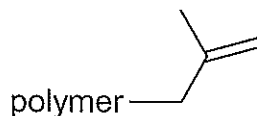


Process for preparing high-reactivity isobutene homo- or copolymers

Description

- 5 The present invention relates to a novel process for preparing high-reactivity isobutene homo- or copolymers with a content of terminal vinylidene double bonds per polyisobutene chain end of at least 50 mol%. The present invention further relates to novel isobutene polymers.
- 10 In contrast to so-called low-reactivity polymers, high-reactivity isobutene homo- or copolymers are understood to mean those polyisobutenes which comprise a high content of terminal ethylenic double bonds (α -double bonds), specifically in practice usually of at least 80 mol%, based on the individual chain ends of the polyisobutene macromolecules. In the context of the present application, vinylidene groups are
- 15 understood to mean those double bonds whose position in the polyisobutene macromolecule is described by the general formula



- i.e. the double bond is present in an α position in the polymer chain. "Polymer" represents the polyisobutene radical shortened by one isobutene unit. The vinylidene groups exhibit the highest reactivity, for example in the thermal addition onto sterically demanding reactants such as maleic anhydride, whereas a double bond further toward the interior of the macromolecules in most cases exhibits lower reactivity, if any, in functionalization reactions. The uses of high-reactivity polyisobutenes include use as
- 20 intermediates for preparing additives for lubricants and fuels, as described, for example, in DE-A 27 02 604.

- Such high-reactivity polyisobutenes are obtainable, for example, by the process of DE-A 27 02 604 by cationic polymerization of isobutene in the liquid phase in the presence of boron trifluoride as a catalyst. A disadvantage here is that the polyisobutenes obtained have a relatively high polydispersity. The polydispersity is a measure of the molecular weight distribution of the resulting polymer chains and corresponds to the quotient of weight-average molecular weight M_w and number-average molecular weight M_n ($PDI = M_w/M_n$).

- 35 Polyisobutenes with a similarly high proportion of terminal double bonds but with a narrower molecular weight distribution are, for example, obtainable by the process of EP-A 145 235, US 5 408 018 and WO 99/64482, the polymerization being effected in the presence of a deactivated catalyst, for example of a complex of boron trifluoride with alcohols and/or ethers.
- 40

High-reactivity polyisobutenes are also obtainable by living cationic polymerization of isobutene and subsequent dehydrohalogenation of the resulting polymerization product, for example by the process from US 5 340 881. However, such a process is complex since the halogen end group introduced with the living cationic polymerization
5 has to be eliminated in a separate step in order to generate the double bond.

It has additionally been known for some time that the Lewis acid aluminum trichloride can also be used as a polymerization catalyst for isobutene, for example from High Polymers, volume XXIV (part 2), p. 713-733 (editor: Edward C. Leonard), J. Wiley &
10 Sons publishers, New York, 1971.

In the literature article "Cationic polymerization using heteropolyacid salt catalysts" in Topics in Catalysis Vol. 23, p. 175-181 (2003), James D. Burrington et al. indicate that, with aluminum trichloride as a polymerization catalyst for isobutene, only low-reactivity
15 polyisobutenes with a low content of terminal vinylidene double bonds (α -double bonds) can be obtained. For instance, table 1 on page 178 of this literature article cites an example of a polyisobutene prepared with AlCl_3 , which has a number-average molecular weight M_n of 1000-2000, a polydispersity M_w/M_n of 2.5-3.5 and a content of vinylidene isomer (α -double bond) of only 5% (in addition to 65% "tri", 5% " β " and 25%
20 "tetra").

In the literature article "Novel initiating system based on AlCl_3 etherate for quasiliving cationic polymerization of styrene" in Polymer Bulletin Vol. 52, p. 227-234 (2004), Sergei V. Kostjuk et al. describe a catalyst system composed of 2-phenyl-2-propanol
25 and an aluminum trichloride/di-n-butyl ether complex for polymerization of styrene. The polydispersities M_w/M_n of the styrene polymers thus prepared are " ~ 2.5 " (see summary) or " ~ 3 " (see page 230).

It was an object of the present invention to provide a process for preparing high-
30 reactivity isobutene homo- or copolymers with a content of terminal vinylidene double bonds per polyisobutene chain end of at least 80 mol% and simultaneously with a narrow molecular weight distribution (i.e. low polydispersities) in acceptable yields. The catalyst system should at the same time have sufficient activity and service life, the handling thereof should be unproblematic and it should not be prone to failure.

35 The object was achieved by a process for preparing high-reactivity isobutene homo- or copolymers with a content of terminal vinylidene double bonds per polyisobutene chain end of at least 50 mol%, which comprises polymerizing isobutene or an isobutene-comprising monomer mixture in the presence of an aluminum trihalide-donor complex
40 effective as a polymerization catalyst or of an alkylaluminum halide-donor complex, said complex comprising, as the donor, an organic compound with at least one ether function or a carboxylic ester function.

Isobutene homopolymers are understood in the context of the present invention to mean those polymers which, based on the polymer, are formed from isobutene to an extent of at least 98 mol%, preferably to an extent of at least 99 mol%. Accordingly, isobutene copolymers are understood to mean those polymers which comprise more than 2 mol% of copolymerized monomers other than isobutene, for example linear butenes.

