7 TMPCl is an abbreviation of 2-chloro-2,4,4-trimethylpentane.

8 bDCC is an abbreviation of 1,3-di(2-chloro-2-propyl)-5-tert-butylbenzene.

9 25DMPy is an abbreviation of 2,5-dimethylpyrrole.

10 2345TeMPy is an abbreviation of 2,3,4,5-tetramethylpyrrole.

11 2MIn is an abbreviation of 2-methylindole.

12 23DMIn is an abbreviation of 2,3-dimethylindole.

13 125TMPy is an abbreviation of 1,2,5-trimethylpyrrole.

14 1MPy is an abbreviation of 1-methylpyrrole.

15 24DMPy is an abbreviation of 2,4-dimethylpyrrole.

16 2,5-DMPy/TiCl₄ is an abbreviation for the mixture of 2,5-dimethylpyrrole and
17 titanium tetrachloride.

18 The diluent used in Examples 1-20 and Comparative Examples A-E was a
19 mixture of hexane and methyl chloride in a volume ratio of 60:40.

20 Below are given descriptions of superscripts "a-h" used in Tables I and II
21 below:

22 a. These quenching agents are solids at room temperature. They were
23 first dissolved in approximately 10 milliliters pre-chilled MeCl, and the

- 1 resulting solution was charged to the reaction medium. The volume of
2 solvent used to dissolve the quenching agent is not included in total
3 reaction volume.
- 4 b. In these reactions, the 2,6-dimethylpyridine is replaced by the common
5 ion salt, tetra-n-butylammonium salt, and the masses in these cells
6 indicate the specific amount used. The salt was first dissolved in
7 approximately 10 milliliters pre-chilled methyl chloride and the resulting
8 solution was charged to the reaction medium.
- 9 c. In these reactions, the reactor was a 60 milliliter tube.
- 10 d. Numbers in parentheses are final concentrations after polymerization
11 reaction and pre-reacted quencher/ TiCl_4 were combined.
- 12 e. Final conditions after polymerization reaction and pre-reacted
13 quencher/ TiCl_4 were combined.
- 14 f. Pre-reacted with 1.062 g of TiCl_4 and 0.0475 liter diluent for 25 minutes
15 prior to addition to the polymerization reactor
- 16 g. Final volume after polymerization reaction and pre-reacted
17 quencher/ TiCl_4 were combined.
- 18 h. In these reactions, the 2,6-dimethylpyridine is replaced by the common
19 ion salt, tetra-n-butylammonium salt, and the molarity in these cells
20 indicate the concentration used. The salt was first dissolved in
21 approximately 10 milliliters pre-chilled methyl chloride and the resulting
22 solution was charged to the reaction medium.

Table I

Example	Initiator	Initiator (grams)	2,6-Dimethyl pyridine (grams)	Isobutylene (grams)	Titanium Tetrachloride (grams)	Quenching Agent	Quenching Agent (grams)	Total Reaction Volume (liters)	Total Diluent Volume (liters)	Temperature (°C)
1	TMPCl	0.3122	0.1607	4.2083	2.3616	25DMPy	0.2797	0.150	0.142	-60
2	TMPCl	0.8326	0.4286	11.2220	6.2977	25DMPy	0.7460	0.400	0.379	-50
3	TMPCl	0.4163	0.2143	5.6110	3.1489	25DMPy	0.3730	0.200	0.189	-40
4	bDCC	0.4726	0.3751	9.8193	5.5105	25DMPy	0.4383	0.350	0.332	-60
5	bDCC	3.5920	1.8110	47.4130	26.6078	25DMPy	3.3318	1.690	1.604	-60
6	bDCC	7.1715	1.7038	44.6075	25.0334	25DMPy	6.6506	1.590	1.509	-60
7	bDCC	0.9021	0.2143	5.6110	6.2977	25DMPy	0.8366	0.200	0.188	-60
8	bDCC	0.9021	0.2143	5.6110	11.0210	25DMPy	0.8366	0.200	0.185	-50
9	TMPCl	0.3122	0.1607	4.2083	2.3616	25DMPy	0.5595	0.150	0.142	-60
10	TMPCl	0.4163	0.2143	5.6110	6.4495	25DMPy	0.7460	0.200	0.187	-60
11	TMPCl	0.8326	0.4286	11.2220	6.2977	25DMPy	0.7460	0.400	0.379	-60
12	TMPCl	0.4163	0.2143	5.6110	3.1489	2345TeMPy ^a	0.4782	0.200	0.189	-60
13	TMPCl	0.4163	0.2143	5.6110	3.1489	23DMin ^a	0.5692	0.200	0.189	-60
14	TMPCl	0.4163	0.2143	5.6110	3.1489	25DMPy	0.1332	0.200	0.189	-60
15 ^b	TMPCl	0.4163	0.2779	5.6110	3.1489	25DMPy	0.1332	0.200	0.189	-60
16 ^b	TMPCl	0.4163	0.2779	5.6110	3.1489	25DMPy	0.3761	0.200	0.189	-60
17	TMPCl	0.3122	0.1607	4.2083	2.3616	25DMPy	0.2797	0.150	0.142	-70
18 ^c	TMPCl	0.0416	0.0214	1.1222	0.3149	Carbazole	0.094	0.02	0.018	-60
19	TMPCl	0.417	0.214	5.611	3.149 ^e	25DMPy/TiCl ₄	0.534 ^f	0.201 ^g	0.19	-60
20	TMPCl	0.4163	0.2143	5.6110	3.1489	2Min ^a	0.5142	0.200	0.189	-60
A ^c	TMPCl	0.083	0.043	1.122	0.630	Pyrrrole	0.040	0.040	0.038	-70
B ^c	TMPCl	0.083	0.043	1.122	0.630	1MPy	0.049	0.040	0.038	-70
C ^c	TMPCl	0.083	0.043	1.122	0.630	24DMPy	0.057	0.040	0.038	-70
D	TMPCl	0.4163	0.2143	5.6110	3.1489	125TMPy	0.4279	0.200	0.189	-60

