

Process for Improving the Stability of Polyisobutenes

Description

- 5 The present invention concerns a process for improving the stability of polyisobutenes, especially the stability of highly reactive polyisobutenes under thermal or oxidative stress, such as under storage conditions.

10 In the past efforts were made to prepare low molecular polyisobutene with a high reactivity for subsequent chemical reactions, e.g. subsequent hydroformylation, thermal ene-reaction with maleic anhydride, or *Friedel-Crafts* alkylation of aromatic compounds. As a result, highly reactive polyisobutene (also referred to as HRPIB) was developed with a high content of alpha-double bonds up to 80 to 90 mol% (see below for the designation of the isomers) or even higher contents up 95, 97 or even 98 %. These efforts mainly concern low molecular polyisobutene,
15 i.e. polyisobutene with a number average molecular weight of not more than 10000 g/mol.

Efforts to prepare polyisobutene with medium or high molecular weight and a high content of reactive double bonds are known from e.g. EP 807641 in which the cationic polymerisation of isobutene with a boron trifluoride complex catalyst is described. Claimed is a content of at least
20 50 mol% terminal double bonds although the terminal double bond content actually achieved in the explicitly disclosed examples is not given.

A high content of alpha- and/or beta-double bonds is necessary for low or medium molecular polyisobutene in order to achieve a high reactivity in thermal reactions, e.g. against maleic acid
25 anhydride, see e.g. WO 2017/216022.

However, it is a disadvantage of such highly reactive polyisobutenes that they age during storage, which may e.g. result in loss of molecular weight, loss of reactivity and/or development of free isobutene monomer. Basis for these effects can be thermal and/or oxidative stress as well
30 as irradiation with UV or visible light.

The development and release of monomeric isobutene is particularly disadvantageous if the polyisobutene is later to be used in foodstuffs, such as chewing gum, or medical products, e.g. as an adhesive for plasters.
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Against such effects stabilisers often are added to polyisobutene which does not remove the reason for degradation, but just suppress or delay degradation as long as enough active stabi-

liser is present in the polyisobutene. Furthermore, the addition of stabilisers disqualifies the stabilised polyisobutene for use in food or medical applications if the stabiliser is not expressly approved for these applications.

- 5 Therefore, a need exists for improving the stability of polyisobutenes, especially the storage stability, without the need to add stabilisers and which can easily be implemented in existing manufacturing plants for high reactivity polyisobutene.

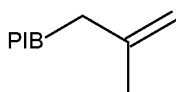
- Subject matter of the present invention is a process for improving the storage stability of polyisobutene, comprising the steps of
- 10 - choosing as a starting material
- in the case of polyisobutene with a number average molecular weight M_n (determined by gel permeation chromatography (GPC) with polystyrene as standard) of less than 10000 g/mol, a polyisobutene composition with a content of polyisobutene species (A) bearing an alpha-double bond of at least 50 mol%, preferably at least 60 mol%, more preferably at least 70 mol%, most preferably at least 75 mol% and especially at least 80 mol% or even 85 mol%,
 - in the case of polyisobutene with a number average molecular weight M_n of from 10000 to 100000 g/mol, a polyisobutene composition with a content of polyisobutene species (A) bearing an alpha-double bond of at least 20 to 60 mol%, preferably at least 25 to 45 mol%, and more
 - 20 preferably at least 30 to 40 mol%,
 - in the case of polyisobutene with a number average molecular weight M_n of more than 100000 to 5000000 g/mol, a polyisobutene composition with a content of polyisobutene species (A) bearing an alpha-double bond of at least 10 to 50 mol%, preferably at least 15 to 45 mol%, and more preferably at least 15 to 40 mol%,
- 25 - optionally at least one solvent,
- treating the optionally dissolved polyisobutene composition
 - in the presence of at least one Brønsted-acid, preferably an acidic solid state catalyst, optionally treated with at least one Brønsted-base
 - for a period of from 5 minutes to 36 hours
 - 30 -- at a temperature of from 40 °C to 250 °C,
- and store the thus obtained polyisobutene composition at a temperature from ambient temperature up to 100 °C, preferably in the absence of oxygen.

- WO 2022/258417 A1 and WO 2023/152258 A1 disclose processes for the isomerisation of medium molecular polyisobutenes with a high content of alpha-double bonds into isomers with beta-double bonds resp. higher substituted double bonds in order to increase the reactivity of such polyisobutene mixtures in photo reactions.
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Both documents are silent about the stability of the thus treated polyisobutene. In contrast, it is the target of these documents to provide polyisobutene species with an increased reactivity, while subject matter of the present invention is the provision of polyisobutene, preferably low molecular polyisobutene, which exhibits an increased stability, especially under storage conditions.

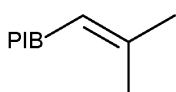
In the context of the present document the double bond isomers are denoted as follows:

A double bond in the terminal carbon-carbon bond



is referred to as alpha-double bond, sometimes the terms terminal- or exo-double bond are used synonymously.

The polyisobutene



bears a beta-double bond, also referred to as endo-double bond.

Furthermore, isomers with other substitution patterns of the double bond, preferably isomers with a tetra-substituted double bond, or with internal double bonds, i.e. double bonds in the backbone of the polymer chain which are neither alpha- nor beta-double bonds, are possible, see e.g. WO 2022/258417 A1 and WO 2023/152258 A1, preferably isomers (C1) to (C8) disclosed therein.

It has now been found that polyisobutene isomers not bearing an alpha-double bond, but preferably a beta-double bond, a tetra-substituted double bond or internal double bonds, are more stable than those bearing an alpha-double bond.

"Stability" in this context means one or more of the following:

- depletion of molecular weight,
- development of isobutene monomer,
- colouration of the polymer (yellowish to orange brown), and/or
- increase of polydispersity (broadening of molecular weight distribution).

The depletion of molecular weight resp. increase of polydispersity may take place by depolymerisation, i.e. by reverse reaction of the polymerisation described below. This kind of reaction is usually characterised by a shift of the GPC graph (gel permeation chromatography) to lower molecular weight compared with the starting material, formation of peaks at lower molecular weight (detectable as a shoulder in the GPC graph), and/or broadening of the GPC graph.

If not explicitly mentioned otherwise the number average molecular weight M_n is determined by gel permeation chromatography with polystyrene as standard.

Another mechanism of depletion of molecular weight is the cleavage of the polymer backbone of the polyisobutene. Such cleavage may be observed by the occurrence of low molecular fragments in GPC while the average molecular weight of the high molecular fraction remains unchanged. Of course, the integrated molecular weight of the whole composition lessens. Usually both reactions may occur at the same time, however, the depolymerisation dominates at moderate temperature. At very high temperature the cleavage may become the main reaction.

As pointed out above the depolymerisation is one of the reasons for presence and/or development of isobutene in the polyisobutene. Another source may also be an incomplete degassing or distillation of the polyisobutene reaction mixture after polymerisation.

The stability of the polyisobutene is determined in the period of time between its manufacturing and its use in the target product or the final use. This period of time may be up to two years at room temperature, preferably up to 18 months, more preferably up to 12 months at room temperature.

The temperature of the storage may be from ambient temperature up to 100 °C, preferably from 0 to 80 °C, more preferably from 5 to 70, even more preferably from 10 to 60, and especially from 15 to 50 °C.

Especially low molecular polyisobutene is stored at a temperature up to 100 °C, preferably up to 80 °C, more preferably up to 70, and even more preferably up to 60 °C to keep the viscosity of the polyisobutene low resp. to keep it fluid.

Especially if stored at temperatures above room temperature the polyisobutene is preferably stored in the absence of oxygen, e.g. from air, under cover of an inert gas. Inert gases may be nitrogen, carbon dioxide or noble gases, such as argon or helium, preferably nitrogen. However,

oxygen may also be present, e.g. by permeation of air into the package or by using oxygen-depleted air (lean air) rather than an inert gas. Usually polyisobutene is more stable in the absence of oxygen than in its presence.

- 5 However, if the polyisobutene is stored at ambient temperature usually no inert gas is necessary but air or lean air is used as gas cover for the product.

In the above-listed formulae the group "PIB" together with the explicitly shown substructures add up to a polyisobutene polymer with a number-average molecular weight M_n of less than
10 10000 g/mol for low molecular weight polyisobutene, from 10000 and up to 100000 g/mol for medium molecular weight polyisobutene and more than 100000 to 5000000 g/mol for high molecular polyisobutene. In other words, the group "PIB" refers to a polyisobutene polymer shortened by the explicitly shown substructures.

- 15 The reactivity of polyisobutene at least against thermal reactions is usually determined by its content of alpha-double bonds.

In the context of the present invention low, medium and high molecular polyisobutene is defined by its number average molecular weight M_n :

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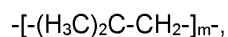
For low molecular polyisobutene with a number-average molecular weight M_n of up to 10000 g/mol the average degree of polymerisation is up to 177, preferably from 5 to 134 (M_n ca. 280 to 7500), more preferably 6 to 107 (M_n ca. 340 to 6000), even more preferably 9 to 89 (M_n ca. 500 to 5000), especially 13 to 45 (M_n ca. 730 to 2500), and even 16 to 20 (M_n ca. 900 to 1130).

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For medium molecular polyisobutene with a number-average molecular weight M_n of from 10000 and up to 100000 g/mol the average degree of polymerisation is from 178 to 1786.

- 30 High molecular polyisobutene exhibits a number-average molecular weight M_n of more than 100000 and up to 5000000 g/mol (degree of polymerisation 1787 to 89285).

In an ideal homopolymer of isobutene the residue "PIB" stands for



- wherein the polymer chain "PIB" may be started on an appropriate initiator, see below, preferably may be connected to hydrogen,
35 with m being a positive integer,

with the proviso that m plus the monomer units in the shown substructures match the degree of polymerisation of the polyisobutene of the respective molecular weight.

In a copolymer some isobutene units may be replaced by other monomer units, e.g. 1-butene,
5 cis or trans 2-butene, see below.

In the case of polyisobutene with an alpha- or beta-double bond the integer m is the degree of polymerisation of the polyisobutene minus 1.

10 The content of the isomers is determined with the help of ^1H -NMR spectroscopy, the detection level is determined by the frequency used. Preferably ^1H -NMR spectroscopy at 700 MHz at 25 °C is used. Very preferably the content of isomers is determined as described in Guo et al., Journal of Polymer Science, Part A: Polymer Chemistry, 2013, 51, 4200–4212.

15 Since the isomers are part of a polymeric mixture with a molecular weight distribution the content of each single isomer in the mixture in weight% and mol% is the same.

Subject matter of the present invention is a process for improving the storage stability of polyisobutene, comprising the steps of

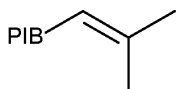
- 20 - choosing as a starting material a preferably low or medium molecular polyisobutene composition with a content of polyisobutene species (A)
-- in the case of polyisobutene with a number average molecular weight M_n of less than 10000 g/mol, a polyisobutene composition with a content of polyisobutene species (A) bearing an alpha-double bond of at least 50 mol%, preferably at least 60 mol%, more preferably at least 70
25 mol%, most preferably at least 75 mol% and especially at least 80 mol% or even 85 mol%,
-- in the case of polyisobutene with a number average molecular weight M_n of from 10000 to 100000 g/mol, a polyisobutene composition with a content of polyisobutene species (A) bearing an alpha-double bond of at least 20 to 60 mol%, preferably at least 25 to 45 mol%, and more preferably at least 30 to 40 mol%,
30 - optionally at least one solvent,
- treating the optionally dissolved polyisobutene composition
-- in the presence of at least one Brønsted-acid, preferably at least one acidic solid state catalyst, optionally treated with at least one Brønsted-base
-- for a period of from 5 minutes to 36 hours
35 -- at a temperature of from 40 °C to 250 °C,
and store the thus obtained polyisobutene composition at a temperature from ambient temperature up to 100 °C, preferably in the absence of oxygen.

According to the present invention the treatment of low- and medium molecular polyisobutene compositions is preferred, even more preferred is the treatment of low molecular polyisobutene.

In a preferred embodiment a low molecular polyisobutene composition is chosen as the starting material with a content of polyisobutene species (A) bearing an alpha-double bond of at least 50 mol%, preferably at least 60 mol%, more preferably at least 70 mol%, even more preferably at least 75 mol%, and especially at least 80 mol% or even at least 85 mol%. The content of polyisobutene species (A) bearing an alpha-double bond can be up to 95 mol%, up to 90 or up to 85 mol%. Low molecular weight polyisobutene with such a high content of alpha-double bonds is often referred to as "highly reactive polyisobutene".

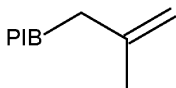
In another preferred embodiment a medium molecular polyisobutene composition is chosen as the starting material with a content of polyisobutene species (A) bearing an alpha-double bond of 20 to 60 mol%, preferably at least 25 to 45 mol%, and more preferably at least 30 to 40 mol%. It is an advantage of such an embodiment that the relatively low content of thermally reactive double bonds, especially alpha-double bonds in such a medium or high molecular polyisobutene composition can be further depleted in the process according to the present invention.

In the context of the present invention the term isomers bearing a "beta-double bond" refers to polyisobutene isomers (B) with the sub-structure



in which "PIB" stands for the polymeric backbone of the polyisobutene except for the final incorporated isobutene unit.

In contrast, the term isomers bearing an "alpha-double bond" refers to polyisobutene isomers (A) with the sub-structure



In the context of the present invention medium molecular polyisobutene is defined as polyisobutene compositions with a number-average molecular weight M_n of from 10000 and up to 100000 g/mol.

- 5 The number-average molecular weight M_n (determined by gel permeation chromatography) of the medium molecular polyisobutene according to the present invention is from 10000 to 100000, preferably from 11000 to 90000, more preferably from 12000 to 80000, most preferably from 13000 to 75000, and especially from 14000 to 70000.
- 10 In contrast, low molecular polyisobutene is defined as polyisobutene compositions with a number-average molecular weight M_n of not more than 10000 g/mol, preferably 280 to 7500, more preferably 330 to 6000, even more preferably 500 to 5000, especially 750 to 2500, and even 900 to 1100 g/mol.
- 15 The polydispersity of the polyisobutene is from 1.2 to 10, preferably from 1.3 to 9, more preferably from 1.4 to 8, even more preferably from 1.5 to 6 and especially from 2 to 5.

As pointed out above, the reactivity of the different double bond isomers in polyisobutene depends on the molecular weight. Furthermore, due to the different manufacturing processes low,
20 medium, and high molecular polyisobutene usually exhibits a different distribution of double bond isomers.

It is an advantage of the process of the present invention that it can easily be implemented in the existing process for the production of polyisobutene with a high content of alpha-double
25 bonds simply by leading the polyisobutene with a high content of alpha-double bonds into the process according to the invention.

