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(54) Title: POLYMERIZATION INITIATING SYSTEM AND METHOD TO PRODUCE HIGHLY REACTIVE OLEFIN FUNCTIONAL POLYMERS

(57) Abstract: A method for producing highly reactive olefin polymers wherein at least 50 mol. % of the polymer chains have terminal double bonds, and a novel polymerization initiating system for accomplishing same.

POLYMERIZATION INITIATING SYSTEM AND METHOD TO PRODUCE
HIGHLY REACTIVE OLEFIN FUNCTIONAL POLYMERS

5 RELATED APPLICATIONS

This application is a continuation of and claims priority to USSN 13/328,569, filed 16 December 2011 (16.12.2011), the entire teachings of which are incorporated herein by reference.

10

The invention is directed to a method for producing highly reactive olefin polymers wherein at least 50 mol. % of the polymer chains have terminal double bonds, and a novel polymerization initiating system for accomplishing same.

15 BACKGROUND OF THE INVENTION

The carbocationic polymerization of isobutylene (IB) is the subject of great scientific and industrial interest. The unique properties of polyisobutylene (PIB), a chemically stable fully saturated polymer make it a desirable material with applications ranging from medical devices to ashless (metal-free) dispersants/detergents suitable for use as motor oil and fuel additives. These ashless dispersants/detergents can be characterized as oil soluble surfactants with oligoamine end-groups derived from low molecular weight (number average molecular weight (M_n) of from about 500 to about 5000) PIB or polybutenes (copolymers of IB with C4 olefins) having olefinic end groups.

25 Two major industrial methods have been developed to produce low molecular weight IB homo or copolymers with olefinic end groups. The "conventional" method uses a C4 mixture and an aluminum halide based catalyst system and produces polybutenes with high tri-substituted olefinic contents. Due to the low reactivity of the tri-substituted olefinic end groups, polybutenes need to be chlorinated to react with maleic anhydride to give polybutenylsuccinic anhydride, which is subsequently reacted with oligoalkylenimines to yield polybutenylsuccinimide-type ashless dispersant/detergent. The other method employs a pure IB feed stream and a BF_3 complex-based catalyst with either alcohols, or ethers in a polymerization reaction run

at low temperature, which yields highly reactive PIB (HR PIB) with high exo-olefinic end-group contents. In contrast to the tri-substituted olefins of conventional polybutenes, PIB exo-olefins readily react with maleic anhydride in a thermal "ene" reaction to produce PIB succinic anhydride and subsequently

5 polyisobutenylsuccinimide ashless dispersants. Because the final product does not contain chlorine, HR PIB is more desirable than conventional polybutenes. However, BF_3 is difficult to handle and the polymer may contain fluorine. Further, as noted above, this method requires a pure IB feed steam and low temperature (e.g., -30°C) and therefore results in a more expensive product.

10 The above-described commercial process for producing HR PIB has been reported by US Pat. No. 5,408,018 (and DE-A 2702604) to Rath. A range of process enhancements were subsequently reported in. US Pat. Nos, 6,407,186, 6,753,389, and 7,217,773 to Rath et al. and US Pat. Nos. 6,846,903, 6,939,943 and 7,038,008 to Wetling et al. A modified process using a different temperature regime and a low 15 residence time was also previously described (e.g., US Pat. Nos. 6,562,913 and 6,683,138 to Baxter et al.). All of these disclosures describe polymerizations carried out with BF_3 catalyst and an alcohol or ether co-catalyst. Such catalytic processes can leave residual fluorine in the polymer especially when utilized with the commonly available mixed C_4 Raffmate I stream. The presence of even small amounts of 20 fluorine cause problems in downstream functionalization reactors due to the release of HF and therefore require expensive fluorine removal post-treatment.

Many attempts have therefore been made to find other methods for producing HR PIB. For instance PIB with nearly quantitative *exo-ohfm* endgroup has been obtained by reacting *tert*-chloride-terminated PIB (PIB-Cl) with strong bases such as 25 potassium *teri*-butoxide and alkali ethoxides in refluxing tetrahydrofuran (THF) for 20-24 h, (Kennedy, J.P.; Chang, V.S.C.; Smith, R.A.; Ivan, B. *Polym. Bull.* 1979, **1**, 575); quenching living PIB with methyltrimethylsilane, (Nielsen, L.V.; Nielson, R.R.; Gao, B.; Kops, J.; Ivan, B. *Polymer* 1997, **38**, 2528.); quenching living PIB with a hindered base (e.g., 2,5-dimethylpyrrole or 1,2,2,6,6-pentamethylpiperidine), 30 (Simison, K.L.; Stokes, CD.; Harrison, J.J.; Storey, R.F. *Macromolecules* 2006, **39**, 2481); quenching living PIB with an alkoxy silane or an ether compound (Storey, R.F.; Kemp, L.L. U.S. Patent Application Publication, 2009/031 8624 A1, Dec. 24, 2009); and reacting living PIB with a mono-sulfide followed by decomposition of the resulting sulfonium salt with a base (Morgan, D.L.; Stokes, CD.; Meierhoefer, M.A.;

Storey, R.F. *Macromolecules* 2009, 42, 2344). However, all of the above methods are expensive as they involve living cationic polymerization at low temperature in a moderately polar solvent and employ expensive reactants.

A broad disclosure of halogen -free metal catalysts based on oxides of Groups 5 V and VI of the Periodic Table of Elements was described in US Pat. No. 6,441,110 to Sigwart et al., but these catalysts were heterogenous and gave poor monomer conversions, with only modest amounts of exo-olefins. Another catalyst system, based on metals from the 3rd to the 12th periods of the periodic system of elements with nitrile ligands and weakly coordinating anions was described in US Pat. No. 7,291,758 to Bohnepoll et al. These catalysts were used only in a polar dichloromethane solution; not in an apolar, all-hydrocarbon media.