Table II

Example	Initiator Type	Initiator (moles per liter)	2,6-Dimethyl pyridine (moles per liter)	Isobutylene (moles per liter)	Titanium Tetrachloride (moles per liter)	Quenching Agent Type	Quenching Agent (moles per liter)	Total Reaction Volume (liters)	Total Diluent Volume (liters)	Temperature (°C)
1	TMPCl	0.014	0.010	0.500	0.083	25DMPy	0.0196	0.150	0.142	-60
2	TMPCl	0.014	0.010	0.500	0.083	25DMPy	0.0196	0.400	0.379	-50
3	TMPCl	0.014	0.010	0.500	0.083	25DMPy	0.0196	0.200	0.189	-40
4	bDCC	0.0047	0.010	0.500	0.083	25DMPy	0.0132	0.350	0.332	-60
5	bDCC	0.0074	0.010	0.500	0.083	25DMPy	0.0207	1.690	1.604	-60
6	bDCC	0.0157	0.010	0.500	0.083	25DMPy	0.0440	1.590	1.509	-60
7	bDCC	0.0157	0.010	0.500	0.166	25DMPy	0.0440	0.200	0.188	-60
8	bDCC	0.0157	0.010	0.500	0.291	25DMPy	0.0440	0.200	0.185	-50
9	TMPCl	0.014	0.010	0.500	0.083	25DMPy	0.0392	0.150	0.142	-60
10	TMPCl	0.014	0.010	0.500	0.170	25DMPy	0.0392	0.200	0.187	-60
11	TMPCl	0.014	0.010	0.500	0.083	25DMPy	0.0196	0.400	0.379	-60
12	TMPCl	0.014	0.010	0.500	0.083	2345TeMPy ^a	0.0196	0.200	0.189	-60
13	TMPCl	0.014	0.010	0.500	0.083	23DMin ^a	0.0196	0.200	0.189	-60
14	TMPCl	0.014	0.010	0.500	0.083	25DMPy	0.007	0.200	0.189	-60
15 ⁿ	TMPCl	0.014	0.005	0.500	0.083	25DMPy	0.007	0.200	0.189	-60
16 ⁿ	TMPCl	0.014	0.005	0.500	0.083	25DMPy	0.0196	0.200	0.189	-60
17	TMPCl	0.014	0.010	0.500	0.083	25DMPy	0.0196	0.150	0.142	-70
18 ^c	TMPCl	0.014	0.01	1.00	0.083	Carbazole	0.028	0.02	0.018	-60
19	TMPCl	0.018 (0.014) ^d	0.013 (0.01) ^d	0.655 (0.5) ^d	0.072 (0.083) ^d	25DMPy/TiCl ₄	0.028 ^e	0.201 ^g	0.19	-60
20	TMPCl	0.014	0.010	0.500	0.083	2MIn ^a	0.0196	0.200	0.189	-60
A ^c	TMPCl	0.014	0.010	0.500	0.083	Pyrrole	0.015	0.040	0.038	-70
B ^c	TMPCl	0.014	0.010	0.500	0.083	1MPy	0.015	0.040	0.038	-70
C ^c	TMPCl	0.014	0.010	0.500	0.083	24DMPy	0.015	0.040	0.038	-70
D	TMPCl	0.014	0.010	0.500	0.083	125TMPy	0.0196	0.200	0.189	-60

1 Polyisobutylene samples were analyzed using ^1H NMR and GPC as
2 described below.

3 Procedure for Fourier Transform Infrared
4 Spectroscopy Monitoring of Isobutylene

5 The polymerization reaction was followed by Fourier Transform Infrared
6 spectroscopy monitoring of isobutylene peak at 887 cm^{-1} . This procedure is
7 described in Storey, R.F.; Thomas, Q.A. *Macromolecules*, 2003, 36,
8 5065-5071.

9 Procedure for Collecting ^1H NMR Data

10 ^1H NMR spectra were collected using a Bruker AC-300 (300MHz)
11 spectrophotometer using samples concentrations of 3 percent to 5 percent
12 (weight/weight) in CDCl_3 . ^1H NMR spectra were used for analysis of the end
13 groups. Fractions of exo-olefin, endo-olefin, tert-chloride and coupled olefin
14 chain ends were obtained using ^1H NMR integration as described in the
15 following section.

16 Procedure for Collecting GPC Data

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

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

22 The fractions of exo-olefin, endo-olefin, and tert-chloride chain ends, and
23 EAS, di-EAS, and coupled products in the polyisobutylene samples were
24 quantified using ^1H NMR integration. It was assumed that these six species
25 represent 100 percent of the chain ends. In some instances, EAS, di-EAS,
26 and coupled products were deemed to be absent by qualitative inspection of
27 the ^1H NMR spectrum, and for di-EAS and coupled products, by confirming

1 the absence of a shoulder on the low elution volume side of the main polymer
 2 peak in the GPC chromatogram. Two procedures are given below. The
 3 "General Procedure" was used when coupled product was detected; the
 4 "Special Procedure" was used when coupled product was deemed to be
 5 absent.