- Therefore, another aspect of the present invention is a process for the production and improving the storage stability of polyisobutene, comprising the steps of
- 30 - (I) first polymerising isobutene or an isobutene-containing monomer mixture
- in the presence of at least one Lewis Acid-donor complex and
- at least one initiator,
- (II) terminating the polymerisation by adding water or basic material to the reaction mixture,
- (III) distilling off unreacted monomer and lower oligomers of isobutene,
35 yielding a polyisobutene composition
-- in the case of polyisobutene with a number average molecular weight M_n of less than 10000 g/mol, a polyisobutene composition with a content of polyisobutene species (A) bearing an al-

- pha-double bond of at least 50 mol%, preferably at least 60 mol%, more preferably at least 70 mol%, most preferably at least 75 mol% and especially at least 80 mol% or even 85 mol%,
-- in the case of polyisobutene with a number average molecular weight M_n of from 10000 to 100000 g/mol, a polyisobutene composition with a content of polyisobutene species (A) bearing
5 an alpha-double bond of at least 20 to 60 mol%, preferably at least 25 to 45 mol%, and more preferably at least 30 to 40 mol%,
-- in the case of polyisobutene with a number average molecular weight M_n of more than 100000 to 5000000 g/mol, a polyisobutene composition with a content of polyisobutene species (A) bearing an alpha-double bond of at least 10 to 50 mol%, preferably at least 15 to 45 mol%,
10 and more preferably at least 15 to 40 mol%,
followed by
- (IV) afterwards optionally adding at least one solvent to this polyisobutene composition,
- treating the optionally dissolved polyisobutene composition
-- in the presence of at least one Brønsted-acid, preferably at least one acidic solid state cata-
15 lyst, optionally treated with at least one Brønsted-base
-- for a period of from 5 minutes to 36 hours
-- at a temperature of from 40 °C to 250 °C,
- (V) washing the reaction mixture with water,
wherein the washing step (V) may take place after step (III) and/or step (IV) ,
20 followed by storage of the thus obtained polyisobutene for a period of time up to two years at room temperature, preferably from ambient temperature up to 100 °C, more preferably in the absence of oxygen.
- 25 A preferred embodiment of the present invention is a process for the production of polyisobutene, comprising the steps of
- (I) first polymerising isobutene or an isobutene-containing monomer mixture
- in the presence of at least one Lewis Acid-donor complex,
wherein the Lewis Acid is a chloride or fluoride,
30 and
- at least one initiator,
- (II) terminating the polymerisation by adding water or basic material to the reaction mixture,
- (III) distilling off unreacted monomer and lower oligomers of isobutene,
wherein hydrofluoric acid or hydrochloric acid originating from deactivation of the fluorine- or
35 chlorine-containing Lewis acids is at least partly left in the reaction mixture,
yielding a polyisobutene composition
-- in the case of polyisobutene with a number average molecular weight M_n of less than 10000

- g/mol, a polyisobutene composition with a content of polyisobutene species (A) bearing an alpha-double bond of at least 50 mol%, preferably at least 60 mol%, more preferably at least 70 mol%, most preferably at least 75 mol% and especially at least 80 mol% or even 85 mol%,
- in the case of polyisobutene with a number average molecular weight M_n of from 10000 to 100000 g/mol, a polyisobutene composition with a content of polyisobutene species (A) bearing an alpha-double bond of at least 20 to 60 mol%, preferably at least 25 to 45 mol%, and more preferably at least 30 to 40 mol%,
- in the case of polyisobutene with a number average molecular weight M_n of more than 100000 to 5000000 g/mol, a polyisobutene composition with a content of polyisobutene species (A) bearing an alpha-double bond of at least 10 to 50 mol%, preferably at least 15 to 45 mol%, and more preferably at least 15 to 40 mol%,
- followed by
- (IV) afterwards optionally adding at least one solvent to this polyisobutene composition,
 - treating the optionally dissolved polyisobutene composition
- in the presence of hydrofluoric acid or hydrochloric acid,
- for a period of from 5 minutes to 36 hours
- at a temperature of from 40 °C to 250 °C,
- at a pressure from 10 bar gauge to 20 mbar,
- (V) optionally washing the reaction mixture with water,
- wherein the washing step (V) may take place after step (IV).

In this embodiment the fluorine- or chlorine-containing Lewis acid is preferably selected from the group consisting of boron trifluoride, boron trichloride, aluminium trichloride, alkyl aluminium dichloride, and dialkyl aluminium chloride, more preferably boron trifluoride or aluminium trichloride.

It is an advantage of this preferred embodiment that the remaining hydrofluoric acid or hydrochloric acid present in the polyisobutene can be utilised for stabilisation of the polyisobutene and may be removed later in step (V).

The amount of hydrofluoric acid or hydrochloric acid present in the polyisobutene after hydrolysis is preferably at least 10 ppm by weight, preferably at least 20, more preferably at least 30, even more preferably at least 50, and especially at least 100 ppm by weight.

Usually, the amount of hydrofluoric acid or hydrochloric acid does not exceed 1000 ppm by weight, preferably not more than 750, more preferably not more than 500, even more preferably not more than 350, and especially not more than 250 ppm by weight.

In a preferred embodiment, the thus treated polyisobutene is washed with water or aqueous base solutions afterwards in step (V) to remove traces of hydrofluoric acid or hydrochloric acid.

- An especially preferred embodiment of the present invention is a process for the production and improving the storage stability of polyisobutene, comprising the steps of
- (I) first polymerising isobutene or an isobutene-containing monomer mixture
 - in the presence of at least one Lewis Acid-donor complex and
 - at least one initiator,
 - (II) terminating the polymerisation by adding water or basic material to the reaction mixture,
 - (III) distilling off unreacted monomer and lower oligomers of isobutene,
- yielding a polyisobutene composition
- in the case of polyisobutene with a number average molecular weight M_n of less than 10000 g/mol, a polyisobutene composition with a content of polyisobutene species (A) bearing an alpha-double bond of at least 50 mol%, preferably at least 60 mol%, more preferably at least 70 mol%, most preferably at least 75 mol% and especially at least 80 mol% or even 85 mol%,
 - in the case of polyisobutene with a number average molecular weight M_n of from 10000 to 100000 g/mol, a polyisobutene composition with a content of polyisobutene species (A) bearing an alpha-double bond of at least 20 to 60 mol%, preferably at least 25 to 45 mol%, and more preferably at least 30 to 40 mol%,
 - in the case of polyisobutene with a number average molecular weight M_n of more than 100000 to 5000000 g/mol, a polyisobutene composition with a content of polyisobutene species (A) bearing an alpha-double bond of at least 10 to 50 mol%, preferably at least 15 to 45 mol%, and more preferably at least 15 to 40 mol%,
- followed by
- (IV) afterwards optionally adding at least one solvent to this polyisobutene composition,
 - treating the optionally dissolved polyisobutene composition
 - in the presence of at least one acidic solid state catalyst, optionally treated with at least one Brønsted-base
 - for a period of from 5 minutes to 36 hours
 - at a temperature of from 40 °C to 250 °C,
 - (V) washing the reaction mixture with water,
- wherein the washing step (V) may take place after step (III) and/or step (IV).

The addition of at least one solvent in step (IV) is less preferred since such a solvent would have to be removed later again.

The amounts of isomers given throughout the text refer to mol%, unless explicitly stated otherwise. Since the determination of the individual or groups of isomers is conducted by NMR analysis (details see below) the result of such NMR analysis is a percental distribution of certain NMR signals of these isomers relative to the integral of the respective nucleus determined.

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In one embodiment of the present invention such process uses low molecular polyisobutene as a starting material.

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In another embodiment of the present invention such process uses medium molecular polyisobutene as a starting material.

In another embodiment of the present invention such process uses high molecular polyisobutene as a starting material.

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Processes for the preparation of such polyisobutene compositions with a higher content of alpha-double bonds are known in the prior art and are relevant for the present invention insofar that they are required for the preparation of the starting material of the process according to the present invention.

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For the preparation of such polyisobutene compositions with a higher content of alpha-double bonds usually isobutene or an isobutenic starting material is polymerised in the presence of at least one Lewis Acid-donor complex and an initiator.

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As a Lewis Acid usually metal halides are used, preferably halides of boron, aluminium, iron, gallium, titanium, zinc or tin.

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Typical examples are boron trifluoride, boron trichloride, aluminum trihalide, alkylaluminum dihalide, dialkylaluminum halide, iron trihalide, gallium trihalide, titanium tetrahalide, zinc dihalide, tin dihalide, tin tetrahalide, wherein the halide is preferably fluoride or chloride, more preferably chloride.

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Preferred are boron trifluoride, aluminum trichloride, alkyl aluminum dichloride, dialkyl aluminum chloride, and iron trichloride, more preferred are boron trifluoride, aluminum trichloride, and alkyl aluminum dichloride, most preferred are boron trifluoride and aluminum trichloride with boron trifluoride being especially preferred.

Examples for suitable donor compounds comprise at least one oxygen and/or nitrogen atom with at least one lone electron pair, preferably at least one oxygen atom with at least one lone electron pair and very preferably are selected from the group consisting of organic compounds with at least one ether function, organic compounds with at least one carboxylic ester function, organic compounds with at least one aldehyde function, organic compounds with at least one keto function, and organic compounds with at least one nitrogen containing heterocyclic ring.

Solely oxygen containing donor compounds are preferred over nitrogen-containing donor compounds.

Preferably the donor is selected from the group consisting of organic compounds with at least one ether function, organic compounds with at least one carboxylic ester function and organic compounds with at least one keto function, more preferably selected from the group consisting of organic compounds with at least one ether function and organic compounds with at least one carboxylic ester function, very preferably donors are organic compounds with at least one ether function, and especially organic compounds with exactly one ether function.

Compounds with at least one ether function are also understood to mean acetals and hemiacetals. The ether compound may comprise one or more ether functions, e.g. one, two, three, four or even more ether functions, preferably one or two ether functions and very preferably one ether function.

The mixture of donors may comprise one, two, three, four or even more different compounds, preferably compounds with at least one ether function, preferably one or two different compounds and very preferably one compound.

It may be an advantage to use a mixture of two different donors, especially two different ethers, see e.g. WO 2017/1140603 for aluminium halide-donor complexes

In a preferred embodiment of the present invention, a boron trihalide-donor complex, an aluminum trihalide-donor complex or an alkylaluminum halide complex, or an iron trihalide-donor complex, or a gallium trihalide-donor complex or a titanium tetrahalide-donor complex or a zinc dihalide-donor complex or a tin dihalide-donor complex or the tin tetrahalide-donor complex or the boron trihalide-donor complex, very preferably a boron trihalide-donor complex, an aluminum trihalide-donor complex or an iron trihalide-donor complex or a boron trihalide-donor complex and especially a boron trihalide-donor complex or an aluminum trihalide-donor complex is used, which comprises, as the donor, at least one dihydrocarbyl ether the general formula R^8-O-

R⁹ in which the variables R⁸ and R⁹ are each independently C₁- to C₂₀-alkyl radicals, preferably C₁- to C₈ alkyl radicals especially C₁- to C₄ alkyl radicals, C₁- to C₂₀-haloalkyl radicals, preferably C₁- to C₈ haloalkyl radicals especially C₁- to C₄ haloalkyl radicals, C₅- to C₈-cycloalkyl radicals, preferably C₅- to C₆-cycloalkyl radicals, C₆- to C₂₀-aryl radicals, especially C₆- to C₁₂ aryl radicals, C₆- to C₂₀-haloaryl radicals, especially C₆- to C₁₂ haloaryl radicals, or C₇- to C₂₀-arylalkyl radicals, especially C₇- to C₁₂-arylalkyl radicals. Preference is given to C₁- to C₄ alkyl radicals, C₁- to C₄ haloalkyl radicals, C₆- to C₁₂ aryl radicals, and C₇- to C₁₂-arylalkyl radicals

Haloalkyl and haloaryl mean preferably chloroalkyl or bromoalkyl and chloroaryl or bromoaryl, very preferably chloroalkyl and chloroaryl. Especially preferred are ω-haloalkyl radicals.

Preferred examples are chloromethyl, 1-chloroeth-1-yl, 2-chloroeth-1-yl, 2-chloroprop-1-yl, 2-chloroprop-2-yl, 3-chloroprop-1-yl, and 4-chlorobut-1-yl.

Preferred examples for chloroaryl are 2-chlorophenyl, 3-chlorophenyl, and 4-chlorophenyl.

The dihydrocarbyl ethers mentioned may be open-chain or cyclic, where the two variables R⁸ and R⁹ in the case of the cyclic ethers may join to form a ring, where such rings may also comprise two or three ether oxygen atoms. Examples of such open-chain and cyclic dihydrocarbyl ethers are dimethyl ether, chloromethyl methyl ether, bis (chloromethyl) ether, diethyl ether, chloromethyl ethyl ether, 2-chloroethyl ethyl ether (CEE), bis (2-chloroethyl) ether (CE), di-n-propyl ether, diisopropyl ether, di-n-butyl ether, di-sec-butyl ether, diisobutyl ether, di-n-pentyl ether, di-n-hexyl ether, di-n-heptyl ether, di-n-octyl ether, di-(2-ethylhexyl) ether, methyl n-butyl ether, methyl sec-butyl ether, methyl isobutyl ether, methyl tert-butyl ether, ethyl n-butyl ether, ethyl sec-butyl ether, ethyl isobutyl ether, ethyl tert-butyl ether, n-propyl-n-butyl ether, n-propyl sec-butyl ether, n-propyl isobutyl ether, n-propyl tert-butyl ether, isopropyl n-butyl ether, isopropyl sec-butyl ether, isopropyl isobutyl ether, isopropyl tert-butyl ether, methyl n-hexyl ether, methyl n-octyl ether, methyl 2-ethylhexyl ether, ethyl n-hexyl ether, ethyl n-octyl ether, ethyl 2-ethylhexyl ether, n-butyl n-octyl ether, n-butyl 2-ethylhexyl ether, tetrahydrofuran, tetrahydropyran, 1,2-, 1,3- and 1,4-dioxane, dicyclohexyl ether, diphenyl ether, alkyl aryl ethers, such as anisole and phenetole, ditolyl ether, dixylyl ether and dibenzyl ether.

Furthermore, difunctional ethers such as dialkoxybenzenes, preferably dimethoxybenzenes, very preferably veratrol, and ethylene glycol dialkylethers, preferably ethylene glycol dimethylether and ethylene glycol diethylether, are preferred.

Among the dihydrocarbyl ethers mentioned, diethyl ether, 2-chloroethyl ethyl ether, diisopropyl ether, di-n-butyl ether and diphenyl ether have been found to be particularly advantageous as donors for the boron trihalide-donor complexes, the aluminum trihalide-donor complexes or the alkylaluminum halide complexes or the iron trihalide-donor complexes or the gallium trihalide-donor complex or the titanium tetrahalide-donor complex or the zinc dihalide-donor complex or the tin dihalide-donor complex or the tin tetrahalide-donor complex or the boron trihalide-donor complex, very preferably boron trihalide-donor complexes, the aluminum trihalide-donor complexes or iron trihalide-donor complexes or boron trihalide-donor complex and especially the a boron trihalide-donor complexes or the aluminum trihalide-donor complexes.