More recently it has been reported that $\text{AlCl}_3\text{-OBu}_2$ complexes in conjunction with a range of initiators or adventitious water initiate the polymerization of IB and in polar solvent (CH_2Cl_2 /hexane 80/20 v/v) yield PIB with high exo-olefmic end groups up to 95% in a range of temperatures (-60 to -20 °C) (Vasilenko, I.V.; Frolov, A.N.; Kostjuk, S.V. *Macromolecules* 2010, 43(13), 5503-5507). Independently, similar results were reported with adventitious water as initiator in conjunction with AlCl_3 or FeCl_3 dialkyl ether complexes in CH_2Cl_2 at temperatures ranging from -20 to 20°C (Lui, Q.; Wu Y.; Zhang, Y.; Yan. P.F.; Xu, R.W. *Polymers* 2010, 51, 5960-5969).

20 However, due to the need for the polar solvent CH_2Cl_2 the commercial potential of this method is questionable. $\text{AlCl}_3\text{-OBu}_2$ has been reported to produce PIB with terminal vinylidene bonds in the absence of solvent and without added initiator, or with water as an added initiator (USPG 2011/0201772A1 of Konig et al.). However, none of the conventional cationic initiators such as alkyl halides, ethers, esters, 25 alcohols and Bronsted acids were found to initiate directly the polymerization in apolar media with AlCl_3 . Therefore there remains a need for a robust and economic method for the preparation of highly reactive PIB or polybutene in a non-polar hydrocarbon media.

30 SUMMARY OF THE INVENTION

It has now been found that conventional cationic initiators used in conjunction with certain combinations of Lewis acid/Lewis base complexes initiate the polymerization of IB in hydrocarbon solvents at temperatures of -30°C to +50°C and provide high yields of highly reactive PIB.

The catalyst of the catalyst-initiator system of the present invention comprises a Lewis acid catalyst ($MR''Y_n$) complexed to a Lewis base (B) in an apolar medium. The affinity of the Lewis acid for the Lewis base should be such that the Lewis acid can interact at least partially with a conventional cationic initiator (RX) enabling the 5 formation of R^+ , which initiates cationic polymerization of isobutylene. The initially complexed Lewis base should be capable of effecting rapid deprotonation of the growing carbocation chain to form an exo-olefin prior to isomerization of the cationic chain or diffusion of the base into free solution. If the Lewis base does not complex to the Lewis acid, at least initially, deprotonation of the growing carbocation will not 10 be sufficiently rapid relative to isomerization to give the desired high yields of exo-olefin. If the interaction of the Lewis acid and the Lewis base is so strong that it prevents interaction with a conventional initiator, polymerization will be inefficient or not occur at all. The Lewis acid or Lewis acid-Lewis base complex must further be capable of interacting with a conventional initiator either in the presence or absence of 15 adventitious water. Catalysts with which monomer conversion is substantially dependent on adventitious water, even in the presence conventional initiators, as evidenced by complete loss of conversion in the presence of a proton trap (e.g., 2, 6-ditert-butylpyridine or "DTBP"), are not suitable.

20 DETAILED DESCRIPTION OF THE INVENTION

Lewis acid catalysts useful in the practice of the present invention can be represented by the general formula ($MR''_m Y_n$), wherein M is selected from Fe, Ga, Hf, Zr and W; preferably Ga or Fe, more preferably Ga; R'' is a hydrocarbyl group, preferably a C_1 to C_8 hydrocarbyl group, more preferably a C_1 to C_8 alkyl group; m is 25 0 or an integer of 1 to 5, preferably 0 or 1, more preferably 0; Y is halogen (F, Cl, Br), preferably either Cl or Br, more preferably Cl, and n is an integer of 1 to 6, preferably 3 to 5; with the proviso that $m+n$ is equal to the valency of M. As used herein, the term "hydrocarbyl" means a chemical group of a compound that contains hydrogen and carbon atoms and that is bonded to the remainder of the compound directly via a 30 carbon atom. The group may contain one or more atoms other than carbon and hydrogen ("hetero atoms") provided they do not affect the essentially hydrocarbyl nature of the group.

The Lewis base (B) is selected from oxygen- and/or sulfur-containing nucleophiles, such as ethers, alcohols, ketones, aldehydes and esters, and sulfur-

containing nucleophiles such as thioethers and thioketones. Specific examples of suitable Lewis bases include acyclic dihydrocarbyl ethers, wherein each hydrocarbyl group is independently selected from C₁ to C₁₂ hydrocarbyl, cyclic ethers having a 5 to 7 membered cyclic group, dihydrocarbyl ketones, wherein each hydrocarbyl group 5 is independently selected from C₁ to C₁₂ hydrocarbyl, C₁ to C₁₂ aliphatic alcohols, C₁ to C₁₂ aliphatic aldehydes, acyclic aliphatic esters wherein each hydrocarbyl group is independently selected from C₁ to C₁₂ hydrocarbyl, cyclic aliphatic esters having a 5 to 7 membered cyclic group, dihydrocarbyl sulfides, wherein each hydrocarbyl group is independently selected from C₁ to C₁₂ hydrocarbyl and dihydrocarbyl thiocarbonyl 10 compounds, wherein each hydrocarbyl group is independently selected from C₁ to C₁₂ hydrocarbyl. The hydrocarbyl groups of the above Lewis bases are preferably alkyl groups and are more preferably C₁ to C₄ alkyl. The hydrocarbyl groups and cyclic aliphatic groups of the above Lewis bases may each independently be substituted with a heteroatom or a heteroatom-containing moiety and may further be substituted with 15 other substituent groups that do not interfere significantly with the ability of such compounds to function as a Lewis base (e.g., C₁ to C₄ "lower alkyl" groups).

An "initiator" is defined as a compound that can initiate polymerization, in the presence or absence of adventitious water and in the presence of a proton trap. The initiator of the present invention (RX) comprises a hydrocarbyl R group wherein the 20 carbon linking group R to X is tertiary, benzylic or allylic, which hydrocarbyl group can form a stable carbocation (e.g., t-butyl⁺), and an X group, which is a halogen.