6 General Procedure

7 The fractional molar amount of each type of chain end was obtained using an
 8 equation analogous to the equation given below for determining the fractional
 9 amount of exo-olefin,

$$10 \quad F(\text{exo}) = (A_{\text{exo}}) / (A_{\text{exo}} + A_{\text{endo}} + A_{\text{tert-Cl}} + A_{\text{EAS}} + 2A_{\text{di-EAS}} + 2A_{\text{coupled}}) \quad (1)$$

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

$$14 \quad A_{\text{tert-Cl}} = (A_{1.65-1.72}/6) - A_{\text{endo}} \quad (2)$$

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

$$25 \quad A_{\text{coupled}} = (A_{5.0-4.75} - A_{4.5-4.75})/2 \quad (3)$$

26 where $A_{5.0-4.75}$ is the integrated area of the convoluted peaks associated with
 27 one of the exo-olefin protons and the two identical protons of the coupled

1 product, and where $A_{4.5-4.75}$ is the integrated area of the peak associated with
2 the other exo-olefin proton.

3 Special Procedure

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

$$7 \quad F(\text{exo}) = (A_{\text{exo}}) / (A_{\text{exo}} + A_{\text{endo}} + A_{\text{tert-Cl}} + A_{\text{EAS}} + 2A_{\text{di-EAS}}) \quad (1)$$

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

12

13 The ^1H NMR results obtained on the polyisobutylene samples prepared in
14 Example 1 above are given below in Table III as the mole percent of the total
15 end groups.

16 Table III

Quench Time (minutes after the addition of 2,5-dimethyl pyrrole)					
Pre-quench	15.9	30.9	45.3	61.3	75.3
Exo-olefin yield (mole %)					
8	99	100	100	100	100

17

18 The data in Table III shows that near quantitative conversion of chain ends to
19 exo-olefin was achieved within 15.9 minutes after the addition of the
20 2,5-dimethyl pyrrole.

Example 2Preparation of Polyisobutylene Using a Mono-functional
Initiator and 2,5-dimethylpyrrole

Polyisobutylene was prepared as described in Example 1 and the conditions listed in Table 1 above. Example 2 conditions were identical to those used in Example 1 above except the temperature was 10°C warmer and the reaction volume was increased from 150 milliliters to 400 milliliters.

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

The ¹H NMR results obtained on the polyisobutylene samples prepared in Example 2 above are given below in Table IV as the mole percent of the total end groups.

Table IV

Pre-quench (minutes)	Quench Time (minutes after the addition of 2,5-dimethyl pyrrole)		
	10	15	60
Exo-olefin yield (mole %)			
18	100	100	100

Example 3Preparation of Polyisobutylene Using a Mono-functional
Initiator and 2,5-dimethylpyrrole -
Reaction Temperature -40°C

Polyisobutylene was prepared according to the procedure of Example 1 using the conditions listed in Table 1. Example 3 conditions are identical to Example 1 conditions except that the temperature was -40°C, and the total volume of the reaction was 200 milliliters instead of 150 milliliters.

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

3 The results, shown in Table V, demonstrated that 2,5-dimethylpyrrole
4 quenching produced exo-olefin at -40°C without coupling; however, the overall
5 reaction was slower and additional time was allowed for complete quenching
6 to occur.

7 Example 4

8 Preparation of Polyisobutylene Using a Di-functional

9 Initiator and 2,5-dimethylpyrrole -

10 Target Molecular Weight 6,000 grams per mole

11 Polyisobutylene was prepared using the procedure described in Example 1
12 and the conditions listed in Table 1. Example 4 conditions were similar to
13 Example 1 conditions except that the mono-functional initiator,
14 2-chloro-2,4,4-trimethylpentane was replaced with a di-functional initiator,
15 1,3-di(2-chloro-2-propyl)-5-tert-butylbenzene and that the reaction volume
16 was increased from 150 milliliters to 350 milliliters. All conditions are given in
17 Table I.

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

20 The ¹H NMR data were used to calculate the exo-olefin as the mole percent of
21 the total chain ends in the polyisobutylene samples prepared in Example 4
22 above.

Example 5

Large Scale Preparation of Polyisobutylene Using a Di-functional

Initiator and 2,5-dimethylpyrrole -

Target Molecular Weight 4,000 grams per mole

Polyisobutylene was prepared using the procedure described in Example 4 and the conditions listed in Table 1. Example 5 conditions are identical to Example 4 conditions except that the initiator concentration and quenching agent concentration were increased. The reactor volume was increased and the target molecular weight was decreased to 4,000 g/mol.

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

The ¹H NMR data were used to calculate the exo-olefin as the mole percent of the total chain ends in the polyisobutylene samples prepared in Example 5 above.

Example 6

Large Scale Preparation of Polyisobutylene Using a Di-functional

Initiator and 2,5-dimethylpyrrole -

Target Molecular Weight 2,000 grams per mole

Polysisobutylene was prepared as described in Example 5 above, except the initiator concentration and quenching agent concentration were increased; exact conditions are given in Table I.

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

The ^1H NMR data were used to calculate the exo-olefin as the mole percent of the total chain ends in the polyisobutylene samples prepared in Example 6 above.

1 The results, shown in Table V, demonstrated that increasing the chain end
2 concentration and quenching agent concentration without a corresponding
3 increase in the Lewis acid concentration caused retardation in the rate of
4 exo-olefin formation.