In a preferred embodiment dihydrocarbyl ethers with at least one secondary or tertiary dihydrocarbyl group are preferred over dihydrocarbyl groups with primary groups only. Ethers with primary dihydrocarbyl groups are those ethers in which both dihydrocarbyl groups are bound to the ether functional group with a primary carbon atom, whereas ethers with at least one secondary or tertiary dihydrocarbyl group are those ethers in which at least one dihydrocarbyl group is bound to the ether functional group with a secondary or tertiary carbon atom.

For the sake of clarity, e.g. diisobutyl ether is deemed to be an ether with primary dihydrocarbyl groups, since the secondary carbon atom of the isobutyl group is not bound to the oxygen of the functional ether group but the hydrocarbyl group is bound via a primary carbon atom.

Preferred examples for ethers with primary dihydrocarbyl groups are diethyl ether, di-n-butyl ether, and di-n-propyl ether.

Preferred examples for ethers with at least one secondary or tertiary dihydrocarbyl group are diisopropyl ether, methyl tert-butyl ether, ethyl tert-butyl ether, and anisole.

In addition, particularly advantageous dihydrocarbyl ethers as donors for the boron trihalide-donor complexes, the aluminum trihalide-donor complexes or the alkylaluminum halide complexes, have been found to be those in which the donor compound has a total carbon number of 3 to 16, preferably of 4 to 16, especially of 4 to 12, in particular of 4 to 8.

In another preferred embodiment halide-substituted ethers are preferred in combination with aluminum halide-donor complex or iron halide-donor complex or boron halide-donor complex.

Organic compounds with at least one carboxylic ester function are preferably hydrocarbyl carboxylates of the general formula $R^{10}\text{-COOR}^{11}$ in which the variables R^{10} and R^{11} are each inde-

pendently C₁- to C₂₀-alkyl radicals, especially C₁- to C₈ alkyl radicals, C₅- to C₈-cycloalkyl radicals, C₆- to C₂₀-aryl radicals, especially C₆- to C₁₂ aryl radicals, or C₇- to C₂₀-arylalkyl radicals, especially C₇- to C₁₂-arylalkyl radicals.

- 5 Examples of the hydrocarbyl carboxylates mentioned are methyl formate, ethyl formate, n-propyl formate, isopropyl formate, n-butyl formate, sec-butyl formate, isobutyl formate, tert-butyl formate, methyl acetate, ethyl acetate, n-propyl acetate, isopropyl acetate, n-butyl acetate, sec-butyl acetate, isobutyl acetate, tert-butyl acetate, methyl propionate, ethyl propionate, n-propyl propionate, isopropyl propionate, n-butyl propionate, sec-butyl propionate, isobutyl propionate, tert-butyl propionate, methyl butyrate, ethyl butyrate, n-propyl butyrate, isopropyl butyrate, n-butyl butyrate, sec-butyl butyrate, isobutyl butyrate, tert-butyl butyrate, methyl cyclohexanecarboxylate, ethyl cyclohexanecarboxylate, n-propyl cyclohexanecarboxylate, isopropyl cyclohexanecarboxylate, n-butyl cyclohexanecarboxylate, sec-butyl cyclohexanecarboxylate, isobutyl cyclohexanecarboxylate, tert-butyl cyclohexanecarboxylate, methyl benzoate, ethyl benzoate, n-propyl benzoate, isopropyl benzoate, n-butyl benzoate, sec-butyl benzoate, isobutyl benzoate, tert-butyl benzoate, methyl phenylacetate, ethyl phenylacetate, n-propyl phenylacetate, isopropyl phenylacetate, n-butyl phenylacetate, sec-butyl phenylacetate, isobutyl phenylacetate and tert-butyl phenylacetate. Among the hydrocarbyl carboxylates mentioned, ethyl acetate has been found to be particularly advantageous as a donor for the complexes.

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In addition, particularly advantageous hydrocarbyl carboxylates as donors, have been found to be those in which the donor compound has a total carbon number of 3 to 16, preferably of 4 to 16, especially of 4 to 12, in particular of 4 to 8, preference is given in particular to those having a total of 3 to 10 and especially 4 to 6 carbon atoms.

25

Organic compounds with at least one aldehyde function, preferably exactly one aldehyde function and organic compounds with at least one keto function, preferably exactly one keto function typically have from 1 to 20, preferably from 2 to 10 carbon atoms. Functional groups other than the carbonyl group are preferably absent.

30

Preferred organic compounds with at least one aldehyde function are those of formula R¹⁰-CHO, in which R¹⁰ has the above-mentioned meaning, very preferably are selected from the group consisting of formaldehyde, acetaldehyde, propionaldehyde, n-butyraldehyde, isobutyraldehyde, and benzaldehyde.

35

Preferred organic compounds with at least one keto function are those of formula R¹⁰-(C=O)-R¹¹, in which R¹⁰ and R¹¹ have the above-mentioned meaning, very preferably are selected from

the group consisting of acetone, methyl ethyl ketone, diethyl ketone, methyl isobutyl ketone, cyclohexanone, acetophenone, and benzophenone. Greatest preference is given to acetone.

Organic compounds with at least one nitrogen containing heterocyclic ring are preferably saturated, partly unsaturated or unsaturated nitrogen-containing five-membered or six-membered heterocyclic rings which comprises one, two or three ring nitrogen atoms and may have one or two further ring heteroatoms from the group of oxygen and sulphur and/or hydrocarbyl radicals, especially C₁- to C₄-alkyl radicals and/or phenyl, and/or functional groups or heteroatoms as substituents, especially fluorine, chlorine, bromine, nitro and/or cyano, for example pyrrolidine, pyrrole, imidazole, 1,2,3- or 1,2,4-triazole, oxazole, thiazole, piperidine, pyrazane, pyrazole, pyridazine, pyrimidine, pyrazine, 1,2,3-, 1,2,4- or 1,2,5-triazine, 1,2,5-oxathiazine, 2H-1,3,5-thiadiazine or morpholine.

However, a very particularly suitable nitrogen-containing basic compound of this kind is pyridine or a derivative of pyridine (especially a mono-, di- or tri-C₁- to C₄-alkyl-substituted pyridine) such as 2-, 3-, or 4-methylpyridine (picolines), 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, 3,5- or 3,6-dimethylpyridine (lutidines), 2,4,6-trimethylpyridine (collidine), 2-, 3-, or 4-tert-butylpyridine, 2-tert-butyl-6-methylpyridine, 2,4-, 2,5-, 2,6- or 3,5-di-tert-butylpyridine or else 2-, 3-, or 4-phenylpyridine.

20 Initiator:

The polymerization is preferably performed with additional use of a mono- or polyfunctional, especially mono-, di- or trifunctional, initiator which is selected from organic hydroxyl compounds, organic halogen compounds and water. It is also possible to use mixtures of the initiators mentioned, for example mixtures of two or more organic hydroxyl compounds, mixtures of two or more organic halogen compounds, mixtures of one or more organic hydroxyl compounds and one or more organic halogen compounds, mixtures of one or more organic hydroxyl compounds and water, or mixtures of one or more organic halogen compounds and water. The initiator may be mono-, di- or polyfunctional, i.e. one, two or more hydroxyl groups or halogen atoms, which start the polymerization reaction, may be present in the initiator molecule. In the case of di- or polyfunctional initiators, telechelic isobutene polymers with two or more, especially two or three, polyisobutene chain ends are typically obtained.

Organic hydroxyl compounds which have only one hydroxyl group in the molecule and are suitable as monofunctional initiators include especially alcohols and phenols, in particular those of the general formula R¹²-OH, in which R¹² denotes C₁- to C₂₀-alkyl radicals, especially C₁- to C₈-alkyl radicals, C₅- to C₈-cycloalkyl radicals, C₆- to C₂₀-aryl radicals, especially C₆- to C₁₂-aryl

radicals, or C₇- to C₂₀-arylalkyl radicals, especially C₇- to C₁₂-arylalkyl radicals. In addition, the R¹² radicals may also comprise mixtures of the abovementioned structures and/or have other functional groups than those already mentioned, for example a keto function, a nitroxide or a carboxyl group, and/or heterocyclic structural elements.

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Typical examples of such organic monohydroxyl compounds are methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, isobutanol, tert-butanol, n-pentanol, n-hexanol, n-heptanol, n-octanol, 2-ethylhexanol, cyclohexanol, phenol, p-methoxyphenol, o-, m- and p-cresol, benzyl alcohol, p-methoxybenzyl alcohol, 1- and 2-phenylethanol, 1- and 2-(p-methoxyphenyl)ethanol, 10 1-, 2- and 3-phenyl-1-propanol, 1-, 2- and 3-(p-methoxyphenyl)-1-propanol, 1- and 2-phenyl-2-propanol, 1- and 2-(p-methoxyphenyl)-2-propanol, 1-, 2-, 3- and 4-phenyl-1-butanol, 1-, 2-, 3- and 4-(p-methoxyphenyl)-1-butanol, 1-, 2-, 3- and 4-phenyl-2-butanol, 1-, 2-, 3- and 4-(p-methoxyphenyl)-2-butanol, 9-methyl-9H-fluoren-9-ol, 1,1-diphenylethanol, 1,1-diphenyl-2-propyn-1-ol, 1,1-diphenylpropanol, 4-(1-hydroxy-1-phenylethyl)benzonitrile, cyclopropyldiphenylmethanol, 15 1-hydroxy-1,1-diphenylpropan-2-one, benzilic acid, 9-phenyl-9-fluorenol, triphenylmethanol, diphenyl(4-pyridinyl)methanol, alpha,alpha-diphenyl-2-pyridinemethanol, 4-methoxytrityl alcohol (especially polymer-bound as a solid phase), alpha-tert-butyl-4-chloro-4'-methylbenzhydrol, cyclohexyldiphenylmethanol, alpha-(p-tolyl)-benzhydrol, 1,1,2-triphenylethanol, alpha,alpha-diphenyl-2-pyridineethanol, alpha,alpha-4-pyridylbenzhydrol N-oxide, 2-fluorotriphenylmethanol, 20 triphenylpropargyl alcohol, 4-[(diphenyl)hydroxymethyl]benzonitrile, 1-(2,6-dimethoxyphenyl)-2-methyl-1-phenyl-1-propanol, 1,1,2-triphenylpropan-1-ol and p-anisaldehyde carbinol.

In a preferred embodiment it is possible to use a mixture of primary and secondary alcohols as initiators, as described in WO 2013/120859.

25

Organic hydroxyl compounds which have two hydroxyl groups in the molecule and are suitable as bifunctional initiators are especially dihydric alcohols or diols having a total carbon number of 2 to 30, especially of 3 to 24, in particular of 4 to 20, and bisphenols having a total carbon number of 6 to 30, especially of 8 to 24, in particular of 10 to 20, for example ethylene glycol, 1,2- 30 and 1,3-propylene glycol, 1,4-butylene glycol, 1,6-hexylene glycol, 1,2-, 1,3- or 1,4-bis(1-hydroxy-1-methylethyl)benzene (o-, m- or p-dicumyl alcohol), bisphenol A, 9,10-di-hydro-9,10-dimethyl-9,10-anthracenediol, 1,1-diphenylbutane-1,4-diol, 2-hydroxytriphenylcarbinol and 9-[2-(hydroxymethyl)phenyl]-9-fluorenol.

Organic halogen compounds which have one halogen atom in the molecule and are suitable as 35 monofunctional initiators are in particular compounds of the general formula R¹³-Hal in which Hal is a halogen atom selected from fluorine, iodine and especially chlorine and bromine, and R¹³ denotes C₁- to C₂₀-alkyl radicals, especially C₁- to C₈-alkyl radicals, C₅- to C₈-cycloalkyl radi-

cals or C₇- to C₂₀-arylalkyl radicals, especially C₇- to C₁₂-arylalkyl radicals. In addition, the R¹³ radicals may also comprise mixtures of the abovementioned structures and/or have other functional groups than those already mentioned, for example a keto function, a nitroxide or a carboxyl group, and/or heterocyclic structural elements.

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Typical examples of such monohalogen compounds are methyl chloride, methyl bromide, ethyl chloride, ethyl bromide, 1-chloropropane, 1-bromopropane, 2-chloropropane, 2-bromopropane, 1-chlorobutane, 1-bromobutane, sec-butyl chloride, sec-butyl bromide, isobutyl chloride, isobutyl bromide, tert-butyl chloride, tert-butyl bromide, 1-chloropentane, 1-bromopentane, 1-chloro-
10 hexane, 1-bromohexane, 1-chloroheptane, 1-bromoheptane, 1-chlorooctane, 1-bromooctane, 1-chloro-2-ethylhexane, 1-bromo-2-ethylhexane, cyclohexyl chloride, cyclohexyl bromide, benzyl chloride, benzyl bromide, 1-phenyl-1-chloroethane, 1-phenyl-1-bromoethane, 1-phenyl-2-chloroethane, 1-phenyl-2-bromoethane, 1-phenyl-1-chloropropane, 1-phenyl-1-bromopropane, 1-phenyl-2-chloropropane, 1-phenyl-2-bromopropane, 2-phenyl-2-chloropropane, 2-phenyl-2-bromo-
15 propane, 1-phenyl-3-chloropropane, 1-phenyl-3-bromopropane, 1-phenyl-1-chlorobutane, 1-phenyl-1-bromobutane, 1-phenyl-2-chlorobutane, 1-phenyl-2-bromobutane, 1-phenyl-3-chlorobutane, 1-phenyl-3-bromobutane, 1-phenyl-4-chlorobutane, 1-phenyl-4-bromobutane, 2-phenyl-1-chlorobutane, 2-phenyl-1-bromobutane, 2-phenyl-2-chlorobutane, 2-phenyl-2-bromobutane, 2-phenyl-3-chlorobutane, 2-phenyl-3-bromobutane, 2-phenyl-4-chlorobutane and 2-phenyl-4-
20 bromobutane.

Organic halogen compounds which have two halogen atoms in the molecule and are suitable as difunctional initiators are, for example, 1,3-bis(1-bromo-1-methylethyl)benzene, 1,3-bis(2-chloro-2-propyl)benzene (1,3-dicumyl chloride) and 1,4-bis(2-chloro-2-propyl)benzene (1,4-dicumyl
25 chloride).

The initiator is more preferably selected from organic hydroxyl compounds in which one or more hydroxyl groups are each bonded to an sp³-hybridized carbon atom, organic halogen compounds, in which one or more halogen atoms are each bonded to an sp³-hybridized carbon
30 atom, and water. Among these, preference is given in particular to an initiator selected from organic hydroxyl compounds in which one or more hydroxyl groups are each bonded to an sp³-hybridized carbon atom.

In the case of the organic halogen compounds as initiators, particular preference is further given
35 to those in which the one or more halogen atoms are each bonded to a secondary or especially to a tertiary sp³-hybridized carbon atom.