The polymerization medium must be a substantially or completely apolar medium, such as a mixture of hexanes or saturated and unsaturated C₄ hydrocarbons,

In the polymerization process of the present invention, the feedstock may be 25 pure isobutylene or a mixed C₄ hydrocarbyl feedstock containing isobutylene, such as a C₄ cut resulting from the thermal or catalytic cracking operation of, for example, naphtha. Thus, suitable feedstocks will typically contain at least 10%, and up to 100% isobutylene, by mass, based on the total mass of the feed. In addition to isobutylene, conventional C₄ cuts suitable for use as feedstocks that are of industrial 30 importance typically will contain between about 5% and about 50% butene-1, between about 2% and about 40% butene-2, between about 2% and about 60% isobutane, between about 2% and about 20% n-butane, and up to about 0.5% butadiene, all percentages being by mass, based on the total feed mass. Feedstocks containing isobutylene may also contain other non-C₄ polymerizable olefin monomers in minor

amounts, e.g., typically less than 25%, preferably less than about 10%, and most preferably less than 5%, such as propadiene, propylene and C₅ olefins. The C₄ cut may be purified by conventional means to remove water, polar impurities and dienes.

The term "polybutene", as employed herein is intended to include not only

5 homopolymers of isobutylene, but also copolymers of isobutylene and one or more other C₄ polymerizable monomers of conventional C₄ cuts as well as non-C₄ ethylenically unsaturated olefin monomers containing 5 carbon atoms, provided such copolymers contain typically at least 50%, preferably at least 65%, and most preferably at least 80% isobutylene units, by mass, based on the polymer number

10 average molecular weight (\overline{M}_n).

The Lewis acid and Lewis base can be complexed by, for example, dissolving the Lewis acid in a solvent (e.g., dichloromethane or 1, 2-dichloroethane) to form a solution and then adding the Lewis base to the solution, while the solution is stirred. The complex may be added to the polymerization medium with the solvent;

15 alternatively, the solvent may be removed prior to the addition of the complex to the polymerization medium.

The molar ratio of Lewis acid to Lewis base in the complex will typically be maintained within a range of from about 1:0.5 to about 1:2, preferably from about 1:0.7 to about 1:1.5, more preferably from about 1:0.8 to about 1:1.2, such as from

20 about 1:0.9 to about 1:1.1 or 1:1.

The amount of the Lewis acid-Lewis base complex employed in the process of the present invention can be controlled, in conjunction with the concentration of initiator and monomer, reaction time and temperature, to achieve the target \overline{M}_n of the polybutene polymer product, the conversion of butene and yield of polybutene. In

25 view of the above, the Lewis acid-Lewis base complex is typically employed in an amount sufficient to contact the butene monomer in a liquid phase reaction mixture at a concentration of millimoles of Lewis acid-Lewis base complex per liter of reaction mixture of from about 1 mM to about 200 mM, preferably from about 5 mM to about 100 mM, and more preferably from about 10 mM to about 50 mM, such as from about

30 10 mM to about 30 mM.

The initiator will typically be employed in an amount sufficient to contact the butene monomer in a liquid phase reaction mixture at a concentration of millimoles of initiator per liter of medium, and independent from the amount of Lewis acid-Lewis

base complex, of from about 1mM to about 200 mM, preferably from about 5 mM to about 100 mM, and more preferably from about 10 mM to about 50 mM, such as from about 10 mM to about 30 mM.

The polymerization reaction can be conducted batch-wise, semi-continuously, 5 or continuously. On an industrial scale, the polymerization reaction is preferably conducted continuously. Conventional reactors, such as tubular reactors, tube-bundle reactors or loop reactors, ie, tube or tube-bundle reactors with continuous circulation of the reaction material, may be used.

The polymerization reaction is conducted in the liquid phase to induce linear 10 or chain-type polymerization, as opposed to ring or branch formation. Thus, if a feed is used that is gaseous under ambient temperature, it is preferred to control the reaction pressure and/or dissolve the feed in an inert solvent or liquid diluent, in order to maintain the feed in the liquid phase. Typical C₄ cuts comprising the feed are liquid under pressure and do not require a solvent or diluent. Typical diluents suitable 15 for use with the process include C₃ to C₆ alkanes, such as propane, butane, pentane, isobutane and the like.

The Lewis acid-Lewis base complex is typically introduced into the reactor as a liquid partially or completely dissolved in a solvent, or as a solid. Polymerization is 20 preferably conducted at a pressure sufficient to maintain the C₄ feed in a liquid state at the reaction temperature, or at higher pressures. The initiator may be introduced to the monomer feed or the reaction mixture in liquid form together with the Lewis acid-Lewis base complex or, preferably, is introduced to the monomer feed or the reaction mixture in liquid form by a line separate from the Lewis acid-Lewis base complex addition line.

25 The liquid phase reaction mixture temperature is controlled by conventional means to be typically from about -30°C to about +50°C, preferably from about -10°C to about +30°C, more preferably from 0°C to about +20°C, such as from 0°C to about +10°C.

The residence time of the butene to be polymerized may be from about 5 30 seconds to several hours, but will typically be from about 1 to about 300 minutes, such as 2 to about 120 minutes, preferably from about 5 to about 60 minutes.

In order to insure even distribution of the catalyst within the reactor, turbulent flow of the reactor contents can be generated by mixing, or with suitable baffles, such

as baffle plates or oscillating baffles, or by dimensioning the reactor tube cross sections so that a suitable flow velocity is established.

The process of the present invention is typically conducted in a manner achieving an isobutylene conversion in the range of from about 20% up to about 5 100%, preferably from about 50% to about 100%, and more preferably from about 70% to about 100%. The combined use of temperature control and catalyst feed rate permits formation of polybutenes having a \overline{M}_n of from about 400 Daltons to about 4000 Daltons, preferably from about 700 Daltons to about 3000 Daltons, more preferably from about 1000 Daltons to about 2500 Daltons; a molecular weight 10 distribution (MWD) of typically from about 1.1 to about 4.0, preferably from about 1.5 to about 3.0, an exo-oiefin content of greater than 50 mol. %, preferably greater than 60 mol. %, more preferably greater than 70 mol. %, such as from about 80 mol. % to about 95 mol. %; a tetrasubstituted olefin content of less than about 20 mol. %, such as less than about 15 mol. %, preferably less than about 10 mol. %, 15 more preferably less than about 5 mol. %; and a chlorine content of less than about 10 mol. %, such as less than about 5 moi. %, preferably less than about 2 mol. %, more preferably less than about 1 moi. %, based on the total moles of polymer.