5 Example 7

6 Effect of Titanium Tetrachloride Concentration 7 on Preparation of Polyisobutylene - 8 Target Molecular Weight 2,000 grams per mole

9 Polyisobutylene was prepared as in Example 6 above, except the
10 concentration of titanium tetrachloride was increased; exact conditions are
11 given in Table I.

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

14 The ^1H NMR data were used to calculate the exo-olefin as the percent of the
15 total chain ends in the polyisobutylene samples prepared in Example 7 above.

16 The results, shown in Table V, demonstrated that doubling the Lewis acid
17 concentration increased the rate of exo-olefin formation but coupling occurred
18 due to the high chain end concentration.

19 Example 8

20 Effect of Titanium Tetrachloride Concentration 21 and Temperature on Preparation of Polyisobutylene

22 Polyisobutylene was prepared according to the procedure of Example 7 using
23 the conditions listed in Table 1. Example 8 conditions are identical to
24 Example 7 conditions except that the concentration of titanium tetrachloride
25 was doubled and the temperature was raised to -50°C .

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

3 The ^1H NMR data were used to calculate the exo-olefin as the percent of the
4 total chain ends in the polyisobutylene samples prepared in Example 8 above.

5 The results, shown in Table V, demonstrated that increasing the Lewis acid
6 concentration and the temperature reduced the rate of coupling relative to
7 exo-olefin formation.

8 Example 9

9 Preparation of Polyisobutylene Using a Mono-functional 10 Initiator and 2,5-dimethylpyrrole - 11 Effect of Doubling Quenching Agent Concentration 12 with All Other Conditions Held Constant

13 Polyisobutylene was prepared according to the procedure of Example 1 using
14 the conditions listed in Table 1. Example 9 conditions are identical to
15 Example 1 conditions except that the concentration of 2,5-dimethylpyrrole was
16 doubled.

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

19 The ^1H NMR data were used to calculate the exo-olefin as the percent of the
20 total chain ends in the polyisobutylene samples prepared in Example 9 above.

21 The results, shown in Table V, demonstrated that increasing the quenching
22 agent concentration without a corresponding increase in the Lewis acid
23 concentration, caused retardation of the rate of exo-olefin formation.

Example 10

Preparation of Polyisobutylene Using a Mono-functional Initiator and 2,5-dimethylpyrrole - Effect of Doubling Quenching Agent Concentration and Doubling Lewis Acid Concentration with All Other Conditions Held Constant

Polyisobutylene was prepared according to the procedure of Example 1 using the conditions listed in Table 1. Example 10 conditions are identical to Example 1 conditions except that the concentration of 2,5-dimethylpyrrole was doubled and the concentration of titanium tetrachloride was doubled.

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

The ^1H NMR data were used to calculate the exo-olefin as the percent of the total chain ends in the polyisobutylene samples prepared in Example 10 above. The results, shown in Table V, demonstrated that an increase in the quenching agent concentration must be accompanied by a corresponding increase in the Lewis acid concentration to maintain an acceptable rate of exo-olefin formation.

Example 11

Preparation of Polyisobutylene Using a Mono-functional Initiator and 2,5-dimethylpyrrole - Effect of Reaction Scale

Polyisobutylene was prepared according to the procedure of Example 1 using the conditions listed in Table 1. Example 11 conditions are identical to Example 1 conditions except that the scale (total reaction volume) of Example 10 is approximately 3 times that of Example 1.

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

3 The ^1H NMR data were used to calculate the exo-olefin as the percent of the
4 total chain ends in the polyisobutylene samples prepared in Example 11
5 above. The results, shown in Table V, demonstrated that the scale of the
6 reaction essentially had no effect upon the results.

7 Example 12

8 Preparation of Polyisobutylene Using a Mono-functional 9 Initiator and 2,3,4,5-tetramethylpyrrole

10 Polyisobutylene was prepared using the conditions listed in Table 1,
11 according to the procedure of Example 1, except that 2,3,4,5-tetramethyl
12 pyrrole, a solid at room temperature, was added as a pre-chilled methyl
13 chloride solution. Example 12 conditions are similar to Example 1 conditions
14 except for identity of the quenching agent, its mode of introduction to the
15 reactor and the scale of the reaction.

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

18 The ^1H NMR data were used to calculate the exo-olefin as the percent of the
19 total chain ends in the polyisobutylene samples prepared in Example 12
20 above. This example illustrated a preferred embodiment of the invention.

21 The results, shown in Table V, demonstrated that 2,3,4,5-tetramethylpyrrole is
22 virtually identical in effectiveness compared to 2,5-dimethylpyrrole.

1 Example 13

2 Preparation of Polyisobutylene using a Mono-functional
3 Initiator and 2,3-dimethylindole

4 Polyisobutylene was prepared using the conditions listed in Table 1,
5 according to the procedure of Example 1, except that 2,3-dimethylindole, a
6 solid at room temperature, was added as a pre-chilled methyl chloride
7 solution. Example 13 conditions were similar to Example 12 conditions
8 except for identity of the quenching agent.

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

11 The ^1H NMR data were used to calculate the exo-olefin as the percent of the
12 total chain ends in the polyisobutylene samples prepared in Example 13.

13 Example 14

14 Preparation of Polyisobutylene Using a Mono-functional
15 Initiator and 2,5-dimethylpyrrole -
16 The Molar Ratio of Quenching Agent to Chain End 0.5 to 1.0

17 Polyisobutylene was prepared according to the procedure of Example 1 using
18 the conditions listed in Table 1. Example 19 conditions are identical to
19 Example 1 conditions except that the molar ratio of quenching agent to chain
20 end was 0.5 to 1.0 instead of 1.4 to 1.0 and the total reaction volume was
21 200 milliliters instead of 150 milliliters.