Preference is given in particular to initiators which may bear, on such an sp^3 -hybridized carbon atom, in addition to the hydroxyl group, the R^{12} , R^{13} and R^{14} radicals, which are each independently hydrogen, C_1 - to C_{20} -alkyl, C_5 - to C_8 -cycloalkyl, C_6 - to C_{20} -aryl, C_7 - to C_{20} -alkylaryl or phenyl, where any aromatic ring may also bear one or more, preferably one or two, C_1 - to C_4 -alkyl, C_1 - to C_4 -alkoxy, C_1 - to C_4 -hydroxyalkyl or C_1 - to C_4 -haloalkyl radicals as substituents, where not more than one of the variables R^{12} , R^{13} and R^{14} is hydrogen and at least one of the variables R^{12} , R^{13} and R^{14} is phenyl which may also bear one or more, preferably one or two, C_1 - to C_4 -alkyl, C_1 - to C_4 -alkoxy, C_1 - to C_4 -hydroxyalkyl or C_1 - to C_4 -haloalkyl radicals as substituents.

10

For the present invention, very particular preference is given to initiators selected from water, methanol, ethanol, 1-phenylethanol, 1-(p-methoxyphenyl)ethanol, n-propanol, isopropanol, 2-phenyl-2-propanol (cumene), n-butanol, isobutanol, sec.-butanol, tert-butanol, 1-phenyl-1-chloroethane, 2-phenyl-2-chloropropane (cumyl chloride), tert-butyl chloride and 1,3- or 1,4-bis(1-hydroxy-1-methylethyl)benzene. Among these, preference is given in particular to initiators selected from water, methanol, ethanol, 1-phenylethanol, 1-(p-methoxyphenyl)ethanol, n-propanol, isopropanol, 2-phenyl-2-propanol (cumene), n-butanol, isobutanol, sec.-butanol, tert-butanol, 1-phenyl-1-chloroethane and 1,3- or 1,4-bis(1-hydroxy-1-methylethyl)benzene.

20 Special preference is given to water as initiator.

Starting material for polymerisation

- The raw material of C4 compounds may be selected from the group consisting of
- 25 (a) a C4 compound material in which an isobutene amount is adjusted to 50 to 75% by weight, obtained by adding high purity isobutene having the isobutene amount of 90 to 100% by weight to C4 raffinate-1 which is a remainder after extracting 1,3-butadiene from a C4 compound derived during a naphtha degrading process;
 - (b) a C4 compound material in which an isobutene amount is adjusted to 50 to 75% by weight, 30 obtained by adding high amount isobutene mixture having isobutene amount of 80 to 97% by weight, which is generated in an olefin conversion unit (OCU) process that produces propylene by the metathesis of ethylene and 2-butene, to C4 raffinate-1 which is a remainder after extracting 1,3-butadiene from a C4 compound derived during a naphtha degrading process;
 - (c) a C4 compound material in which an isobutene amount is adjusted to 50 to 75% by weight, 35 obtained by adding high purity isobutene having the isobutene amount of 90 to 100% by weight to butane-butene oil (B-B oil) derived from crude oil refining process;
 - (d) a C4 compound material in which an isobutene amount is adjusted to 50 to 75% by weight,

obtained by adding high amount isobutene mixture having the isobutene amount of 80 to 97% by weight, which is generated in an olefin conversion unit (OCU) process that produces propylene by the metathesis of ethylene and 2-butene, to butane-butene oil (B-B oil) derived from crude oil refining process;

5 (e) a C₄ compound material in which an isobutene amount is adjusted to 50 to 75% by weight, obtained by adding a dilute solvent to high purity isobutene having an isobutene amount of 90 to 100% by weight;

(f) a C₄ compound material in which an isobutene amount is adjusted to 50 to 75% by weight, obtained by adding a dilute solvent to high amount isobutene mixture having the isobutene
10 amount of 80 to 97% by weight, which is generated in an olefin conversion unit (OCU) process that produces propylene by the metathesis of ethylene and 2-butene;

(g) a C₄ compound material in which an isobutene amount is adjusted to 50 to 75% by weight, obtained by adding high purity isobutene having the isobutene amount of 90 to 100% by weight to a mixture generated in dehydrogenation reaction that converts isobutane to isobutene; and

15 (h) a C₄ compound material in which an isobutene amount is adjusted to 50 to 75% by weight, obtained by adding high amount isobutene mixture having the isobutene amount of 80 to 97% by weight, which is generated in an olefin conversion unit (OCU) process that produces propylene by the metathesis of ethylene and 2-butene to a mixture generated in dehydrogenation reaction that converts isobutane to isobutene.

20

For the use of isobutene or of an isobutene-comprising monomer mixture as the monomer to be polymerized, suitable isobutene sources are both pure isobutene and isobutenic C₄ hydrocarbon streams, for example C₄ raffinates, especially "raffinate 1", C₄ cuts from isobutane dehydrogenation, C₄ cuts from steam crackers and from FCC crackers (fluid catalyzed cracking), provided that they have been substantially freed of 1,3-butadiene present therein. A C₄ hydrocarbon stream from an FCC refinery unit is also known as "b/b" stream. Further suitable isobutenic C₄ hydrocarbon streams are, for example, the product stream of a propylene-isobutane cooxidation or the product stream from a metathesis unit, which are generally used after customary purification and/or concentration. Suitable C₄ hydrocarbon streams generally comprise less than
25 500 ppm, preferably less than 200 ppm, of butadiene. The presence of 1-butene and of cis- and trans-2-butene is substantially uncritical. Typically, the isobutene concentration in the C₄ hydrocarbon streams mentioned is in the range from 40 to 60% by weight. For instance, raffinate 1 generally consists essentially of 30 to 50% by weight of isobutene, 10 to 50% by weight of 1-butene, 10 to 40% by weight of cis- and trans-2-butene, and 2 to 35% by weight of butanes; in
30 the polymerization process according to the invention, the unbranched butenes in the raffinate 1 generally behave virtually inertly, and only the isobutene is polymerized.

In a preferred embodiment, the monomer source used for the polymerization is a technical C₄ hydrocarbon stream with an isobutene content of 1 to 100% by weight, especially of 1 to 99% by weight, in particular of 1 to 90% by weight, more preferably of 30 to 60% by weight, especially a raffinate 1 stream, a b/b stream from an FCC refinery unit, a product stream from a propylene-isobutane cooxidation or a product stream from a metathesis unit.

Especially when a raffinate 1 stream is used as the isobutene source, the use of water as the sole initiator or as a further initiator has been found to be useful, in particular when polymerization is effected at temperatures of -20°C to +30°C, especially of 0°C to +20°C. At temperatures of -20°C to +30°C, especially of 0°C to +20°C, when a raffinate 1 stream is used as the isobutene source, it is, however, also possible to dispense with the use of an initiator.

The isobutenic monomer mixture mentioned may comprise small amounts of contaminants such as water, carboxylic acids or mineral acids, without there being any critical yield or selectivity losses. It is appropriate to prevent enrichment of these impurities by removing such harmful substances from the isobutenic monomer mixture, for example by adsorption on solid adsorbents such as activated carbon, molecular sieves or ion exchangers.

The isobutene or the isobutene containing C₄ hydrocarbon stream can at least partially, preferably completely, originate from renewable sources, as described for example in WO 2012/40859 A1, particularly from page 5, line 9 to page 6, line 24. The proportion of isobutene from renewable sources in the total amount of isobutene used, measured according to ASTM D 6866 as described in WO 2012/40859 A1, is advantageously at least 1 wt%, preferably at least 2 wt%, particularly preferably at least 10 wt%, especially preferably at least 25 wt%, and specifically at least 50 wt%. The proportion of isobutene from renewable sources can be up to 100 wt%, preferably up to 95 wt%, particularly preferably up to 90 wt%, especially preferably up to 85 wt%, and specifically up to 80 wt%.

In a preferred embodiment of the present invention, the isobutene used in the isobutene-comprising monomer mixture resp. in the polyisobutene has a biobased fraction, measured as a ¹⁴C:¹²C ratio ASTM-D6866, of more than 0%, preferably at least 1%, particularly preferably at least 5%, even more preferably at least 10%, especially at least 20%, and specifically at least 25%.

Advantageously, this biobased fraction can be at least 30%, preferably at least 40%, particularly preferably at least 50%, even more preferably at least 66%, especially at least 75%, and specifically at least 85%.

At a fraction of at least 90%, preferably at least 95%, particularly preferably at least 98%, and even 100%, this can be referred to as significantly predominant or completely biobased isobutene.

- 5 According to this embodiment, resources are conserved and the product is produced at least partially with renewable raw materials.

In another embodiment of the present invention, the isobutene used in the polymerization can be obtained entirely from renewable raw materials or consist of mixtures of isobutene from re-
10 newable and fossil sources.

The latter embodiment is particularly preferred as long as isobutene from renewable sources is not available in industrially sufficient quantities and economically viable.

- 15 The terms "renewable" or "bio-based" used herein with regard to a material or a compound (such as alcohols, alkyl, olefins, di-olefins, etc.) denote a material or compound obtained from a "new carbon" source as measured by ASTM test method designated as D 6866, "Determining the Biobased Content of Natural Range Materials Using Radiocarbon and Isotope Ratio Mass Spectrometry Analysis", incorporated herein by reference in its entirety. This test method
20 measures the $^{14}\text{C}/^{12}\text{C}$ isotope ratio in a sample and compares it to the $^{14}\text{C}/^{12}\text{C}$ isotope ratio in a standard 100% bio-based material to give percent biobased content of the sample.

"Renewable" or "bio-based" compounds can be prepared from biomass using thermochemical methods (e.g., Fischer-Tropsch catalysts), biocatalysts (e.g., fermentation), or other processes.
25

- All types of polymers made with the isobutene of this invention are verifiable as being made with isobutene that did not originate from a petrochemical source. Additionally, the isobutene containing polymers of this invention can also be distinguished from isobutene containing polymers that come from natural sources, such as natural rubber. Accordingly, the isobutene containing
30 polymers of this invention are analytically verifiable as coming from the bio- renewable, environmentally friendly sources. Assessment of the renewably based carbon content of a material can be performed through standard test methods, e.g. using radiocarbon and isotope ratio mass spectrometry analysis. ASTM International (formally known as the American Society for Testing and Materials) has established a standard method for assessing the biobased content of mate-
35 rials. The ASTM method is designated ASTM-D6866.

The application of ASTM-D6866 to derive "biobased content" is built on the same concepts as radiocarbon dating, but without use of the age equations. The analysis is performed by deriving a ratio of the amount of radiocarbon (^{14}C) in an unknown sample compared to that of a modern reference standard. This ratio is reported as a percentage with the units "pMC"(percent modern carbon). If the material being analyzed is a mixture of present day radiocarbon and fossil carbon (containing very low levels of radiocarbon), then the pMC value obtained correlates directly to the amount of biomass material present in the sample. "Biobased materials" are organic materials in which the carbon comes from recently (on a human time scale) fixated CO_2 present in the atmosphere using sunlight energy (photosynthesis). On land, this CO_2 is captured or fixated by plant life (e.g., agricultural crops or forestry materials). In the oceans, the CO_2 is captured or fixated by photosynthesizing bacteria or phytoplankton. For example, a biobased material has a $^{14}\text{C}/^{12}\text{C}$ isotope ratio greater than 0. Contrarily, a fossil-based material, has a $^{14}\text{C}/^{12}\text{C}$ isotope ratio of about 0.

A small amount of the carbon atoms of the carbon dioxide in the atmosphere is the radioactive isotope ^{14}C , which is created when atmospheric nitrogen is struck by a cosmic ray generated neutron, causing the nitrogen to lose a proton and form carbon of atomic mass 14 (^{14}C), which is then immediately oxidized to carbon dioxide. A small but measurable fraction of atmospheric carbon is present in the form of $^{14}\text{CO}_2$. Atmospheric carbon dioxide is processed by green plants to make organic molecules during the process known as photosynthesis. Virtually all forms of life on Earth depend on this green plant production of organic molecules to produce the chemical energy that facilitates growth and reproduction. Therefore, the ^{14}C that forms in the atmosphere eventually becomes part of all life forms and their biological products, enriching biomass and organisms which feed on biomass with ^{14}C . In contrast, carbon from fossil fuels does not have the signature $^{14}\text{C}:^{12}\text{C}$ ratio of renewable organic molecules derived from atmospheric carbon dioxide.

To achieve a desired biobased content in an isobutene-based polymer, the mixture ratio of biobased isobutene to petroleum based isobutene in the polymer may be varied. In one embodiment, the biobased content for the isobutene-based elastomer of the present invention is greater than 0%. In another embodiment, the biobased content for the isobutene-based elastomer is greater than 20%. In another embodiment, the biobased content for the isobutene-based elastomer is greater than 40%. In another embodiment, the biobased content for the isobutene-based elastomer is greater than 60%. In another embodiment, the biobased content for the isobutene-based elastomer is greater than 80%. In another embodiment, the biobased content for the isobutene-based elastomer is greater than 90%. Alternatively or additionally, the multiolefin content of the final polymer can be modified by adjusting the multiolefin monomer feed for the

polymerization reaction. For example, 4 mol% (petroleum-based isoprene, renewable isoprene or mixtures thereof) incorporation of isoprene into the final butyl polymer would result in a biobased content of between 5 to 95% (ASTM D6866). As another example, 0.9 mol% (petroleum-based isoprene, renewable isoprene or mixtures thereof) incorporation of isoprene into the

5 final butyl polymer would result in a biobased content of between 1 to 99% (ASTM D6866). Polymerization of a butyl rubber polymer using biobased isoprene and bio-isobutene will yield a bio-butyl rubber with a bio-based content of 100% (ASTM D6866).

The present invention also relates to a method for verifying that a polymer having repeating

10 units derived from isobutene contains isobutene that is obtained from a renewable non-petroleum derived hydrocarbon source. This method involves (a) determining the biobased content of the polymer; and (b) verifying that the polymer is from a renewable non-petroleum derived source if the biobased content (as described in ASTM D6866) of greater than 0%.

15 The verification method can be applied to homopolymers or copolymer of isobutene. In one embodiment, the method relates to verifying if a block copolymer having repeating units derived from isobutene contains isobutene that is from a renewable, sustainable non-petroleum derived source which comprises: (a) determining the percent modern carbon of at least one polyisobutene block in the copolymer; and (b) verifying that the isobutene from the copolymer is from a

20 renewable, sustainable non-petroleum derived source if polyisobutene block has a total biobased content (ASTM D6866-08) greater than 0%.

The polymerization of isobutene or the isobutene-containing C4-mixture can be effected either continuously or batchwise. Continuous processes can be performed in analogy to known prior

25 art processes for continuous polymerization of isobutene in the presence of boron trifluoride-based catalysts in the liquid phase.

It is also possible to convert monomer mixtures of isobutene or of the isobutenic hydrocarbon mixture with olefinically unsaturated monomers copolymerizable with isobutene. When monomer mixtures of isobutene are to be copolymerized with suitable comonomers, the monomer

30 mixture preferably comprises at least 5% by weight, more preferably at least 10% by weight and especially at least 20% by weight of isobutene, and preferably at most 95% by weight, more preferably at most 90% by weight and especially at most 80% by weight of comonomers.