Once the target molecular weight of the polymer is achieved, the polymer product can be discharged from the reactor and passed into a medium that deactivates 20 the polymerization catalyst and terminates the polymerization. Suitable deactivation media include water, amines, alcohols and caustics. The polyisobutylene product can then be separated by distilling off the remaining C_4 hydrocarbons and low molecular weight oligomers. Preferably residual amounts of catalyst are removed, usually by washing with water or caustic.

25 This invention will be further understood by reference to the following examples, which are not intended, and should not be construed as listing all possible embodiments within the scope of the invention.

EXAMPLES

30 Preparation of Lewis acid (LA) Lewis base (LB) complex

All operations were performed in a dry N_2 atmosphere MBraun 150-M glove box (Innovative Technology Inc., Newburyport, MA). LA (3.9 mmol) was first dissolved in 3.36 ml of dichloromethane in a 20 ml vial equipped with a screw top with a septum. The vial was cooled down to 0°C. to form a 1M complex. LB (3.9 mmol)

was then added drop wise for 1 minute, while the solution was stirred. The solution was kept at +25 °C and it was used within 1 hour of preparation.

Polymerizations

5 Polymerization was performed in a dry N₂ atmosphere MBraun 150-M glove box (Innovative Technology Inc., Newburyport, MA). Yields were determined gravimetrically. Number average molecular weights (\overline{M}_n) and polydispersity indices (PDI) were determined by size exclusion chromatography. The distribution of end-groups was determined by ¹H NMR. The amount of unreacted chlorinated PIB (PIB-Cl), which is one indicator of whether the reaction can be driven further to completion, was determined by proton NMR spectroscopy.

10

EXAMPLE 1 (Comparative)

The LA.LB complex AlCl₃.dibutyl ether (0.022 M), in a 1:1 molar ratio, was used to 15 polymerize isobutylene (IB) (1 M) in hexanes at -20°C for 20 minutes. IB and hexanes were premixed in a 75 mL culture tube, equipped with a screw top with septum. The LA.LB complex was added last. Polymerization was quenched using an excess of aqueous NH₄OH.

20

Monomer Conversion (%)	Mn	PDI	end-group distribution (mol. %)				
			exo olefins	endo olefins	trisubstituted olefins	tetrasubstituted olefins	PIB-Cl
8	1800	10	86	8	-	7	-

As shown, AlCl₃ polymerizes IB in hexanes without added initiator. Initiation is by adventitious water which is inefficient and the amount of which is difficult to control. Monomer conversion was low and polydispersity was high.

25

EXAMPLE 2 (Comparative)

Polymerization of IB was performed as in Example 1 but with the LA.LB complex AlCl₃.diisopropyl ether (0.02 M) at 0°C.

Monomer	Mn	PDI	end-group distribution (mol. %)

Conversion (%)			exo olefins	endo olefins	trisubstituted olefins	tetrasubstituted olefins	PIB-Cl
31	3400	3.6	64	-	-	23	-

Monomer conversion remained low and polydispersity remained high. The higher polymerization temperature increased yield but concurrently resulted in more isomerization.

5 EXAMPLE 3 (Comparative)

The LA.LB complex AJCb.dibutyl ether (0.022 M), in a 1:1 molar ratio, was used to polymerize IB (1 M) in dichloromethane/hexanes 80/20 (v/v) in the presence of cumyl alcohol (CumOH, 0.018 M) and 2,6-ditert.-butylpyridine (DTBP, 0.006 M) at -40°C for 3 minutes. IB, hexanes, CumOH, and DTBP were premixed in a 75 ml culture tube, equipped with a screw top with a septum. The LA.LB complex was added last. The polymerization was quenched with excess of aqueous NH4OH.

10 Monomer conversion: 0 %.

No conversion achieved with added initiator when chain transfer is suppressed with DTBP (proton trap) demonstrates that initiation is only via adventitious water. Cumyl alcohol, as added initiator, cannot be ionized by AlCl3 in hexanes.

15

EXAMPLE 4 (Comparative)

Polymerization of **1B** was performed as in Example 1 but for 60 min.

Monomer Conversion (%)	Mn	PDI	end-group distribution (mol. %)				
			exo olefins	endo olefins	trisubstituted olefins	tetrasubstituted olefins	PIB-Cl
21	2000	8.7	82	8	0	10	-

20 Monomer conversion remained low and polydispersity remained high, although polymerization time was increased.

EXAMPLE 5 (Comparative)

Polymerization of IB was performed as in Example 4 but in the presence of 2-chloro-
2, 4, 4-trimethylpentane, or "TMPC1" (0.015M).

Monomer Conversion	Mn	PDI	end-group distribution (mol. %)					
			exo	endo	trisubstituted	tetrasubstituted	PIB-Cl	

(%)			olefins	olefins	olefins	olefins	
21	2000	2.3	79	9	0	11	-

Comparing Example 5 to Example 4 demonstrates that TMPC1 does not initiate the polymerization when AlCl_3 is the LA. Conversion, Mn and end-group distribution remained substantially the same.

EXAMPLE 6 (Comparative)

5 The LA.LB complex AlCl_3 .diisobutyl ether (0.022 M), in a 1:1 molar ratio, was used to polymerize IB (1 M) in hexanes in the presence of TMPC1 (0.015 M) and DTBP (0.006 M) at 0°C for 20 minutes. IB, hexanes, TMPC1, and DTBP were premixed in a 75 mL culture tube, equipped with a screw top with a septum. The LA.LB complex was added last. The polymerization was quenched with excess of aqueous Ni^{3+}OH .

10 Monomer conversion: 0 %

As with Example 3, no conversion achieved with added initiator when chain transfer is suppressed with DTBP (proton trap) demonstrating that initiation is only via adventitious water. TMPC1, as added initiator cannot be ionized by AlCl_3 .diisobutyl ether in hexanes.

15

EXAMPLE 7 (Comparative)

The LA.LB complex AlCl_3 .diisopropyl ether (0.02 M), in a 1:1 molar ratio, was used to polymerize IB (1 M) in hexanes in the presence of t-butyl alcohol or "tBuOH" (0.015 M) at 0°C for 20 minutes. IB, hexanes, and tBuOH were premixed in a 75 mL culture tube, equipped with a screw top with a septum. The LA.LB complex was added last. The polymerization was quenched with excess of methanol.