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

24 The results, shown in Table V, demonstrated that the moles of exo-olefin
25 produced exceeded the moles of 2,5-dimethylpyrrole charged to the reaction.
26 Without being bound by any theory, it is believed that 2,5-dimethylpyrrole

1 removed a proton from the carbenium ion and subsequently transferred the
2 proton to the electron donor. The quenching agent was serving as a catalyst
3 for elimination, and the electron donor was serving as a proton acceptor.

4 Example 15

5 Preparation of Polyisobutylene Using a Mono-functional
6 Initiator and 2,5-dimethylpyrrole -
7 Molar Ratio of Quenching Agent to Chain End 0.5 to 1.0
8 and Electron Donor Replaced by Common Ion Salt Precursor

9 Polyisobutylene was prepared according to the procedure of Example 1 using
10 the conditions listed in Table 1. Example 15 conditions were identical to
11 Example 14 conditions except that the electron donor was replaced by a
12 common ion salt precursor.

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

15 The results, summarized in Table V, demonstrated that in the absence of an
16 electron donor, the quenching agent served both as catalyst and proton
17 acceptor. They also showed that the reaction of the quenching agent with the
18 chains ends was quantitative since the yield of 32 percent exo-olefin plus the
19 yield of 34 percent coupled product indicated that a total of 49 percent of the
20 chains underwent elimination by the quenching agent. A high coupling
21 fraction occurred because depletion of the quenching agent caused the rate of
22 elimination to diminish dramatically relative to the rate of coupling. The results
23 suggest that complete conversion of the chain ends to exo-olefin, in the
24 absence of a basic electron donor, required a stoichiometric or higher
25 concentration of quenching agent.

Example 16

Preparation of Polyisobutylene Using a Mono-functional

Initiator and 2,5-dimethylpyrrole -

Molar Ratio of Quenching Agent to Chain End 1.4 to 1.0

and Electron Donor replaced by Common Ion Salt Precursor

Polyisobutylene was prepared according to the procedure of Example 1 using the conditions listed in Table 1. Example 16 conditions were identical to Example 15 conditions except that the molar ratio of quenching agent to chain end was 1.4 to 1.0 instead of 0.5 to 1.0.

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

The results, shown in Table V, further demonstrated that in the absence of an electron donor, the quenching agent served both as catalyst and proton acceptor. Conversion to exo-olefin was more nearly complete and coupling was considerably reduced because an excess of quenching agent was used.

Example 17

Preparation of Polyisobutylene Using a Mono-functional

Initiator and 2,5-dimethylpyrrole -

Reaction Temperature equals -70°C

Polyisobutylene was prepared according to the procedure of Example 1 using the conditions listed in Table 1. Example 17 conditions are identical to Example 1 conditions except that the temperature was -70°C instead of -60°C.

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

1 The results, shown in Table V, demonstrated that lower temperatures,
2 particularly -70°C and lower, undesirably promoted coupling.

3 Example 18

4 Preparation of Polyisobutylene Using a Mono-functional
5 Initiator and Carbazole

6 A four-neck 250 milliliter round-bottom flask was equipped with an overhead
7 mechanical stirrer and platinum resistance thermometer. This assembly was
8 immersed into a heptane bath at -60°C under dry nitrogen gas in a
9 substantially inert atmosphere glovebox. The flask was then charged with the
10 following reactants:

11 108 milliliters hexane equilibrated at -60°C,

12 72 milliliters methylchloride equilibrated at -60°C,

13 0.48 milliliters 2-chloro-2,4,4-trimethylpentane equilibrated at room
14 temperature,

15 0.23 milliliters 2,6-dimethylpyridine equilibrated at room temperature,

16 16.4 milliliters of isobutylene equilibrated at -60°C, and

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

18 With continued stirring, next 1.82 milliliters titanium tetrachloride was charged
19 to the flask. The reaction was allowed to proceed 12 minutes and then 20
20 milliliters of the polymerization solution was charged to four 60 milliliter test
21 tubes, equipped with threaded caps.

22 The polymerization was allowed to continue in each test tube for 4 additional
23 minutes (16 total reaction minutes) at which point 1 of the 4 tubes was
24 terminated with 5 milliliters of methanol to provide a comparative example
25 prior to addition of quenching agents. The remaining 3 solutions were

1 allowed to continue reacting for 8 minutes with intermittent shaking (24 total
2 reaction minutes), at which time 0.094 g carbazole was added to one of the
3 test tubes containing a reactive polymerization. After addition of carbazole, 1
4 of the remaining polymerizations was terminated with 5 milliliters of methanol
5 to provide another comparative example. The carbazole quenching reaction
6 was allowed to proceed 15 minutes at which time 5 milliliters of methanol was
7 charged in order to terminate the reaction. The final polymerization test tube
8 was then terminated with 5 milliliters of methanol to provide a final
9 comparative example. Non-quencher-containing reactions were used to
10 provide a comparative baseline for the quenching reactions and to provide
11 references for structural and molecular weight characterization in the absence
12 of a quenching agent.