35 Useful copolymerizable monomers include: vinylaromatics such as styrene and α -methylstyrene, C₁- to C₄-alkylstyrenes such as 2-, 3- and 4-methylstyrene, and 4-tert-butylstyrene, halostyrenes such as 2-, 3- or 4-chlorostyrene, and isoolefins having 5 to 10 carbon at-

oms, such as 2-methylbutene-1, 2-methylpentene-1, 2-methylhexene-1, 2-ethylpentene-1, 2-ethylhexene-1 and 2-propylheptene-1. Further useful comonomers include olefins which have a silyl group, such as 1-trimethoxysilylethene, 1-(trimethoxysilyl)propene, 1-(trimethoxysilyl)-2-methylpropene-2, 1-[tri(methoxyethoxy)-silyl]ethene, 1-[tri(methoxyethoxy)silyl]propene, and
5 1-[tri(methoxyethoxy)silyl]-2-methylpro-pene-2. In addition - depending on the polymerization conditions – useful comonomers also include isoprene, 1-butene and cis- and trans-2-butene.

When the process according to the invention is to be used to prepare copolymers, the process can be configured so as to preferentially form random polymers or to preferentially form block
10 copolymers. To prepare block copolymers, for example, the different monomers can be supplied successively to the polymerization reaction, in which case the second comonomer is especially not added until the first comonomer is already at least partly polymerized. In this manner, di-block, triblock and higher block copolymers are obtainable, which, according to the sequence of monomer addition, have a block of one or the other comonomer as a terminal block. In some
15 cases, however, block copolymers also form when all comonomers are supplied to the polymerization reaction simultaneously, but one of them polymerizes significantly more rapidly than the other(s). This is the case especially when isobutene and a vinylaromatic compound, especially styrene, are copolymerized in the process according to the invention. This preferably forms block copolymers with a terminal polystyrene block. This is attributable to the fact that the vi-
20 nylaromatic compound, especially styrene, polymerizes significantly more slowly than isobutene.

The polymerization can be effected either continuously or batchwise. Continuous processes can be performed in analogy to known prior art processes for continuous polymerization of isobutene in the presence of boron trifluoride-based catalysts in the liquid phase.

25

The process according to the invention is suitable either for performance at low temperatures, e.g. at -90°C to 0°C, or at higher temperatures, i.e. at at least 0°C, e.g. at 0°C to +30°C or at 0°C to +50°C. The polymerization in the process according to the invention is, however, preferably performed at relatively low temperatures, generally at -70°C to -10°C, especially at -60°C to
30 -15°C.

When the polymerization in the process according to the invention is effected at or above the boiling temperature of the monomer or monomer mixture to be polymerized, it is preferably performed in pressure vessels, for example in autoclaves or in pressure reactors.

35

The polymerization in the process may be performed in the presence of an inert diluent. The inert diluent used should be suitable for reducing the increase in the viscosity of the reaction

solution which generally occurs during the polymerization reaction to such an extent that the removal of the heat of reaction which evolves can be ensured. Suitable diluents are those solvents or solvent mixtures which are inert toward the reagents used. Suitable diluents are, for example, aliphatic hydrocarbons such as n-butane, n-pentane, n-hexane, n-heptane, n-octane and isooctane, cycloaliphatic hydrocarbons such as cyclopentane and cyclohexane, aromatic hydrocarbons such as benzene, toluene and the xylenes, and halogenated hydrocarbons, especially halogenated aliphatic hydrocarbons, such as methyl chloride, dichloromethane and trichloromethane (chloroform), 1,1-dichloroethane, 1,2-dichloroethane, trichloroethane and 1-chlorobutane, and also halogenated aromatic hydrocarbons and alkylaromatics halogenated in the alkyl side chains, such as chlorobenzene, monofluoromethylbenzene, difluoromethylbenzene and trifluoromethylbenzene, and mixtures of the aforementioned diluents. The diluents used, or the constituents used in the solvent mixtures mentioned, are also the inert components of isobutenic C₄ hydrocarbon streams. A non-halogenated solvent is preferred over the list of halogenated solvents.

The polymerization may be performed in a halogenated hydrocarbon, especially in a halogenated aliphatic hydrocarbon, or in a mixture of halogenated hydrocarbons, especially of halogenated aliphatic hydrocarbons, or in a mixture of at least one halogenated hydrocarbon, especially a halogenated aliphatic hydrocarbon, and at least one aliphatic, cycloaliphatic or aromatic hydrocarbon as an inert diluent, for example a mixture of dichloromethane and n-hexane, typically in a volume ratio of 10:90 to 90:10, especially of 50:50 to 85:15. Prior to use, the diluents are preferably freed of impurities such as water, carboxylic acids or mineral acids, for example by adsorption on solid adsorbents such as activated carbon, molecular sieves or ion exchangers.

In a preferred embodiment, the polymerization is performed in halogen-free aliphatic or especially halogen-free aromatic hydrocarbons, especially toluene. For this embodiment, water in combination with the organic hydroxyl compounds mentioned and/or the organic halogen compounds mentioned, or especially as the sole initiator, have been found to be particularly advantageous.

In another preferred embodiment, the polymerization is performed in halogen-free aliphatic or cycloaliphatic, preferably aliphatic hydrocarbons, especially hexane, pentane, heptane, cyclohexane, cyclopentane, and mixtures comprising them.

The polymerization is preferably performed under substantially aprotic and especially under substantially anhydrous reaction conditions. Substantially aprotic and substantially anhydrous reaction conditions are understood to mean that, respectively, the content of protic impurities

and the water content in the reaction mixture are less than 50 ppm and especially less than 5 ppm. In general, the feedstocks will therefore be dried before use by physical and/or chemical measures. More particularly, it has been found to be useful to admix the aliphatic or cycloaliphatic hydrocarbons used as solvents, after customary prepurification and predrying with an organometallic compound, for example an organolithium, organomagnesium or organoaluminum compound, in an amount which is sufficient to substantially remove the water traces from the solvent. The solvent thus treated is then preferably condensed directly into the reaction vessel. It is also possible to proceed in a similar manner with the monomers to be polymerized, especially with isobutene or with the isobutenic mixtures. Drying with other customary desiccants such as molecular sieves or predried oxides such as aluminum oxide, silicon dioxide, calcium oxide or barium oxide is also suitable. The halogenated solvents for which drying with metals such as sodium or potassium or with metal alkyls is not an option are freed of water or water traces with desiccants suitable for that purpose, for example with calcium chloride, phosphorus pentoxide or molecular sieves. It is also possible in an analogous manner to dry those feedstocks for which treatment with metal alkyls is likewise not an option, for example vinylaromatic compounds. Even if some or all of the initiator used is water, residual moisture should preferably be very substantially or completely removed from solvents and monomers by drying prior to reaction, in order to be able to use the water initiator in a controlled, specified amount, as a result of which greater process control and reproducibility of the results are obtained.

The polymerization reaction is appropriately terminated by adding excess amounts (relative to the Lewis acid) of water or of basic material, for example gaseous or aqueous ammonia or aqueous basic solutions, preferably aqueous solutions of (earth)alkali metal hydroxide, (earth)alkali metal oxides, (earth)alkali metal carbonates or (earth)alkali metal hydrogencarbonates. Alkali metals are preferred over earth alkali metals.

A preferred earth alkali metal is calcium, preferred alkali metals are sodium or potassium, more preferably sodium.

In a preferred embodiment water is used for terminating the polymerisation.

By adding water the Lewis acid used as catalyst is hydrolysed leaving traces of the metal, usually as oxide or hydroxide, and the halide in the reaction mixture. Since as Lewis acid preferably fluorides or chlorides are used, the latter is present as a Brønsted-acid in the form of hydrofluoric or hydrochloric acid. If it is intended to leave the Brønsted-acid in the reaction mixture, preferably no washing step is performed directly after addition of water.

If it is intended to hydrolyse the Lewis Acid and remove it afterwards in a washing step, the ten- to thousandfold amount of water relative to the Lewis Acid (wt/wt) is used for its hydrolysis and washing, preferably the 50 to 900-fold, and more preferably the 100 to 800 fold amount.

- 5 If it is intended to hydrolyse the Lewis Acid and leave the fluorine- or chlorine-containing hydrolysis products at least partly in the reaction mixture usually an amount of water up to 500 (wt/wt) relative to the Lewis Acid is used, preferably up to 250, more preferably up to 100 (wt/wt).

- 10 After unconverted C₄ monomers have been removed, the crude polymerization product is typically washed once or repeatedly with distilled or deionized water, in order to remove adhering inorganic constituents and the Brønsted-acid formed by hydrolysis of the Lewis acid. To achieve high purities or to remove undesired low and/or high molecular weight fractions, the polymerization reaction mixture can be fractionally distilled under reduced pressure.

- 15 In case a multi-step washing of the reaction mixture is applied to remove water-soluble contaminants the final step is always a treatment with pure water. This is especially preferred if the first washing steps use aqueous basic solutions, preferably aqueous solutions of (earth)alkali metal hydroxide, (earth)alkali metal oxides, (earth)alkali metal carbonates or (earth)alkali metal hydrogencarbonates. The treatment with pure water substantially removes basic and metallic
20 compounds, if used.

- In terms of process technology, all known extraction and washing processes and apparatus can be used for washing or extraction in step d), e.g. those described in Ullmann's Encyclopedia of Industrial Chemistry, 6th ed, 1999 Electronic Release, Chapter: Liquid – Liquid Extraction – Apparatus. For example, these can be single- or multi-stage, preferably single-stage extractions,
25 as well as those in direct or counter-current mode, preferably counter-current operation.

- Preferably, sieve bottom or packed or packing columns, stirring tanks or mixer-settler devices, as well as pulsed columns or those with rotating internals are used.

- 30 The thus obtainable polyisobutene composition with a content of polyisobutene species (A) bearing an alpha-double bond as pointed out above is subjected to the process according the present invention.

- 35 It is also possible to use the reaction mixture from the polymerisation after deactivation of the catalyst and optionally after removal of the hydrolysis products by washing in the process ac-

According to the present invention without further purification. Besides the polyisobutene composition such a reaction mixture may contain unreacted monomer and lower oligomers of isobutene.

5 The undistilled reaction mixture differs from the polyisobutene composition insofar that it additionally comprises isobutene and those lower oligomers of isobutene which are usually separated from the reaction mixture by distillation.

Such lower oligomers of isobutene can be diisobutene, triisobutene, tetraisobutene, pentaisobutene, hexaisobutene, heptaisobutene, and octaisobutene. Higher oligomers of isobutene usually
10 remain in the polyisobutene composition since they are not significantly volatile under distillation conditions, even under reduced pressure.

The content of unreacted isobutene may be up to 40 wt%, preferably up to 30 wt%, more preferably up to 20 wt%.

15 The content of unreacted lower oligomers mentioned above may be up to 5 wt%, preferably up to 3 wt%.

The distribution of double bond isomers among the oligomers is usually comparable to that of the polymer mixture, preferably it is the same.

20 Hence, the content of oligomer species of formula (A) bearing an alpha-double bond is at least 70 mol%, preferably at least 75 mol%, more preferably at least 80 mol%, most preferably at least 85 mol% and especially at least 90 mol%.

25 For the process according to the present invention it is possible to use a solution of the polyisobutene composition in at least one solvent as described above or to use the polyisobutene composition neat. In a preferred embodiment a 10 to 90 wt% solution of the polyisobutene composition in a solvent, preferably in a halogene-free solvent is used in the process according to the present invention, preferably a 15 to 60 wt% solution, more preferably a 20 to 50, and especially
30 25 to 40 wt% solution.

In one embodiment the solvent may be the inert components of isobutenic C₄ hydrocarbon streams.

35 After being subjected to the process according to the present invention the solvent in the reaction mixture is preferably removed, more preferably removed by way of distillation.

Usually a single step evaporation is sufficient without rectification equipment and can be effected in a falling-film evaporator, a rising-film evaporator, a thin-film evaporator, a long-tube evaporator, a helical tube evaporator, a forced-circulation flash evaporator or a paddle dryer, for example a Discotherm® dryer from List Technology AG, Switzerland, or a combination of these apparatuses.

The distillation is effected, as a rule, at 80 – 320°C, preferably 100 – 300°C, and 0.1 – 40, preferably 0.5 – 20 mbar.

Distillation may be assisted by leading an inert stripping through the evaporator, preferably nitrogen.

Such distillation and optionally stripping process yields a polyisobutene with a drastically reduced amount of solvent and monomer, even if n-hexane is used as a solvent. Therefore, another object of the invention are compositions in which the content of n-hexane is not more than 1000 ppm by weight, preferably not more than 900, more preferably not more than 800, and especially not more than 750 ppm by weight, and simultaneously the content of isobutene is not more than 50 ppm by weight, preferably not more than 40, more preferably not more than 30, and especially not more than 25 and even not more than 20 ppm by weight.

Such compositions are especially suitable for chewing gums or plasters.

Process conditions

The process according to the present invention is carried out at a temperature of from 40 °C to 250 °C, preferably 50 to 230, more preferably 60 to 200, even more preferably 70 to 180 and especially 80 to 160 °C for a period of from 5 minutes to 36 hours, preferably 10 minutes to 24 hours, more preferably 15 minutes to 12 hours, and especially 0.5 to 6 hours.

Optimum contact time of the polyisobutene composition with the catalyst and reaction temperature can be determined by systematic variation of the reaction parameters.

In the preferred case of a ion exchange resin (see below) the reaction temperature should not exceed 150 °C, preferably not higher than 140, more preferably not higher than 130, even more preferably not higher than 120 °C, especially not higher than 110 °C for a period of from 10 minutes to 36 hours, preferably 15 minutes to 24 hours, more preferably 30 minutes to 12 hours, especially 1 to 10 hours, and even 2 to 8 hours.

According to the present invention the polyisobutene with a high content of alpha-double bonds is treated with at least one Brønsted-acid for a period of from 10 minutes to 36 hours at a temperature pointed out above.

- 5 In one embodiment of the invention the Brønsted-acid is a mineral acid, preferably selected from the group consisting of hydrofluoric acid (HF), hydrochloric acid (HCl), nitric acid (HNO₃), sulfuric acid (H₂SO₄), sulfurous acid (H₂SO₃), phosphorous acid (H₃PO₃), and phosphoric acid (H₃PO₄), among which hydrofluoric acid, hydrochloric acid, sulfuric acid and phosphoric acid are preferred, hydrofluoric acid, hydrochloric acid, and sulfuric acid are even more preferred.