Monomer Conversion (%)	Mn	PDI	end-group distribution (mol. %)					PIB-Cl
			exo olefins	endo olefins	trisubstituted olefins	tetrasubstituted olefins		
11	900	2.1	92	4	0	4	0	

tBuOH as added initiator did not improve conversion relative to Example 2

(adventitious water as initiator), although exo content increased.

25

EXAMPLE 8 (Comparative)

Polymerization of IB was performed as in Example 6, except that cumy] chloride (CumCl) was used instead of TMPC1, and AlCl_3 .diisopropyl ether was used instead AlCl_3 .diisobutyl ether.

Monomer conversion: 2 %

5 As with Example 6, no conversion achieved with added initiator when chain transfer is suppressed with DTBP (proton trap) demonstrating that initiation is only via adventitious water. CumCl as added initiator cannot be ionized by AlCl_3 .diisopropyl ether in hexanes.

10 EXAMPLE 9 (Comparative)

The LA.LB complex GaCl_3 .diisopropyl ether (0.02 M), in a 1:1 molar ratio, was used to polymerize IB (1 M) in hexanes at 0°C for 20 minutes. IB and hexanes were premixed in a 75 ml culture tube, equipped with a screw top with a septum. Addition of the LA.LB complex started the polymerization. The polymerization was quenched 15 with excess of aqueous NH_4OH .

Monomer Conversion (%)	Mn	PDI	end-group distribution (mol. %)				
			exo olefins	endo olefins	trisubstituted olefins	tetrasubstituted olefins	PIB-Cl
26	1700	1.9	68	16	0	10	5

In the absence of initiator, and with initiation via only adventitious water, monomer 20 conversion remained low.

EXAMPLE 10 (Invention)

The LA.LB complex GaCl_3 .diisopropyl ether (0.02 M), in a 1:1 molar ratio, was used to polymerize IB (1 M) in hexanes in the presence of TMPC1, (0.02 M) at 0°C for 20 minutes. IB, hexanes, and TMPC1 were premixed in a 75 ml culture tube, equipped with a screw top with a septum. Addition of the LA.LB complex started the polymerization. The polymerization was quenched with excess of aqueous NH_4OH .

Monomer Conversion (%)	Mn	PDI	end-group distribution (mol. %)				
			exo olefins	endo olefins	trisubstituted olefins	tetrasubstituted olefins	PIB-Cl

100	900	2.1	77	9	0	8	7
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EXAMPLE 11 (Comparative)

The LA GaCl_3 (0.02 M) was used to polymerize IB (1 M) in hexanes in the presence of TMPCl (0.02 M) and isopropyl ether (0.02 M) at 0°C for 20 minutes. IB, hexanes, 5 isopropyl ether, and TMPCl were premixed in a 75 ml culture tube, equipped with a screw top with a septum. Addition of 1M solution of GaCl_3 in hexane (0.02 M) started the polymerization. The polymerization was quenched with excess of aqueous NH_4OH .

Monomer Conversion (%)	Mn	PDI	end-group distribution (mol. %)				
			exo olefins	endo olefins	trisubstituted olefins	tetrasubstituted olefins	PIB-Cl
82	700	2.1	33	0	36	18	14

Compare to Example 10. When the Lewis base (isopropyl ether) is not complexed 10 initially to GaCl_3 , exo-olefin content is reduced due to isomerization and cleavage.

EXAMPLE 12 (Invention)

Polymerization of IB was performed as in Example 10, except that 2-chloro-2- 15 methylpropane (tBuCl) was used instead of TMPCl. [tBuCl] = 0.01 M.

Monomer Conversion (%)	Mn	PDI	end-group distribution (mol. %)				
			exo olefins	endo olefins	trisubstituted olefins	tetrasubstituted olefins	PIB-Cl
57	1700	1.5	70	8	0	6	16

Compare to Example 10. Lower concentration of tBuCl relative to TMPCl resulted in 1 a higher MW and similar exo-olefin content.

EXAMPLE 13 (Comparative)

20 Polymerization of IB was performed as in Example 10, but 2-hydroxy-2-methylpropane (tBuOH) was used instead of TMPCl.

Monomer Conversion (%)	Mn	PDI	end-group distribution (mol. %)				
			exo olefins	endo olefins	trisubstituted olefins	tetrasubstituted olefins	PIB-Cl
4	900	3.0	52	0	27	13	0

Compare to Example 10. Significant isomerization and cleavage with tBuOH as initiator relative to TMPCl and almost no conversion

EXAMPLE 14 (Invention)

5 Polymerization of IB was performed as in Example 12 except that polymerization time was increased to 40 minutes.

Monomer Conversion (%)	Mn	PDI	end-group distribution (mol. %)				
			exo olefins	endo olefins	trisubstituted olefins	tetrasubstituted olefins	PIB-Cl
77	1700	1.6	80	11	0	7	2

Compare to Example 12. Longer reaction time increased conversion, reduced PIB-Cl and increased exo-olefin content at constant MW.

10

EXAMPLE 15 (Comparative)

Polymerization of IB was performed as in Example 12, but without TMPCl.

Monomer Conversion (%)	Mn	PDI	end-group distribution (mol. %)				
			exo olefins	endo olefins	trisubstituted olefins	tetrasubstituted olefins	PIB-Cl
26	1700	1.9	68	16	0	10	5

15 Compare to Example 12. In the absence of initiator, and with initiation via only adventitious water, monomer conversion is low.

EXAMPLE 16 (Comparative)

Polymerization of IB was performed as in Example 15 but in the presence of 2,6-di-tertbutyl pyridine (DTBP); [DTBP] = 0.005 M.

Monomer Conversion (%)	Mn	PDI	end-group distribution (mol. %)				
			exo olefins	endo olefins	trisubstituted olefins	tetrasubstituted olefins	PIB-Cl
2	---	---	93	0	0	0	7

20 Compare to Example 15. Chain transfer is suppressed with DTBP (proton trap), demonstrating that initiation is only via adventitious water.

EXAMPLE 17 (Invention)

Polymerization of IB was performed as in Example 10, but in the presence of [DTBP] = 0.005 M.