13 Example 19

14 Preparation of Polyisobutylene Using a Mono-functional Initiator and 2,5- 15 dimethylpyrrole – Pre-reaction of 2,5-dimethylpyrrole with Titanium 16 Tetrachloride Prior to Quenching

17
18 The reactor configuration, ATR-FTIR probe and conduit, FTIR spectrometer
19 and spectroscopic method and analysis, constant-temperature heptane bath,
20 and glovebox were the same as described in Example 1. The 250 milliliter
21 reactor flask was charged with the following reactants:

22
23 85.5 milliliters hexane equilibrated at -60°C,
24 57 milliliters methyl chloride equilibrated at -60°C,
25 0.23 milliliters 2,6-dimethyl pyridine equilibrated at room temperature, and
26 0.48 milliliters 2-chloro-2,4,4-trimethyl pentane equilibrated at room
27 temperature.

28
29 A reference absorbance at 887 cm⁻¹ was established and then 8.18 milliliters
30 isobutylene equilibrated at -60°C was charged to the 250 milliliter reactor
31 flask.

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

2
3 28.5 milliliters hexane equilibrated at -60°C,
4 19 milliliters methyl chloride equilibrated at -60°C, and
5 0.57 milliliters 2,5-dimethylpyrrole equilibrated at room temperature.

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

7
8 Next, 1.2 milliliters titanium tetrachloride was charged to the 250 milliliter
9 reactor flask followed by the immediate of 0.62 milliliters titanium tetrachloride
10 to the 500 milliliter flask.

11
12 After a polymerization time of 25 minutes, a pre-quench aliquot (5-10 milliliter)
13 was removed from the contents of the 250 milliliter reactor flask and
14 terminated with 10-15 milliliters per-chilled methanol, and then the
15 polymerization was quenched by pouring the contents of the 500 milliliter flask
16 into the 250 milliliter reactor flask. Aliquots were removed at 1, 3, 5, 8, 15,
17 and 30 minutes and terminated with pre-chilled methanol. The balance of the
18 reactor contents was terminated at 60 minutes using pre-chilled methanol.

19
20 Polyisobutylene samples were collected and analyzed as described above for
21 the polyisobutylene samples obtained in Example 1. The data obtained are
22 summarized below in Table V.

23 24 Example 20

25 Preparation of Polyisobutylene Using a Mono-functional 26 Initiator and 2-methylindole - Effect of Indole Substitution 27 on the Quenching Reaction

28 Polyisobutylene was prepared using the conditions listed in Table 1,
29 according to the procedure of Example 1, except that 2-methylindole, a solid
30 at room temperature, was added as a pre-chilled methyl chloride solution.

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

3 The ^1H NMR data were used to calculate the exo-olefin as the percent of the
4 total chain ends in the polyisobutylene samples prepared in Example 20. The
5 data show that 2-methylindole yields a small amount of exo-olefin
6 polyisobutylene.

7 Comparative Examples A-C

8 Preparation of Polyisobutylene Using a Mono-functional 9 Initiator - Effect of Pyrrole Structure on the Quenching Reaction

10 Polyisobutylene was prepared according to the procedure of Example 18
11 using the conditions listed in Table 1. Comparative examples A-C conditions
12 were similar to Example 18 conditions except that the total reaction volume
13 was 40 milliliters, the quenching agent concentration was 0.015 M, and the
14 temperature was $-70\text{ }^{\circ}\text{C}$.

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

17 The results, shown in Table V, demonstrated that the placement of alkyl
18 substituents on the pyrrole ring had a significant influence on the structure of
19 the product. Most notably, reactions quenched with pyrrole and 1-methyl
20 pyrrole did not yield any exo-olefin polyisobutylene, but rather yielded EAS
21 and di-EAS products.

22 Comparative Example D

23 Preparation of Polyisobutylene Using a Mono-functional 24 Initiator - Effect of Pyrrole Structure on the Quenching Reaction

25 Polyisobutylene was prepared according to the procedure of Example 1 using
26 the conditions listed in Table 1. Comparative Example D conditions are very

- 1 similar to Example 1 conditions except for the total volume of the reaction and
- 2 the structure of the pyrrole compound.
- 3 The polyisobutylene samples were collected and analyzed as described
- 4 above for the Example 1 polyisobutylene samples.
- 5 The results, shown in Table V demonstrated that 1,2,5-trimethylpyrrole was
- 6 an ineffective quenching agent relative to 2,5-dimethylpyrrole at -60°C. The
- 7 major product obtained with the 1,2,5-trimethylpyrrole was tert-chloride
- 8 polyisobutylene.

Table V. Composition of Chain Ends after 60 minutes of Quenching

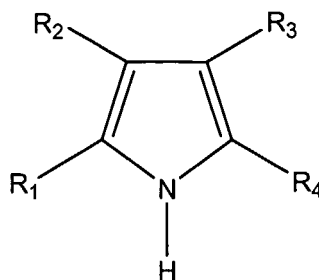
Examples	Quenching Agent	Exo-Olefin Chain End (mole %)	Endo-Olefin Chain End (mole %)	Tert-Cl Chain End (mole %)	EAS ^a Chain End (mole %)	Di-EAS Chain End (mole %)	Coupled Product (mole %)	Reaction Temp. (°C)
1	2,5-dimethylpyrrole	100	0	0	0	0	0	-60
2	2,5-dimethylpyrrole	100 ^a	0	0	0	0	0	-50
3	2,5-dimethylpyrrole	99	1	0	0	0	0	-40
4	2,5-dimethylpyrrole	100	0	0	0	0	0	-60
5	2,5-dimethylpyrrole	100	0	0	0	0	0	-60
6	2,5-dimethylpyrrole	28	0	72	0	0	0	-60
7	2,5-dimethylpyrrole	68	0	1	0	0	31	-50
8	2,5-dimethylpyrrole	83	0	0	0	0	17	-50
9	2,5-dimethylpyrrole	27	0	73	0	0	0	-60
10	2,5-dimethylpyrrole	99	0	1	0	0	0	-60
11	2,5-dimethylpyrrole	100 ^a	0	0	0	0	0	-60
12	2,3,4,5-tetramethylpyrrole	100	0	0	0	0	0	-60
13	2,3-dimethylindole	90	2	3	5	N/A	0	-60
14	2,5-dimethylpyrrole	74	0	15	0	0	11	-60
15	2,5-dimethylpyrrole	32	0	34	0	0	34	-60
16	2,5-dimethylpyrrole	84	0	6	0	0	10	-60
17	2,5-dimethylpyrrole	65	0	7	0	0	28	-70
18	Carbazole	23	<1	70	<4	<1	<3	-60
19	2,5-dimethylpyrrole/TiCl ₄	100	0	0	0	0	0	-60
20	2-methylindole	18	0	2	78	N/A	2	-60
A	Pyrrole ^b	0	0	0	33	66	0	-70
B	1-methylpyrrole	0	0	0	99	0	0	-70
C	2,4-dimethylpyrrole	12	0	72	13	0	2	-70
D	1,2,5-trimethylpyrrole	3	0	97	0	0	0	-60