10

The mineral acid may be added to the reaction mixture and/or may be part of the reaction mixture originating from hydrolysis of the Lewis acid:

- 15 In a preferred embodiment of the present invention the Brønsted-acid is hydrofluoric acid or hydrochloric acid and originates from the hydrolysis of the Lewis acid with which the polyisobutene was polymerised. In this embodiment the polymerisation of the isobutene or isobutene-containing mixture is terminated by adding water or a basic material, preferably water, to the reaction mixture thereby deactivating the Lewis acid. The hydrofluoric acid or hydrochloric acid originating from desactivation of the fluorine- or chlorine-containing Lewis acids is intentionally
20 at least partly left in the reaction mixture and no washing of the reaction mixture is performed and the thus obtain reaction mixture comprising Brønsted-acid and water is subjected to treatment at elevated temperature as pointed out above.

- 25 In this embodiment the treatment of the polyisobutene with the mineral acid usually takes place at ambient pressure or slight excess pressure, e.g. up to 10 bar (gauge), at the beginning of the reaction reducing the pressure in the course of the treatment in vacuo down to 100 mbar, preferably down to 50, more preferably down to 20, and especially down to 10 mbar towards the end of the reaction. By applying pressure the volatile acids hydrofluoric acid or hydrochloric acid are kept in the reaction mixture. By applying vacuum volatile constituents of the reaction mixture
30 are removed, such as isobutene, lower oligomers of isobutene, water, and hydrofluoric acid or hydrochloric acid so that the reaction comes to an end.

Optionally traces of acid can be removed by washing with water.

- 35 If non-volatile mineral acids such as sulfuric acid or phosphoric acid are added to the polyisobutene the acids have to be removed by washing with water or an aqueous basic solution.

In another preferred embodiment at least one acidic solid state catalysts is used in the reaction according to the present invention:

Examples of acidic solid state catalysts are those which exhibit a temperature programmed desorption (TPD) of ammonia which is above the physical adsorption. A method for the determination of the temperature programmed desorption (TPD) of ammonia can be found in Philip M. Kester, Jeffrey T. Miller, and Rajamani Gounder, Ammonia Titration Methods To Quantify Brønsted Acid Sites in Zeolites Substituted with Aluminum and Boron Heteroatoms, *Industrial & Engineering Chemistry Research* 2018 57 (19), 6673-6683, Chapter 2.3.

10

Preferably the acidic solid state catalysts are selected from the group consisting of

- Natural clay minerals: kaolinite, bentonite, attapulgite, montmorillonite, clarit, fuller's earth, zeolites (X, Y, A, H-ZSM etc), cation exchanged zeolites, and clays

- Mounted acids: H_2SO_4 , H_3PO_4 , $\text{CH}_2(\text{COOH})_2$ mounted on silica, quartz sand, alumina or diatomaceous earth

15

- Cation exchange resins

- Metal oxides and sulfides: ZnO , CdO , Al_2O_3 , CeO_2 , ThO_2 , TiO_2 , ZrO_2 , SnO_2 , PbO , As_2O_5 , Bi_2O_3 , Sb_2O_5 , V_2O_5 , Cr_2O_3 , MoO_3 , WO_3 , CdS , ZnS

20

- Metal salts: MgSO_4 , CaSO_4 , SrSO_4 , BaSO_4 , CuSO_4 , ZnSO_4 , CdSO_4 , $\text{Al}_2(\text{SO}_4)_3$, FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, CoSO_4 , NiSO_4 , $\text{Cr}_2(\text{SO}_4)_3$, KHSO_4 , K_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, $\text{Zn}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, $\text{Bi}(\text{NO}_3)_3$, $\text{Fe}(\text{NO}_3)_3$, CaCO_3 , BPO_4 , AlPO_4 , CrPO_4 , FePO_4 , $\text{Cu}_3(\text{PO}_4)_2$, $\text{Zn}_3(\text{PO}_4)_2$, $\text{Mg}_3(\text{PO}_4)_2$, $\text{Ti}_3(\text{PO}_4)_4$, $\text{Zr}_3(\text{PO}_4)_4$, $\text{Ni}_3(\text{PO}_4)_2$, AgCl , CuCl , CaCl_2 , AlCl_3 , TiCl_4 , SnCl_4 , CaF_2 , BaF_2 , AgClO_4 , $\text{Mg}(\text{ClO}_4)_2$,

- Mixed oxides: $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{SiO}_2\text{-TiO}_2$, $\text{SiO}_2\text{-SnO}_2$, $\text{SiO}_2\text{-ZrO}_2$, $\text{SiO}_2\text{-BeO}$, $\text{SiO}_2\text{-MgO}$, $\text{SiO}_2\text{-CaO}$, $\text{SiO}_2\text{-SrO}$, $\text{SiO}_2\text{-ZnO}$, $\text{SiO}_2\text{-Ga}_2\text{O}_3$, $\text{SiO}_2\text{-Y}_2\text{O}_3$, $\text{SiO}_2\text{-La}_2\text{O}_3$, $\text{SiO}_2\text{-MoO}_3$, $\text{SiO}_2\text{-WO}_3$, $\text{SiO}_2\text{-V}_2\text{O}_5$,

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- $\text{SiO}_2\text{-ThO}_2$, $\text{Al}_2\text{O}_3\text{-MgO}$, $\text{Al}_2\text{O}_3\text{-ZnO}$, $\text{Al}_2\text{O}_3\text{-CdO}$, $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-ThO}_2$, $\text{Al}_2\text{O}_3\text{-TiO}_2$, $\text{Al}_2\text{O}_3\text{-ZrO}_2$, $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5$, $\text{Al}_2\text{O}_3\text{-MoO}_3$, $\text{Al}_2\text{O}_3\text{-WO}_3$, $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-Mn}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-Co}_3\text{O}_4$, $\text{Al}_2\text{O}_3\text{-NiO}$, $\text{TiO}_2\text{-CuO}$, $\text{TiO}_2\text{-MgO}$, $\text{TiO}_2\text{-ZnO}$, $\text{TiO}_2\text{-CdO}$, $\text{TiO}_2\text{-ZrO}_2$, $\text{TiO}_2\text{-SnO}_2$, $\text{TiO}_2\text{-Bi}_2\text{O}_3$, $\text{TiO}_2\text{-Sb}_2\text{O}_5$, $\text{TiO}_2\text{-V}_2\text{O}_5$, $\text{TiO}_2\text{-Cr}_2\text{O}_3$, $\text{TiO}_2\text{-MoO}_3$, $\text{TiO}_2\text{-WO}_3$, $\text{TiO}_2\text{-Mn}_2\text{O}_3$, $\text{TiO}_2\text{-Fe}_2\text{O}_3$, $\text{TiO}_2\text{-Co}_3\text{O}_4$, $\text{TiO}_2\text{-NiO}$, $\text{ZrO}_2\text{-CdO}$, ZnO-MgO , $\text{ZnO-Fe}_2\text{O}_3$, $\text{MoO}_3\text{-CoO-Al}_2\text{O}_3$, $\text{MoO}_3\text{-NiO-Al}_2\text{O}_3$,

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- $\text{TiO}_2\text{-SiO}_2\text{-MgO}$, $\text{MoO}_3\text{-Al}_2\text{O}_3\text{-MgO}$, heteropoly acids.

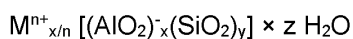
More preferably the acidic solid state catalyst is selected from the group consisting of SiO_2 , Al_2O_3 , TiO_2 , ZrO_2 , B_2O_3 , ZnO_2 , Nb_2O_5 or mixtures thereof.

35

In a preferred embodiment, the acidic solid catalyst is a zeolite, preferably an aluminosilicate or titanosilicate of lattice type FAU (faujasite type), BEA ((beta polymorph A-type), MFI (ZSM-5 type), LTA, MOR (mordenite type), MEL, MFI/MEL mixed lattices, CHA (chabasite type), or FER

(ferrierite type). Zeolites are particularly preferred to be aluminosilicates of the type zeolite A, zeolite X, zeolite Y, zeolite L, ZSM 5 and ZSM 11, with zeolites ZSM 5 being particularly preferred.

- 5 Aluminosilicate have the general composition



wherein

- 10 M is an n-valent cation, preferably of an alkali or alkaline earth metal, especially preferably an alkali metal, particularly preferably sodium or potassium, especially sodium,
n the charge of the cation M, preferably 1 or 2, especially preferably 1,
y/x is the molar ratio of SiO₂ to AlO₂ (modulus), which has a rational number of at least 1, preferably 1 to 10, especially preferably 1 to 5, most preferably 1 to 3, and
15 z is the number of water molecules absorbed by the crystal.

The composition of the unit cells of zeolites, as a rule, is as follows:

Zeolite A: Na₁₂[(AlO₂)₁₂(SiO₂)₁₂] × 27 H₂O

Zeolite X: Na₈₆[(AlO₂)₈₆(SiO₂)₁₀₆] × 264 H₂O

- 20 Zeolite Y: Na₅₆[(AlO₂)₅₆(SiO₂)₁₃₆] × 250 H₂O

Zeolite L: K₉[(AlO₂)₉(SiO₂)₂₇] × 22 H₂O

ZSM 5: Na_{0.3}H_{3.8}[(AlO₂)_{4.1}(SiO₂)_{91.9}] and

ZSM 11: Na_{0.1}H_{1.7}[(AlO₂)_{1.8}(SiO₂)_{94.2}].

- 25 Very preferably the acidic solid state catalyst is selected from the group consisting of silicates, alumina, silico-aluminates, and zeolites.

Especially the acidic solid state catalyst is a molecular sieve.

- 30 The average pore diameter of such molecular sieves is from 0.1 to 1 nm (1 to 10 Å), preferably from 0.1 to 0.6, more preferably from 0.2 to 0.5 nm.

Such molecular sieves are aluminosilicates with a silica-alumina ratio (SiO₂/ Al₂O₃) of from 1 : 0.1 to 1 : 5, preferably from 1 : 0.2 to 1 : 3, and more preferably of 1 : 0.2 to 1 : 1, especially 1 :

- 35 0.5.

The approximate chemical composition of such aluminosilicates is



with

x from 0 to 1, preferably from 0 to 0.7, more preferably from 0 to 0.5, especially 0,

5 y from 0 to 1, preferably from 0.3 to 1, more preferably from 0.5 to 1, especially 1,

wherein $x + y = 1$.

In a preferred embodiment the acidity of the acidic solid state catalysts is adjusted by treatment with at least one Brønsted-base, preferably at least one inorganic base, more preferably hydrox-
10 ides, oxides, C₁-C₄-carboxylates, preferably formates or acetates, more preferably acetates, carbonates or hydrogen carbonates of alkaline or earth alkaline metals, even more preferably of sodium, potassium or calcium.

For this purpose the acidic solid state catalyst is treated with an aqueous solution of the
15 Brønsted-base in an amount sufficient to yield the desired acidity, and afterwards dried or calcinated.

Preferably the impregnated solid state catalyst is calcinated at a temperature of from 400 to
20 1000 °C.

With such a treatment it is possible to adjust the acidity and, therefore, the reactivity of a solid state catalyst so that the reaction can be terminated when the concentration of the desired iso-
mer with tetra-substituted double bonds in the reaction mixture is at its maximum while side- or
follow up-reactions- do not occur significantly.

In a preferred embodiment the solid state catalyst comprises an alumina component, a zeolite
component and optionally an added metal component as the Brønsted-base, preferably the
added metal component is present in the solid state catalyst. In a preferred embodiment the
solid state catalyst is used as described in US 8147588 B2, preferably as described therein
30 from column 2, line 50 to column 5, line 32, which is incorporated herein by reference.

The acidic solid state catalyst, optionally treated with at least one Brønsted-base or ion ex-
changer can be used in different geometrical shapes, such as powder, granules, beads,
spheres, saddles, extrudates, strands, pellets, tablets or meshes.

35 In another preferred embodiment, the heterogeneous acidic inorganic solid catalyst is a metal oxide or clay mineral loaded with at least one mineral acid.

The mineral acids are preferably selected from the group consisting of hydrofluoric acid, hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid and phosphoric acid, among which hydrochloric acid, sulfuric acid and phosphoric acid are preferred, especially preference is sulfuric acid.

5

The above-mentioned compounds can be considered as metal oxides and clay minerals, preferably ZnO, Al₂O₃, TiO₂, ZrO₂ and SiO₂, especially preferably Al₂O₃, TiO₂ and SiO₂, especially preferably Al₂O₃ and SiO₂.

- 10 The degree of loading can range from 2 to 25 wt% mineral acid in relation to the carrier (metal oxide or clay mineral), preferably from 3 to 20, preferably 4 to 17.5 and most preferably 5 to 15 wt%.

The mineral acid can usually be applied to the carrier by spraying or impregnating, then the loaded carrier is dried and optionally calcined according to known methods.

15

The catalyst load, calculated as kg polyisobutene composition per kg solid state catalyst and hour reaction time, can vary from 0.1 to 10, preferably from 0.2 to 8, more preferably from 0.5 to 5 kg/(kg×h).

- 20 The process can optionally be conducted in the presence of at least one solvent, preferably in the presence of at least one solvent.

As solvent those solvents may be used which are listed above in the context of the polymerisation, preferred are non-halogenated solvents, more preferred are aliphatic or aromatic hydrocarbons, especially aliphatic hydrocarbons.

25

In a preferred embodiment the solvent, especially the hydrocarbon, is treated with water, preferably saturated with water prior to conducting the the process according the present invention and the reaction is thus conducted in the presence of a solvent together with water.

30

The the process according the present invention can be conducted in a continuous or discontinuous manner, preferably continuously.

- 35 For a discontinuous reaction polyisobutene composition, optional solvent, and solid state catalyst are placed together in a reactor, heated to the temperature desired and the reaction is conducted under stirring or pumping the reaction mixture in a circular flow.

For a continuous reaction polyisobutene composition, optional solvent, and solid state catalyst are conveyed through a reactor in upflow or downflow procedure, heated to the temperature desired and the reaction is conducted. The liquid flow through the reactor is adjusted so that the residence time in the reactor corresponds to the reaction time desired.

5

Usually the reaction can be conducted at atmospheric pressure, higher pressure may be helpful to prevent the optional solvent from evaporating so that the reaction mixture remains in a single liquid phase.

10 The Langmuir specific surface area of the acidic solid state catalyst, optionally treated with at least one Brønsted-base, employed in the process according to the invention is preferably from 50 to 1000 m²/g, more preferably from 75 to 900 m²/g, particularly preferably from 100 to 800 m²/g, even more preferably 200 to 700, and especially 300 to 500 m²/g. The Langmuir surface area is determined by nitrogen absorption using the DIN 66132 method.

15

The pore volume of the acidic solid state catalyst, optionally treated with at least one Brønsted-base, determined by mercury porosimetry is preferably from 0.01 to 0.3 ml/g, more preferably from 0.03 to 0.2 ml/g. The average pore diameter determined by this method is preferably from 0.1 to 10 nm, more preferably from 0.2 to 9 nm, and more preferably from 0.3 to 5 nm.

20

The mercury pore volume and the pore diameter of pores with 0.3 nm or higher are determined by the DIN 66133 method, for smaller pore diameters the nitrogen pore volume is used.