Monomer Conversion (%)	Mn	PDI	end-group distribution (mol. %)				
			exo olefins	endo olefins	trisubstituted olefins	tetrasubstituted olefins	PIB-Cl
30	1000	1.7	67	6	0	5	22

Compare, to Example 10. Yield is reduced but not eliminated by DTBP. MW and 5 exo-olefin content is maintained. Compare to Example 6 with AlCl₃ where no conversion was achieved in the presence of DTBP.

10 EXAMPLE 18 (Invention)

Polymerization of IB was performed as in Example 10, but at +10 °C.

Monomer Conversion (%)	Mn	PDI	end-group distribution (mol. %)				
			exo olefins	endo olefins	trisubstituted olefins	tetrasubstituted olefins	PIB-Cl
100	1000	2.1	75	11	0	12	2

Compare to Example 10. Conversions, MW and exo-olefin content maintained at higher temperature.

15 EXAMPLE 19 (Invention)

Polymerization of IB was performed as in Example 10, but at [IB] = 4 M.

Monomer Conversion (%)	Mn	PDI	end-group distribution (mol. %)				
			exo olefins	endo olefins	trisubstituted olefins	tetrasubstituted olefins	PIB-Cl
70	1900	1.7	78	9	0	8	5

Compare to Example 10. Lower molar ratio of catalyst to monomer increased MW and decreased yield, but exo-olefin content is maintained.

20 EXAMPLE 20 (Invention)

Polymerization of IB was performed as in Example 10, but using GaCl₃.2, 4-dimethyl-3-pentanone LA.LB complex.

Monomer Conversion (%)	Mn	PDI	end-group distribution (mol. %)				
			exo olefins	endo olefins	trisubstituted olefins	tetrasubstituted olefins	PIB-Cl
65	1200	1.4	81	8	0	7	4

Compare to Example 10. Ketone is effective as the Lewis base with comparable MW and exo-olefin content, but lower conversion.

5

EXAMPLE 21 (Comparative)

10 Polymerization of IB was performed as in Example 10, but using GaCb.triethylamine LA.LB complex.

Monomer conversion: 0 %

Compare to Example 10. Triethylamine is not an effective base,

EXAMPLE 22 (Comparative)

15 Polymerization of IB was performed as in Example 10, but using $\text{SnCl}_4\text{.diisopropyl ether}$ LA.LB complex.

Monomer conversion: 0 %

Compare to Example 10. SnCl_4 is not an effective Lewis acid catalyst,

20 EXAMPLE 23 (Comparative)

Polymerization of IB was performed as in Example 10, but using $\text{SbCl}_5\text{.diisopropyl ether}$ LA.LB complex.

Monomer conversion: 0 %

Compare to Example 10. SbCl_5 is not an effective Lewis acid catalyst.

25

EXAMPLE 24 (Invention)

Polymerization of IB was performed as in Example 10, using $\text{FeCl}_3\text{.diisopropyl ether}$ LA.LB complex.

Monomer	Mn	PDI	end-group distribution (mol. %)
---------	----	-----	---------------------------------

Conversion (%)			exo olefins	endo olefins	trisubstituted olefins	tetrasubstituted olefins	PIB-Cl
47	900	1.5	91	4	0	2	3

Compare to Example 10, FeCl_3 is an effective Lewis acid catalyst with higher exo-olefin content at similar MW, but lower conversion.

EXAMPLE 25 (Invention)

5 The LA.LB complex $\text{FeCl}_3\text{.chloromethyl ethyl ether}$ (0.02 M), in a 1:1 molar ratio, was used to polymerize IB (1 M) in hexanes in the presence of tBuCl (0.02 M) at 0°C for 20 minutes. IB, hexanes, and tBuCl were premixed in a 75 ml culture tube, equipped with a screw top with a septum. Addition of the LA.LB complex started the polymerization. The polymerization was quenched with excess of aqueous NH_4OH .

Monomer Conversion (%)	Mn	PDI	end-group distribution (mol. %)			
			exo olefins	endo and trisubstituted olefins	tetrasubstituted olefins	PIB-Cl
85	600	—	60	14	12	14

EXAMPLE 26

Polymerization of [IB] = 1M, [TMPC1] = 0.02 M in hexanes at 0°C for 20 min. conducted using various Lewis Acid and Lewis Base combinations and complexes. In each case, polymerization was terminated with NH4OH.

#	LA.LB	[LA.LB] (M)	Soluble complex	INV (I) Comp. (C)	Yield (%)	Mn	PDI	[Mn] (NMR)	[PIB] (M)	exo (%)	endo (%)	tri (%)	tetra (%)	PIB-Cl (%)
a	TaCl ₅ .iPr ₂ O	0.01	No	C	4			2200	0.0010	17		19	22	42
b	TaCl ₅ .iPr ₂ O	0.02	No	C	23	1600	6.9	1900	0.0071	22		34	27	17
c	MoCl ₅ .iPr ₂ O	0.01	Yes	C	34	1000	4.8	1200	0.0169	28		30	21	21
d	MoCl ₅ .iPr ₂ O	0.02	Yes	C	100	1400	2.9	900	0.0640	28		37	22	13
e	InCl ₃ .iPr ₂ O	0.01	No	C	0									
f	InCl ₃ .iPr ₂ O	0.02	No	C	0									
g	GaCl ₃ .tBuOH	0.01	Yes	I	8	400	1.3	460	0.0108	75	10			
h	GaCl ₃ .tBuOH	0.02	Yes	I	24	900	1.2	460	0.0316	82	7			
i	GaCl ₃ .γBuL [*]	0.01	Yes	I	16			600	0.0162	50		28	20	2
j	GaCl ₃ .γBuL	0.02	Yes	I	50			600	0.0501	48		29	21	2
k	GaCl ₃ .AcN ^{**}	0.01	No	C	5			1100	0.0028	17		15	9	59
l	GaCl ₃ .AcN	0.02	No	C	25			1100	0.0132	13		27	11	49
m	VCl ₃ .iPr ₂ O	0.01	No	C	0									
n	VCl ₃ .iPr ₂ O	0.02	No	C	0									
o	WCl ₄ .iPr ₂ O	0.01	Yes	I	1			1000	0.0001	80	7		7	6
p	WCl ₄ .iPr ₂ O	0.02	Yes	I	9			700	0.0071	78	8		9	5