^a Data taken from 45 minute quench time^b Data taken from 30 minute quench time

N/A Data not available.

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
5 nitrogen-containing five-membered aromatic ring compounds selected
6 from pyrroles and imidazoles having at least two hydrocarbyl
7 substituents attached to the aromatic ring, provided the nitrogen
8 containing five-membered aromatic ring is not:
- 9 (a) 2,4-dimethylpyrrole;
10 (b) 1,2,5-trimethylpyrrole;
11 (c) 2-phenylindole;
12 (d) 2-methylbenzimidazole;
13 (e) 1,2-dimethylimidazole;
14 (f) 2-phenylimidazole; and
15 (g) 2,4,5-triphenylimidazole.
- 16 2. The method of claim 1, wherein the polyolefin is prepared in situ.
- 17 3. The method of claim 1, wherein the nitrogen-containing five-membered
18 aromatic ring compound is a substituted pyrrole.
- 19 4. The method of claim 3, wherein the substituted pyrrole has the general
20 formula:



1

2

wherein:

3

(a) R₁ and R₄ are independently alkyl containing one carbon atom to about 20 carbon atoms, R₂ and R₃ are independently hydrogen or alkyl containing 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

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(b) R₁ and R₂ form a fused aromatic ring of from 6 carbon atoms to 10 carbon atoms or an aliphatic ring of from 4 carbon atoms to about 8 carbon atoms, R₄ is alkyl containing one carbon atom to about 20 carbon atoms, and R₃ is hydrogen or alkyl containing 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

10

11

12

13

14

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16

17

(c) R₂ and R₃ form a fused aromatic ring of from 6 carbon atoms to 10 carbon atoms or an aliphatic ring of from 4 carbon atoms to about 8 carbon atoms, and R₁ and R₄ are independently alkyl containing one carbon atom to about 20 carbon atoms; or

18

19

20

21

(d) both R₁ and R₂, and R₃ and R₄, taken in pairs, independently form a fused aromatic ring of from 6 carbon atoms to 10 carbon atoms or an aliphatic ring of from 4 carbon atoms to about 8 carbon atoms.

22

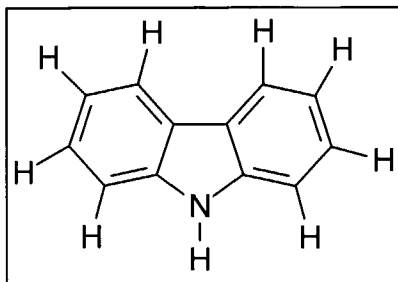
23

24

1 5. The method of claim 4, wherein R₁ and R₄ are methyl and R₂ and R₃
2 are hydrogen.

3 6. The method of claim 4, wherein R₁, R₂, R₃ and R₄ are methyl.

4 7. The method of claim 4, wherein the substituted-pyrrole has the
5 following formula:



6
7 8. The method of claim 1, wherein the polyolefin is polyisobutylene.

8 9. The method of claim 1, wherein the quenching is carried out at a
9 temperature in the range of from about -130°C to about 10°C.

10 10. The method of claim 9, wherein the quenching is carried out at a
11 temperature in the range of from -80°C to about 0°C.

12 11. The method of claim 10, wherein the quenching is carried out at a
13 temperature in the range of from -70°C to about -10°C

14 12. The method of claim 11, wherein the quenching is carried out at a
15 temperature in the range of from about -60°C to about -20°C.

16 13. The method of claim 4, wherein each alkyl group on the substituted
17 pyrrole ring has from one carbon atom to about 12 carbon atoms.

18 14. The method of claim 13, wherein each alkyl group on the substituted
19 pyrrole ring has from one carbon atom to about 4 carbon atoms.