The acidity/basicity of the solid state catalyst is determined using the pH-value of an aqueous
25 slurry of the solid state catalyst, see below in the Analytical Method section.

Preferred solid state catalysts without treatment with a Brønsted-base exhibit a pH-value in the form of a 10 wt% aqueous slurry from 3 to 8, preferably from 3.5 to 7, more preferably from 4 to 6, and especially from 4 to 5.5.

30

Preferred solid state catalysts treated with at least one Brønsted-base exhibit a pH-value in the form of a 10 wt% aqueous slurry from 6 to 13, preferably from 7 to 12.5, more preferably from 8 to 12, and especially from 9 to 11.5.

35 In an especially preferred embodiment acidic ion exchangers may be used as acidic solid state catalyst, preferably strongly acidic ion exchangers.

- Ion exchanger resins usually are based upon styrene or (meth)acrylic acid. Weakly acidic ion exchangers are often based on polymers comprising (meth)acrylic acid with carboxylic acid groups as acidic groups. Strongly acidic ion exchangers are usually based on styrene-divinyl styrene copolymers bearing sulfonic acid groups. Since the backbone of the polymer is organic
- 5 the reaction temperature should not be raised above a certain limit, see above. An exception are perfluorinated polymers, such as Nafion® ion exchangers which can also be used at higher temperatures. Further examples of commercially available ion exchangers are acidic ion exchangers of from the Amberlyst® or Amberlite® product range.
- 10 In the case of acidic ion exchangers the concentration of acid sites based on the dry weight capacity should be at least 1.0 eq/kg, preferably at least 1.5, more preferably at least 2.0, even more preferably at least 2.5, and especially at least 3 eq/kg. The concentration of acid sites usually does not exceed 10.0 eq/kg.
- 15 Preferred ion exchangers exhibit a nitrogen BET surface area from 10 to 100, preferably 20 to 80, and very preferably from 30 to 70 m²/g.
- Preferably the average pore diameter of ion exchangers is from 50 to 1000 Å (Angström), more preferably from 100 to 800, and more preferably from 200 to 500 Å.
- 20 The total pore volume is preferably from 0.1 to 0.9 ml/g, more preferably from 0.2 to 0.8, and even more preferably 0.3 to 0.7 ml/g.
- In a preferred embodiment ion exchanger is used in the form of beads, preferably with an average diameter from 0.1 to 5 mm, more preferably from 0.2 to 3 mm, and even more preferably
- 25 from 0.3 to 2.5 mm.
- Usually a high concentration of acid sites is preferred.
- 30 By executing the process according to the invention, the amount of alpha-double bonds can be reduced by at least 5 %, preferably by at least 10%, more preferably by at least 15%, and especially by at least 20%, using the amount of alpha-double bond in the starting material as reference.
- 35 If for example the starting material has a content of isomers with alpha-double bond of 50 mol%, a 5% reduction means a reduction by 2.5% yielding a product with 47.5 mol% isomer content

with alpha-double bonds. A 10% reduction yields a product with 45 mol% % isomer content with alpha-double bonds and so on.

5 It is an advantage of the process according to the invention that it can be easily added to an existing polyisobutene manufacturing plant by adding a reactor for carrying out the reaction of step (IV). All other reaction steps can basically left unchanged.

10 It is a further advantage of the present invention that the product of the process according to the invention may still comprise isomers with alpha-double bonds which due to their high reactivity may be used for chemical modification of the polyisobutene. In one embodiment of the present invention medium molecular polyisobutene may still contain more than 20% isomers with alpha-double bonds when starting with a composition with a higher content prior to the treatment according to the present invention. The resulting product is on the one hand more stable than the starting material and on the other hand still comprises double bonds suitable for further chemical modification.

15 The situation is similar for low molecular polyisobutene: In one embodiment of the present invention for the same reason may still contain more than 20% isomers with alpha-double bonds when starting with a composition with a higher content prior to the treatment according to the present invention. In another embodiment the content of isomers with alpha-double bonds may even be reduced below 20% in case an especially thermally stable product is desired.

20 Reaction step (IV) can be carried out continuously or discontinuously, preferably continuously. Preferably, the reaction is carried out in at least one stirred tank reactor, preferably a reactor with internal stirring or with a pumping circuit, more preferably with a pumping circuit.

30 In a preferred embodiment, the heterogeneous acidic catalyst is in the pumping circuit, which results in a lower thermal load on the catalyst and allows for a lower reaction temperature.

If the heterogeneous acidic catalyst is not in the pumping circuit but in the reactor, the catalyst can be arranged in the reactor as a full-space reactor or cut-off reactor (horde reactor).

35 In a horde reactor, the catalyst is divided into several successive fills (trays) in one and the same apparatus. It is therefore possible to set the reaction temperature separately for each section, preferably the reaction temperature increases during the course of the reaction.

It is also possible to carry out the reaction in more than one stirred tank reactor, for example in a cascade of at least two stirred tank reactors, preferably 2 to 5, especially preferably 2 to 3 stirred tank reactors.

- 5 This has the advantage that the temperature in each reactor in the cascade can be adjusted independently of the other reactors and, if necessary, additional reactants, e.g. further acid, can be added to the reaction mixture.

In another embodiment, the reaction is carried out in a tubular reactor.

10

In one embodiment, the tubular reactor has at least two temperature zones, preferably increasing the reaction temperature in the course of the reaction.

- In order to enable the separation of a gas phase forming in the course of the reaction, it is advantageous to arrange apparatus for separating the gas phase between tubular reactors arranged on top of each other, for example flashpots or thin-film evaporators, in which the temperature for the next tubular reactor can also be adjusted.
- 15

The embodiment using at least one tubular reactor is preferred both for using an acidic solid state catalyst as well as for using a mineral acid as Brønsted-acid:

20

- It is an advantage that in a tubular reactor the mineral acid is easily kept in the reaction mixture, preferably by conducting the reaction under slight excess pressure. The volatile content of the reaction mixture can be separated off the discharge of the tubular reactor in a flashpots or thin-film evaporator, optionally in vacuo. If necessary, the product can be submitted to a washing to remove inorganic or water-soluble contaminants of the product.
- 25

The thus obtained product exhibits an increased stability, it preferably exhibits less depletion of molecular weight and/or less development of isobutene monomer than the untreated starting material under the same storage conditions, especially under thermal stress.

30

The product obtained according to the present invention may still have alpha-double bond, e.g. up to 50 mol%, preferably up to 45 mol%, more preferably up to 40 mol%, even more preferably up to 35 mol%, and especially up to 30 mol%.

- 35 The product obtained according to the present invention may comprise more than 20 mol% alpha-double bonds, preferably at least 25 mol%.

Despite the presence of the remaining alpha-double bonds the stability of the product obtained according to the present invention is improved compared with the starting material.

5 Since the product obtained by the process according to the present invention comprises resp. develops less monomeric isobutene it is advantageous in applications in which the product must not be skin irritant, harmful or even toxic.

10 Therefore, another subject matter of the present invention is the use of the product obtained by the process according to the present invention in medicinal and/or food applications, preferably as a constituent of adhesives for plasters, sealants or adhesives for food packaging or in chewing gums.

Other aspects of the present invention are:

- 15 - Plasters, comprising product obtained by the process according to the present invention in its adhesive layer.
- Food packages, comprising product obtained by the process according to the present invention in its sealant or adhesive compositions.
- 20 - Chewing gum, comprising product obtained by the process according to the present invention.

25 Because of its increased stability the product obtained by the process according to the present invention is especially suitable for exterior applications, therefore, another object of the present invention is the use of the product obtained by the process according to the present invention in sealants, adhesives, coatings or roofings.

30 Another aspect are sealants, adhesives, coatings and roofings comprising the product obtained by the process according to the present invention.

35 The NMR spectroscopy of the polyisobutene polymers was performed as described in Guo et al., Journal of Polymer Science, Part A: Polymer Chemistry, 2013, 51, 4200–4212, on a Bruker 700 MHz spectrometer using 5 mm o.d. tubes with appropriate concentration of polyisobutene in deuterated chloroform (CDCl₃) as a solvent at 25 °C. The ¹H spectra of polyisobutene solutions in CDCl₃ were calibrated to tetramethylsilane as internal standard ($\delta_H = 0.00$) or to the sol-

vent signal ($\delta_c = 77.0$), respectively. The distortionless enhancement by polarization transfer (DEPT) technique was further used for structural characterization of polyisobutenes.

The examples which follow are intended to illustrate the present invention in detail without re-

Examples

Analytical methods

If not mentioned otherwise in this text, the gel permeation chromatography (GPC) was conducted as follows:

Solvent: Tetrahydrofurane, stabilised with 250 ppm BHT (tert. butyl hydroxy toluene)

Columns: 2 × Agilent PLgel Mixed E 3 μ m 7.5×300 mm

Flow rate: 1ml/min

Detector: Agilent G1362A RID (refraction index detector)

Temperature: 35 °C (columns and detector)

Calibration: Polystyrene 162 - 51950 g/mol, separate measurement

Recommended polymer concentration: 2.5 g/l

Evaluation: Manual evaluation using PSS WinGPC as software

Example 1

Commercially available Oppanol® B12 (Mv 55000 g/mol, available from BASF SE, Ludwigshafen, Germany) was dissolved in octane (25 wt% solution) and stirred at 100 °C with 50 wt% Amberlyst® 15 dry (strongly acidic ion exchanger with sulfonic acid groups bound to styrene-divinylbenzene-copolymer, surface area 53 m²/g (nitrogen BET surface), total pore volume 0.40 cc/g, average pore diameter 300 Å, concentration of acid sites at least 4.7 eq/kg). The content and distribution of double bond was determined by ¹H NMR spectroscopy:

Table 1

Time (h)	Terminal Vinylidene (%)	Trisubstituted Double Bonds (%)	Tetrasubstituted Double Bonds (%)
0	39.0	40.2	19.5
4	23.5	49.4	25.2
8.5	16.5	41.4	38.9

Example 2

Commercially available Glissopal® 1000 (Mn 1000 g/mol, available from BASF SE, Ludwigsha-
fen, Germany) was dissolved in octane (30 wt% solution) and stirred at 100 °C with 50 wt%
5 Amberlyst® 15 dry. The content and distribution of double bond was determined by ¹H NMR
spectroscopy.

The content of free isobutene of selected samples was determined after heating the samples at
220 °C for 5 hours in the presence of air by headspace gas chromatography.

Table 2

Time (h)	Terminal Vinylidene (%)	Trisubstituted Double Bonds (%)	Tetrasubstituted Double Bonds (%)	Isobutene Content [ppm]
0	79.5	12.1	2.1	2082
3	29.8	51.0	17.0	n.d.
7.5	19.6	41.7	36.0	998

Example 3

15 Commercially available Glissopal® 1000 was dissolved in octane (30 wt% solution) and stirred
at 100 °C with 50 wt% Amberlyte® IR120 H (strongly acidic ion exchanger with sulfonic acid
groups bound to styrene-divinylbenzene-copolymer, exchange capacity at least 1.8 eq/l). The
content and distribution of double bond was determined by ¹H NMR spectroscopy.

Table 3

Time (h)	Terminal Vinylidene (%)	Trisubstituted Double Bonds (%)	Tetrasubstituted Double Bonds (%)
0	79.5	12.1	2.1
1	63	21	5
3	55	29	6
5	51	33	6
7	49	34	7

Example 4

Commercially available Glissopal® 1000 was dissolved in hexane (50 wt% solution) and stirred at 90 °C with 25 wt% zeolite which had been acidified with mineral acid prior to use. The content and distribution of double bond was determined by ¹H NMR spectroscopy.

5 Table 4

Time (h)	Terminal Vinylidene (%)	Trisubstituted Double Bonds (%)	Tetrasubstituted Double Bonds (%)
0	79.5	12.1	2.1
2	34.4	48.5	10.0

Example 5

10 Polyisobutene with a number average molecular weight of Mn 2300 g/mol and with a fluorine content of 14 ppm was heated to 220 °C under vacuo (50 mbar). The content and distribution of double bond was determined by ¹H NMR spectroscopy.

Table 5

Time (h)	Terminal Vinylidene (%)	Trisubstituted Double Bonds (%)	Tetrasubstituted Double Bonds (%)	Fluorine Content [ppm]
0	85.3	9.8	1.3	14
1	70.7	18.2	0	< 1

Claims

1. Process for improving the storage stability of polyisobutene, comprising the steps of
- choosing as a starting material
 - in the case of polyisobutene with a number average molecular weight M_n (determined by gel permeation chromatography (GPC) with polystyrene as standard) of less than 10000 g/mol, a polyisobutene composition with a content of polyisobutene species (A) bearing an alpha-double bond of at least 50 mol%, preferably at least 60 mol%, more preferably at least 70 mol%, most preferably at least 75 mol% and especially at least 80 mol% or even 85 mol%,
 - in the case of polyisobutene with a number average molecular weight M_n (determined by gel permeation chromatography (GPC) with polystyrene as standard) of from 10000 to 100000 g/mol, a polyisobutene composition with a content of polyisobutene species (A) bearing an alpha-double bond of at least 20 to 60 mol%, preferably at least 25 to 45 mol%, and more preferably at least 30 to 40 mol%,
 - in the case of polyisobutene with a number average molecular weight M_n (determined by gel permeation chromatography (GPC) with polystyrene as standard) of more than 100000 to 5000000 g/mol, a polyisobutene composition with a content of polyisobutene species (A) bearing an alpha-double bond of at least 10 to 50 mol%, preferably at least 15 to 45 mol%, and more preferably at least 15 to 40 mol%,
 - optionally at least one solvent,
 - treating the optionally dissolved polyisobutene composition
 - in the presence of at least one Brønsted-acid, preferably an acidic solid state catalyst, optionally treated with at least one Brønsted-base
 - for a period of from 5 minutes to 36 hours
 - at a temperature of from 40 °C to 250 °C,
- and store the thus obtained polyisobutene composition at a temperature from ambient temperature up to 100 °C, preferably in the absence of oxygen.
2. Process according to Claim 1, characterised in that the Brønsted-acid is selected from the group consisting of hydrofluoric acid, hydrochloric acid, nitric acid, sulfuric acid, sulfurous acid, phosphorous acid, and phosphoric acid.
3. Process according to Claim 1, characterised in that the Brønsted-acid is an acidic solid state catalyst selected from the group consisting of
- Natural clay minerals: kaolinite, bentonite, attapulgite, montmorillonite, clarit, fuller's earth, zeolites (X, Y, A, H-ZSM etc), cation exchanged zeolites, and clays