^{*}γ-butyro lactone
^{**} acrylonitrile

EXAMPLE 27 (Invention)
Polymerization of [IB] = 1M, [TMPCl] = 0.02 M in hexanes at 0°C for 20 min. Terminated with NH₄OH

#	LA,LB	[LA,LB] (M)	Yield (%)	Mn	PDI	Mn (NMR)	[PIB] (M)	exo (%)	exo-cpld ** (%)	tri (%)	tetra (%)
a	HfCl ₄ .iPr ₂ O	0.01	50			1500	0.0195	40	13	29	19
b	HfCl ₄ .iPr ₂ O	0.02	100			1300	0.0553	52	5	27	17
c*	HfCl ₄ .iPr ₂ O	0.02	92			1500	0.0369	46	10	24	19
d	HfCl ₄ .1.5iPr ₂ O	0.01	15			650	0.0142	53	24	14	10
e	HfCl ₄ .1.5iPr ₂ O	0.02	34			600	0.0328	51	25	14	10

*[tBuCl] = 0.02 M, terminated with MeOH

** exo-olefin that has coupled (dimerized)

EXAMPLE 28 (Invention)
Polymerization of [IB] = 1M, by [HfCl₄.iPr₂O] = 0.02 M (DCM solution filtered through 450 nm PTFE membrane), [tBuCl] = 0.01 M in hexanes at 0°C. Terminated with MeOH.

#	Time (min)	Yield (%)	Mn	PDI	Mn (NMR)	[PIB] (M)	exo (%)	exo-cpld (%)	tri (%)	tetra (%)
a	5	64			1700	0.0229	48	7	25	20
b	10	72			1750	0.0247	47	7	27	19
c	20	89			1500	0.0352	49	7	24	20
d	40	99			1500	0.0403	52	7	23	18
e	60	100			1100	0.0534	56	7	22	16

EXAMPLE 29 (Invention)
 Polymerization of IB in C₄ feed composition IB = 35% 1-butene = 10%, 2-butene = 6% hexanes = 49% at 0°C.

#	[GaCl ₃ .iPr ₂ O]	[TMPCl]	Time (min)	Yield (%)	Mn (NMR)	Mn (GPC)	PDI	exo (%)	PIB-Cl (%)	endo (%)	tetra (%)
a	0.01	0.01	20	9	900	1000	1.9	55	36	6	2
b	0.01	0.01	60	10	1100	1200	3.3	66	21	9	4
c	0.02	0.01	20	19	1200	1700	2.5	75	15	7	4
d	0.02	0.01	60	33	1500	1900	2.4	85	3	8	4
e	0.01	0.02	20	18	1100	1200	3.2	66	23	8	3
f	0.01	0.02	60	19	1100	1300	3.1	69	17	10	4
g	0.02	0.02	20	28	1300	1500	2.7	81	7	7	4
h	0.02	0.02	60	36	1300	1700	2.7	81	7	7	4

EXAMPLE 30 (Invention)
 Polymerization of IB in C₄ feed composition IB = 44% 1-butene = 26.4%, trans 2-butene = 14.7%, hexanes = 14.5% at 0°C.

#	[GaCl ₃ .iPr ₂ O]	[TMPCl]	Time (min)	Yield (%)	Mn (NMR)	Mn (GPC)	PDI	exo (%)	PIB-Cl (%)	endo (%)	tetra (%)
a	0.01	0.01	20	10	1200	1600	3.1	64	27	6	3
b	0.01	0.01	60	14	1600	1700	3.1	70	17	9	4
c	0.02	0.02	20	27	1400	1600	2.6	74	15	8	4
d	0.02	0.02	60	46	1300	1400	3.0	85	4	8	3

While certain representative embodiments and details have been provided to illustrate the invention, it will be apparent to the skilled artisan that various product and process changes from those disclosed herein may be made without departing from the scope of the present invention. The appended claims define the scope of the invention

All cited patents, test procedures, priority documents, and other cited documents are fully incorporated by reference to the extent that such material is consistent with this specification and for all jurisdictions in which such incorporation by reference is permitted.

Certain features of the present invention are described in terms of a set of numerical upper limits and a set of numerical lower limits. This specification discloses all ranges formed by any combination of these limits. It is to be understood that the upper limits and lower limits, as well as range and ratio limits set forth herein may be independently combined, and that all combinations of these limits are within the scope of the invention unless otherwise indicated.

WHAT IS CLAIMED IS:

1. A process for the preparation of polybutene having an exo-olefin content of at least 50 mol. %, which process comprises contacting isobutene or an isobutene-containing monomer mixture, with a Lewis acid catalyst complexed with an oxygen and/or sulfur-containing Lewis base, in a substantially or completely apolar solvent, and initiating polymerization of said isobutene or an isobutene-containing monomer mixture with an initiator, wherein said Lewis acid catalyst is a Lewis acid of the formula MR''_mY_n , wherein M is a metal selected from Fe, Ga, Hf, Zr and W; R" is a hydrocarbyl group; Y is halogen; m is 0 or an integer of 1 to 5; and n is an integer of 1 to 6, with the proviso that m+n is equal to the valency of metal M; and the initiator is a compound of the formula RX, wherein X is a halide; R is a hydrocarbyl group capable of forming a stable carbocation, and wherein the carbon linking group R to group X is tertiary, benzylic or allylic.
2. The process of claim 1, wherein M is Ga or Fe, and R" is a C₁ to C₈ alkyl group.
3. The process of claim 1, wherein m is 0 or 1.
4. The process of claim 1, wherein Y is Cl or Br.
5. The process of claim 1, wherein said Lewis base is selected from acyclic dihydrocarbyl ethers, wherein each hydrocarbyl group is independently selected from C₁ to C₁₂ hydrocarbyl, basic cyclic ethers having a 5 to 7 membered cyclic group, dihydrocarbyl ketones, wherein each hydrocarbyl group is independently selected from C₁ to C₁₂ hydrocarbyl, C₁ to C₁₂ aliphatic alcohols, C₁ to C₁₂ aliphatic aldehydes, acyclic aliphatic esters wherein each hydrocarbyl group is independently selected from C₁ to C₁₂ hydrocarbyl, cyclic aliphatic esters having a 5 to 7 membered cyclic group, dialkyl sulfides, wherein each hydrocarbyl group is independently selected from C₁ to C₁₂ hydrocarbyl, and basic dihydrocarbyl thiocarbonyl compounds, wherein each hydrocarbyl group is independently selected from C₁ to C₁₂ hydrocarbyl, and mixtures thereof.