20 15. The method of claim 1, wherein the polyolefin is prepared by
21 quenching a quasi-living polyolefin polymer product containing terminal

- 1 tert-chloride chain ends or a mixture of terminal tert-chloride chain ends
2 and terminal olefinic chain ends in the presence of a Lewis acid.
- 3 16. The method of claim 15, wherein the quasi-living polyolefin polymer
4 product contains terminal tert-chloride chain ends.
- 5 17. The method of claim 15, wherein the Lewis acid is a titanium or boron
6 halide.
- 7 18. The method of claim 17, wherein the Lewis acid is a titanium halide.
- 8 19. The method of claim 18, wherein the Lewis acid is titanium
9 tetrachloride.
- 10 20. The method of claim 1, wherein the quasi-living polyolefin polymer is
11 formed by contacting at least one cationically polymerizable monomer
12 with an initiator, in the presence of a Lewis acid under reaction
13 conditions suitable for quasi-living polymerization.
- 14 21. The method of claim 20, wherein the at least one cationically
15 polymerizable monomer comprises at least one of isobutylene, 2-
16 methyl-1-butene, 3-methyl-1-butene, 4-methyl-1-pentene, and beta-
17 pinene.
- 18 22. The method of claim 21, wherein the at least one cationically
19 polymerizable monomer is isobutylene.
- 20 23. The method of claim 20, wherein two different cationically
21 polymerizable monomers are employed.
- 22 24. The method of claim 20, wherein the initiator is multi-functional.
- 23 25. The method of claim 24, wherein the initiator is di-functional.
- 24 26. The method of claim 25, wherein the di-functional initiator comprises at
25 least one of 1,3-di(2-chloro-2-propyl)-5-tert-butylbenzene,

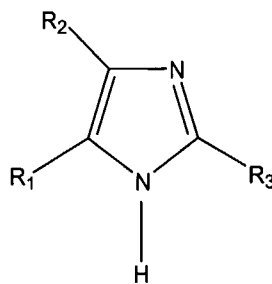
1 1,4-di(2-chloro-2-propyl)benzene, 1,4-di(2-acetoxy-2-propyl)benzene,
 2 1,3-di(2-acetoxy-2-propyl)-5-tert-butylbenzene,
 3 1,3-di(2-methoxy-2-propyl)-5-tert-butylbenzene and
 4 1,4-di(2-methoxy-2-propyl)benzene.

5 27. The method of claim 20, wherein the initiator is mono-functional.

6 28. The method of Claim 27, wherein the mono-functional initiator
 7 comprises at least one of 2-chloro-2-phenylpropane; 2-acetoxy-2-
 8 phenylpropane; 2-propionoxy-2-phenylpropane, 2-methoxy-2-
 9 phenylpropane, 2-ethoxy-2-phenylpropane, 2-chloro-2,4,4-
 10 trimethylpentane, 2-acetoxy-2,4,4-trimethylpentane, 2-propionoxy-
 11 2,4,4-trimethylpentane, 2-methoxy-2,4,4-trimethylpentane, and 2-
 12 ethoxy-2,4,4-trimethylpentane.

13 29. The method of claim 1, wherein the nitrogen-containing five-membered
 14 aromatic ring is a substituted imidazole.

15 30. The method of claim 29, wherein the substituted imidazole has the
 16 general formula:



17

18 wherein R₃ is branched alkyl containing from about 4 carbon atoms
 19 to about 20 carbon atoms, and wherein

20 (a) R₁ and R₂ are independently hydrogen, alkyl of one carbon
 21 atom to about 20 carbon atoms, cycloalkyl of about 3 to
 22 about 7 carbon atoms, aryl of about 6 to about 30 carbon

- 1 atoms, alkaryl of about 7 to about 30 carbon atoms, or
2 aralkyl of about 7 to about 30 carbon atoms; or
- 3 (b) R_1 and R_2 form a fused aromatic ring of from 6 carbon
4 atoms to 10 carbon atoms or an aliphatic ring of from 4
5 carbon atoms to 8 carbon atoms.
- 6 31. The method of claim 30, wherein R_1 is methyl, R_2 is hydrogen and R_3 is
7 tert-butyl.
- 8 32. The method of claim 1, wherein the molecular weight distribution,
9 M_w/M_n , of the polyolefin polymer is present in the range of about 1.01 to
10 about 3.0.
- 11 33. The method of claim 32, wherein the molecular weight distribution,
12 M_w/M_n , of the polyolefin polymer is present in the range of about 1.1 to
13 about 2.0.
- 14 34. The method of claim 33, wherein the molecular weight distribution,
15 M_w/M_n , of the polyolefin polymer is less than 1.5.
- 16 35. A method for preparing a polyolefin containing one or more exo-olefinic
17 end groups on the polymer chain, comprising quenching a cationic
18 quasi-living polyolefin polymer system with one or more
19 nitrogen-containing five-membered aromatic ring compounds selected
20 from pyrroles and imidazoles having at least two hydrocarbyl
21 substituents attached to the aromatic ring, wherein the nitrogen
22 containing five-membered aromatic ring compounds are pre-reacted
23 with a Lewis acid, and provided the nitrogen containing five-membered
24 aromatic ring is not:
- 25 (a) 2,4-dimethylpyrrole;
- 26 (b) 1,2,5-trimethylpyrrole;
- 27 (c) 2-phenylindole;

- 1 (d) 2-methylbenzimidazole;
- 2 (e) 1,2-di-methylimidazole;
- 3 (f) 2-phenylimidazole; and
- 4 (g) 2,4,5-tri-phenylimidazole.

5 36. The method of claim 35 wherein the Lewis acid is TiCl_4 .

6 37. The method of claim 35 wherein the nitrogen containing five-membered
7 aromatic ring compound is 2,5-dimethylpyrrole.

8 38. The method of claim 4, wherein the substituted pyrrole is 2,3-
9 dimethylindole.

10 39. The method of claim 1, wherein the polyolefin has at least 20 percent
11 exo-olefin end groups.

12 40. The method of claim 1, wherein the polyolefin has at least 50 percent
13 exo-olefin end groups.

14 41. The method of claim 1, wherein the polyolefin has at least 70 percent
15 exo-olefin end groups.