- Mounted acids: H_2SO_4 , H_3PO_4 , $\text{CH}_2(\text{COOH})_2$ mounted on silica, quartz sand, alumina or diatomaceous earth
 - Cation exchange resins
 - Metal oxides and sulfides: ZnO , CdO , Al_2O_3 , CeO_2 , ThO_2 , TiO_2 , ZrO_2 , SnO_2 , PbO , As_2O_5 , Bi_2O_3 , Sb_2O_5 , V_2O_5 , Cr_2O_3 , MoO_3 , WO_3 , CdS , ZnS
 - Metal salts: MgSO_4 , CaSO_4 , SrSO_4 , BaSO_4 , CuSO_4 , ZnSO_4 , CdSO_4 , $\text{Al}_2(\text{SO}_4)_3$, FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, CoSO_4 , NiSO_4 , $\text{Cr}_2(\text{SO}_4)_3$, KHSO_4 , K_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, $\text{Zn}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, $\text{Bi}(\text{NO}_3)_3$, $\text{Fe}(\text{NO}_3)_3$, CaCO_3 , BPO_4 , AlPO_4 , CrPO_4 , FePO_4 , $\text{Cu}_3(\text{PO}_4)_2$, $\text{Zn}_3(\text{PO}_4)_2$, $\text{Mg}_3(\text{PO}_4)_2$, $\text{Ti}_3(\text{PO}_4)_4$, $\text{Zr}_3(\text{PO}_4)_4$, $\text{Ni}_3(\text{PO}_4)_2$, AgCl , CuCl , CaCl_2 , AlCl_3 , TiCl_4 , SnCl_4 , CaF_2 , BaF_2 , AgClO_4 , $\text{Mg}(\text{ClO}_4)_2$,
 - Mixed oxides: $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{SiO}_2\text{-TiO}_2$, $\text{SiO}_2\text{-SnO}_2$, $\text{SiO}_2\text{-ZrO}_2$, $\text{SiO}_2\text{-BeO}$, $\text{SiO}_2\text{-MgO}$, $\text{SiO}_2\text{-CaO}$, $\text{SiO}_2\text{-SrO}$, $\text{SiO}_2\text{-ZnO}$, $\text{SiO}_2\text{-Ga}_2\text{O}_3$, $\text{SiO}_2\text{-Y}_2\text{O}_3$, $\text{SiO}_2\text{-La}_2\text{O}_3$, $\text{SiO}_2\text{-MoO}_3$, $\text{SiO}_2\text{-WO}_3$, $\text{SiO}_2\text{-V}_2\text{O}_5$, $\text{SiO}_2\text{-ThO}_2$, $\text{Al}_2\text{O}_3\text{-MgO}$, $\text{Al}_2\text{O}_3\text{-ZnO}$, $\text{Al}_2\text{O}_3\text{-CdO}$, $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-ThO}_2$, $\text{Al}_2\text{O}_3\text{-TiO}_2$, $\text{Al}_2\text{O}_3\text{-ZrO}_2$, $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5$, $\text{Al}_2\text{O}_3\text{-MoO}_3$, $\text{Al}_2\text{O}_3\text{-WO}_3$, $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-Mn}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-Co}_3\text{O}_4$, $\text{Al}_2\text{O}_3\text{-NiO}$, $\text{TiO}_2\text{-CuO}$, $\text{TiO}_2\text{-MgO}$, $\text{TiO}_2\text{-ZnO}$, $\text{TiO}_2\text{-CdO}$, $\text{TiO}_2\text{-ZrO}_2$, $\text{TiO}_2\text{-SnO}_2$, $\text{TiO}_2\text{-Bi}_2\text{O}_3$, $\text{TiO}_2\text{-Sb}_2\text{O}_5$, $\text{TiO}_2\text{-V}_2\text{O}_5$, $\text{TiO}_2\text{-Cr}_2\text{O}_3$, $\text{TiO}_2\text{-MoO}_3$, $\text{TiO}_2\text{-WO}_3$, $\text{TiO}_2\text{-Mn}_2\text{O}_3$, $\text{TiO}_2\text{-Fe}_2\text{O}_3$, $\text{TiO}_2\text{-Co}_3\text{O}_4$, $\text{TiO}_2\text{-NiO}$, $\text{ZrO}_2\text{-CdO}$, ZnO-MgO , $\text{ZnO-Fe}_2\text{O}_3$, $\text{MoO}_3\text{-CoO-Al}_2\text{O}_3$, $\text{MoO}_3\text{-NiO-Al}_2\text{O}_3$, $\text{TiO}_2\text{-SiO}_2\text{-MgO}$, $\text{MoO}_3\text{-Al}_2\text{O}_3\text{-MgO}$, heteropoly acids.
4. Process according to Claim 1, characterised in that the Brønsted-acid is an acidic ion exchanger.
5. Process for improving the storage stability of polyisobutene, comprising the steps of
- (I) first polymerising isobutene or an isobutene-containing monomer mixture
 - in the presence of at least one Lewis Acid-donor complex and
 - at least one initiator,
 - (II) terminating the polymerisation by adding water or basic material to the reaction mixture,
 - (III) distilling off unreacted monomer and lower oligomers of isobutene, yielding a polyisobutene composition
 - in the case of polyisobutene with a number average molecular weight M_n (determined by gel permeation chromatography (GPC) with polystyrene as standard) of less than 10000 g/mol, a polyisobutene composition with a content of polyisobutene species (A) bearing an alpha-double bond of at least 50 mol%, preferably at least 60 mol%, more preferably at least 70 mol%, most preferably at least 75 mol% and especially at least 80 mol% or even 85 mol%,

- 5 -- in the case of polyisobutene with a number average molecular weight M_n (determined by gel permeation chromatography (GPC) with polystyrene as standard) of from 10000 to 100000 g/mol, a polyisobutene composition with a content of polyisobutene species (A) bearing an alpha-double bond of at least 20 to 60 mol%, preferably at least 25 to 45 mol%, and more preferably at least 30 to 40 mol%,
- 10 -- in the case of polyisobutene with a number average molecular weight M_n (determined by gel permeation chromatography (GPC) with polystyrene as standard) of more than 100000 to 5000000 g/mol, a polyisobutene composition with a content of polyisobutene species (A) bearing an alpha-double bond of at least 10 to 50 mol%, preferably at least 15 to 45 mol%, and more preferably at least 15 to 40 mol%, followed by
- 15 - (IV) afterwards optionally adding at least one solvent to this polyisobutene composition,
- treating the optionally dissolved polyisobutene composition
- in the presence of at least one Brønsted-acid, preferably at least one acidic solid state catalyst, optionally treated with at least one Brønsted-base
- for a period of from 5 minutes to 36 hours
- at a temperature of from 40 °C to 250 °C,
- 20 - (V) washing the reaction mixture with water,
- wherein the washing step (V) may take place after step (III) and/or step (IV),
- followed by storage of the thus obtained polyisobutene for a period of time up to two years at room temperature, preferably from ambient temperature up to 100 °C, more preferably in the absence of oxygen.
- 25
6. Process according to Claim 5, characterised in that Lewis acid is selected from the group consisting of boron trifluoride, boron trichloride, aluminum trihalide, alkylaluminum dihalide, dialkylaluminum halide, iron trihalide, gallium trihalide, titanium tetrahalide, zinc dihalide, tin dihalide, tin tetrahalide, wherein the halide is preferably fluoride or
- 30 chloride, more preferably chloride.
7. Process according to Claim 5 or 6, characterised in that
- in step (II) the polymerisation is terminated with water, aqueous ammonia or an aqueous basic solution, preferably water, and
- 35 - the Brønsted-acid in step (IV) is of hydrofluoric acid or hydrochloric acid.

8. Process according to Claim 5 or 6, characterised in that the Brønsted-acid is an acidic solid state catalyst selected from the group consisting of
- Natural clay minerals: kaolinite, bentonite, attapulgite, montmorillonite, clarit, fuller's earth, zeolites (X, Y, A, H-ZSM etc), cation exchanged zeolites, and clays
 - 5 - Mounted acids: H_2SO_4 , H_3PO_4 , $\text{CH}_2(\text{COOH})_2$ mounted on silica, quartz sand, alumina or diatomaceous earth
 - Cation exchange resins
 - Metal oxides and sulfides: ZnO , CdO , Al_2O_3 , CeO_2 , ThO_2 , TiO_2 , ZrO_2 , SnO_2 , PbO , As_2O_5 , Bi_2O_3 , Sb_2O_5 , V_2O_5 , Cr_2O_3 , MoO_3 , WO_3 , CdS , ZnS
 - 10 - Metal salts: MgSO_4 , CaSO_4 , SrSO_4 , BaSO_4 , CuSO_4 , ZnSO_4 , CdSO_4 , $\text{Al}_2(\text{SO}_4)_3$, FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, CoSO_4 , NiSO_4 , $\text{Cr}_2(\text{SO}_4)_3$, KHSO_4 , K_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, $\text{Zn}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, $\text{Bi}(\text{NO}_3)_3$, $\text{Fe}(\text{NO}_3)_3$, CaCO_3 , BPO_4 , AlPO_4 , CrPO_4 , FePO_4 , $\text{Cu}_3(\text{PO}_4)_2$, $\text{Zn}_3(\text{PO}_4)_2$, $\text{Mg}_3(\text{PO}_4)_2$, $\text{Ti}_3(\text{PO}_4)_4$, $\text{Zr}_3(\text{PO}_4)_4$, $\text{Ni}_3(\text{PO}_4)_2$, AgCl , CuCl , CaCl_2 , AlCl_3 , TiCl_4 , SnCl_4 , CaF_2 , BaF_2 , AgClO_4 , $\text{Mg}(\text{ClO}_4)_2$,
 - 15 - Mixed oxides: $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{SiO}_2\text{-TiO}_2$, $\text{SiO}_2\text{-SnO}_2$, $\text{SiO}_2\text{-ZrO}_2$, $\text{SiO}_2\text{-BeO}$, $\text{SiO}_2\text{-MgO}$, $\text{SiO}_2\text{-CaO}$, $\text{SiO}_2\text{-SrO}$, $\text{SiO}_2\text{-ZnO}$, $\text{SiO}_2\text{-Ga}_2\text{O}_3$, $\text{SiO}_2\text{-Y}_2\text{O}_3$, $\text{SiO}_2\text{-La}_2\text{O}_3$, $\text{SiO}_2\text{-MoO}_3$, $\text{SiO}_2\text{-WO}_3$, $\text{SiO}_2\text{-V}_2\text{O}_5$, $\text{SiO}_2\text{-ThO}_2$, $\text{Al}_2\text{O}_3\text{-MgO}$, $\text{Al}_2\text{O}_3\text{-ZnO}$, $\text{Al}_2\text{O}_3\text{-CdO}$, $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-ThO}_2$, $\text{Al}_2\text{O}_3\text{-TiO}_2$, $\text{Al}_2\text{O}_3\text{-ZrO}_2$, $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5$, $\text{Al}_2\text{O}_3\text{-MoO}_3$, $\text{Al}_2\text{O}_3\text{-WO}_3$, $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-Mn}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-Co}_3\text{O}_4$, $\text{Al}_2\text{O}_3\text{-NiO}$, $\text{TiO}_2\text{-CuO}$, $\text{TiO}_2\text{-MgO}$, $\text{TiO}_2\text{-ZnO}$, $\text{TiO}_2\text{-CdO}$, $\text{TiO}_2\text{-ZrO}_2$, $\text{TiO}_2\text{-SnO}_2$, $\text{TiO}_2\text{-Bi}_2\text{O}_3$, $\text{TiO}_2\text{-Sb}_2\text{O}_5$, $\text{TiO}_2\text{-V}_2\text{O}_5$, $\text{TiO}_2\text{-Cr}_2\text{O}_3$, $\text{TiO}_2\text{-MoO}_3$, $\text{TiO}_2\text{-WO}_3$, $\text{TiO}_2\text{-Mn}_2\text{O}_3$, $\text{TiO}_2\text{-Fe}_2\text{O}_3$, $\text{TiO}_2\text{-Co}_3\text{O}_4$, $\text{TiO}_2\text{-NiO}$, $\text{ZrO}_2\text{-CdO}$, ZnO-MgO , $\text{ZnO-Fe}_2\text{O}_3$, $\text{MoO}_3\text{-CoO-Al}_2\text{O}_3$, $\text{MoO}_3\text{-NiO-Al}_2\text{O}_3$, $\text{TiO}_2\text{-SiO}_2\text{-MgO}$, $\text{MoO}_3\text{-Al}_2\text{O}_3\text{-MgO}$, heteropoly acids.
 - 20
9. Process according to Claim 5 or 6, characterised in that the Brønsted-acid is an acidic ion exchanger.
10. Process for the production of polyisobutene, comprising the steps of
- (I) first polymerising isobutene or an isobutene-containing monomer mixture
 - 30 - in the presence of at least one Lewis Acid-donor complex, wherein the Lewis Acid is a chloride or fluoride, and
 - at least one initiator,
 - (II) terminating the polymerisation by adding water or basic material to the reaction mixture,
 - 35 - (III) distilling off unreacted monomer and lower oligomers of isobutene, wherein hydrofluoric acid or hydrochloric acid originating from deactivation of the fluo-

rine- or chlorine-containing Lewis acids is at least partly left in the reaction mixture, yielding a polyisobutene composition

-- in the case of polyisobutene with a number average molecular weight M_n of less than 10000 g/mol, a polyisobutene composition with a content of polyisobutene species (A) bearing an alpha-double bond of at least 50 mol%, preferably at least 60 mol%, more preferably at least 70 mol%, most preferably at least 75 mol% and especially at least 80 mol% or even 85 mol%,

-- in the case of polyisobutene with a number average molecular weight M_n of from 10000 to 100000 g/mol, a polyisobutene composition with a content of polyisobutene species (A) bearing an alpha-double bond of at least 20 to 60 mol%, preferably at least 25 to 45 mol%, and more preferably at least 30 to 40 mol%,

-- in the case of polyisobutene with a number average molecular weight M_n of more than 100000 to 5000000 g/mol, a polyisobutene composition with a content of polyisobutene species (A) bearing an alpha-double bond of at least 10 to 50 mol%, preferably at least 15 to 45 mol%, and more preferably at least 15 to 40 mol%,

followed by

- (IV) afterwards optionally adding at least one solvent to this polyisobutene composition,

- treating the optionally dissolved polyisobutene composition

-- in the presence of hydrofluoric acid or hydrochloric acid,

-- for a period of from 5 minutes to 36 hours

-- at a temperature of from 40 °C to 250 °C,

-- at a pressure from 10 bar gauge to 20 mbar,

- (V) optionally washing the reaction mixture with water,

wherein the washing step (V) may take place after step (IV).

11. Process according to any one of the preceding claims, characterised in that the content of polyisobutene species (A) bearing an alpha-double bond in the starting material is reduced by at least 5 %, preferably by at least 10%, more preferably by at least 15%, and especially by at least 20%, using the amount of alpha-double bond in the starting material as reference.

12. Use of the product obtained by a process according to any one of the preceding claims in medicinal and/or food applications, preferably as a constituent of adhesives for plasters, sealants or adhesives for food packaging or in chewing gums.

13. Plasters, comprising product obtained by a process according to any one of Claims 1 to 10 in its adhesive layer.
14. Food packages, comprising product obtained by a process according to any one of Claims 1 to 10 in its sealant or adhesive compositions.
15. Chewing gum, comprising product obtained by a process according to any one of Claims 1 to 10.