6. The process of claim 5, wherein said Lewis base is selected from acyclic dialkyl ethers, wherein each alkyl group is independently selected from C₁ to C₄ alkyl, cyclic ethers having a 5 to 7 membered cyclic group, basic dialkyl ketones, wherein each alkyl group is independently selected from C₁ to C₄ alkyl, C₁ to C₄ aliphatic alcohols, C₁ to C₄ aliphatic aldehydes, acyclic aliphatic esters wherein each hydrocarbyl group is independently selected from C₁ to C₄ alkyl, cyclic aliphatic esters having a 5 to 7 membered cyclic group, dialkyl sulfides, wherein each alkyl group is independently selected from C₁ to C₄ alkyl, and dialkyl thiocarbonyl compounds, wherein each alkyl group is independently selected from C₁ to C₄ alkyl, and mixtures thereof.

7. The process of claim 1, wherein said apolar medium is selected from saturated C₄ hydrocarbons, unsaturated C₄ hydrocarbons, and mixtures thereof.

8. The process of claim 1, wherein said isobutene or an isobutene-containing monomer mixture is selected from pure isobutene; a C₄ refinery cut containing between about 5% and about 50% butene-1, between about 2% and about 40% butene-2, between about 2% and about 60% iso-butane, between about 2% and about 20% n-butane, and up to about 0.5% butadiene, wherein all percentages are by mass, based on the total mass of the C₄ refinery cut; and mixtures of pure isobutene and said C₄ refinery cut.

9. The process of claim 1, wherein said complex is contacted with said isobutene or an isobutene-containing monomer at a concentration of millimoles of Lewis acid-Lewis base complex per liter of medium of from about 1mM to about 200 mM.

10. The process of claim 1, wherein said Lewis acid and said Lewis base are complexed by dissolving the Lewis acid in solvent to form a solution, and then adding said Lewis base to said solution.

11. The process of claim 1, wherein the polymerization process is conducted continuously.

12. The process of claim 1, wherein said polybutene product has an exo-olefin content of at least 70 mol. %.

13. A catalyst-initiator system for catalyzing the polymerization of isobutene or an isobutene-containing monomer mixture in a substantially or completely apolar solvent to provide a polybutene product having an exo-olefin content of at least 50 mol. %, wherein said catalyst comprising a Lewis acid catalyst complexed with an oxygen and/or sulfur containing Lewis base, wherein said Lewis acid catalyst is a Lewis acid of the formula MR''_mY_n , wherein M is a metal selected from Fe, Ga, Hf, Zr and W; R" is a hydrocarbyl group; Y is halogen; m is 0 or an integer of 1 to 5; and n is an integer of 1 to 6, with the proviso that m+n is equal to the valency of metal M; and the polymerization is initiated via an initiator of the formula RX, wherein X is a halide; R is a hydrocarbyl group capable of forming a stable carbocation, and wherein the carbon linking group R to group X is tertiary, benzylic or allylic

14. The catalyst-initiator system of claim 13, wherein M is Ga or Fe, and R" is a C_1 to C_8 alkyl group.

15. The catalyst-initiator system of claim 13, wherein m is 0 or 1.

16. The catalyst-initiator system of claim 13, wherein Y is Cl or Br.

17. The catalyst-initiator system of claim 13, wherein said Lewis base is selected from acyclic dihydrocarbyl ethers, wherein each hydrocarbyl group is independently selected from C_1 to C_{12} hydrocarbyl, basic cyclic ethers having a 5 to 7 membered cyclic group, dihydrocarbyl ketones, wherein each hydrocarbyl group is independently selected from C_1 to C_{12} hydrocarbyl, C_1 to C_{12} aliphatic alcohols, C_1 to C_{12} aliphatic aldehydes, acyclic aliphatic esters wherein each hydrocarbyl group is independently selected from C_1 to C_{12} hydrocarbyl, cyclic aliphatic esters having a 5 to 7 membered cyclic group, dialkyl sulfides, wherein each hydrocarbyl group is independently selected from C_1 to C_{12}

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hydrocarbyl, and basic dihydrocarbyl thiocarbonyl compounds, wherein each hydrocarbyl group is independently selected from C₁ to C₁₂ hydrocarbyl, and mixtures thereof

18. The catalyst-initiator system of claim 17, wherein said Lewis base is selected from acyclic dialkyl ethers, wherein each alkyl group is independently selected from C₁ to C₄ alkyl, cyclic ethers having a 5 to 7 membered cyclic group, basic dialkyl ketones, wherein each alkyl group is independently selected from C₁ to C₄ alkyl, C₁ to C₄ aliphatic alcohols, C₁ to C₄ aliphatic aldehydes, acyclic aliphatic esters wherein each hydrocarbyl group is independently selected from C₁ to C₄ alkyl, cyclic aliphatic esters having a 5 to 7 membered cyclic group, dialkyl sulfides, wherein each alkyl group is independently selected from C₁ to C₄ alkyl, and dialkyl thiocarbonyl compounds, wherein each alkyl group is independently selected from C₁ to C₄ alkyl, and mixtures thereof.,

19. The catalyst-initiator system of claim 13, wherein said Lewis acid and said Lewis base are complexed by dissolving the Lewis acid in solvent to form a solution, and then adding said Lewis base to said solution.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/069822

A. CLASSIFICATION OF SUBJECT MATTER			
INV. C08F110/10 C08F4/14 C08F4/16 C08F4/22			
ADD.			
According to International Patent Classification (IPC) or to both national classification and IPC			
B. FIELDS SEARCHED			
Minimum documentation searched (classification system followed by classification symbols) C08F			
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched			
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal			
C. DOCUMENTS CONSIDERED TO BE RELEVANT			
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.		<input checked="" type="checkbox"/> See patent family annex.	
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family			
Date of the actual completion of the international search 18 March 2013		Date of mailing of the international search report 22/03/2013	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Kaumann, Edgar	

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Information on patent family members

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