In the context of the present invention, the following definitions apply to generically defined radicals:

10

A C₁- to C₈-alkyl radical is a linear or branched alkyl radical having 1 to 8 carbon atoms. Examples thereof are methyl, ethyl, n-propyl, isopropyl, n-butyl, 2-butyl, isobutyl, tert-butyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, n-hexyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methylpropyl, 1-ethyl-2-methylpropyl, n-heptyl, n-octyl and the constitutional isomers thereof, such as 2-ethylhexyl. Such C₁- to C₈-alkyl radicals may to a small extent also comprise heteroatoms such as oxygen, nitrogen or halogen atoms, for example chlorine, and/or aprotic functional groups, for example carboxyl ester groups, cyano groups or nitro groups.

A C₁- to C₂₀-alkyl radical is a linear or branched alkyl radical having 1 to 20 carbon atoms. Examples thereof are the abovementioned C₁- to C₈-alkyl radicals, and additionally n-nonyl, isononyl, n-decyl, 2-propylheptyl, n-undecyl, n-dodecyl, n-tridecyl, isotridecyl, n-tetradecyl, n-hexadecyl, n-octadecyl and n-eicosyl. Such C₁- to C₂₀-alkyl radicals may to a small extent also comprise heteroatoms such as oxygen, nitrogen or halogen atoms, for example chlorine, and/or aprotic functional groups, for example carboxyl ester groups, cyano groups or nitro groups.

A C₅- to C₈-cycloalkyl radical is a saturated cyclic radical which may comprise alkyl side chains. Examples thereof are cyclopentyl, 2- or 3-methylcyclopentyl, 2,3-, 2,4- or 2,5-dimethylcyclopentyl, cyclohexyl, 2-, 3- or 4-methylcyclohexyl, 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, 3,5- or 3,6-dimethylcyclohexyl, cycloheptyl, 2-, 3- or 4-methylcycloheptyl, cyclooctyl, 2-, 3-, 4- or 5-methylcyclooctyl. Such C₅- to C₈-cycloalkyl radicals may to a small extent also comprise heteroatoms such as oxygen, nitrogen or halogen atoms, for example chlorine, and/or aprotic functional groups, for example carboxyl ester groups, cyano groups or nitro groups.

40

A C₆- to C₂₀-aryl radical or a C₆- to C₁₂-aryl radical is preferably optionally substituted phenyl, optionally substituted naphthyl, optionally substituted anthracenyl or optionally substituted phenanthrenyl. Such aryl radicals may be a 1 to 5 aprotic substituents or

aprotic functional groups, for example C₁- to C₈-alkyl, C₁- to C₈-haloalkyl such as C₁- to C₈-chloroalkyl or C₁- to C₈-fluoroalkyl, halogens such as chlorine or fluorine, nitro, cyano or phenyl. Examples of such aryl radicals are phenyl, naphthyl, biphenyl, anthracenyl, phenanthrenyl, tolyl, nitrophenyl, chlorophenyl, dichlorophenyl,
 5 pentafluorophenyl, pentachlorophenyl, (trifluoromethyl)phenyl, bis(tri-fluoromethyl)-phenyl, (trichloro)methylphenyl and bis(trichloromethyl)phenyl.

A C₇- to C₂₀-arylalkyl radical or a C₇- to C₁₂-arylalkyl radical is preferably optionally substituted C₁- to C₄-alkylphenyl such as benzyl, o-, m- or p-methylbenzyl, 1- or
 10 2-phenylethyl, 1-, 2- or 3-phenylpropyl or 1-, 2-, 3- or 4-phenylbutyl, optionally substituted C₁- to C₄-alkylnaphthyl such as naphthylmethyl, optionally substituted C₁- to C₄-alkylantracenyl such as anthracenylmethyl, or optionally substituted C₁- to C₄-alkyl-phenanthrenyl such as phenanthrenylmethyl. Such arylalkyl radicals may bear 1 to 5 aprotic substituents or aprotic functional groups, especially on the aryl moiety, for
 15 example C₁- to C₈-alkyl, C₁- to C₈-haloalkyl such as C₁- to C₈-chloroalkyl or C₁- to C₈-fluoroalkyl, halogen such as chlorine or fluorine, nitro or phenyl.

A suitable aluminum trihalide is especially aluminum trifluoride, aluminum trichloride or aluminum tribromide. A useful alkylaluminum halide is especially a mono(C₁- to
 20 C₄-alkyl)aluminum dihalide or a di(C₁- to C₄-alkyl)aluminum monohalide, for example methylaluminum dichloride, ethylaluminum dichloride, dimethylaluminum chloride or diethylaluminum chloride. In a preferred embodiment, isobutene or an isobutene-comprising monomer mixture is polymerized in the presence of an aluminum trichloride-donor complex effective as a polymerization catalyst.

25 If the aluminum trihalide-donor complex or alkylaluminum halide-donor complex effective as a polymerization catalyst comprises, as the donor, an organic compound with at least one ether function, compounds with at least one ether function are also understood to mean acetals and hemiacetals.

30 In a preferred embodiment of the present invention, an aluminum trihalide-donor complex or an alkylaluminum halide complex, especially an aluminum trichloride-donor complex, is used, which comprises, as the donor, a dihydrocarbyl ether of the general formula R¹-O-R² in which the variables R¹ and R² are each independently C₁- to
 35 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.

40 The dihydrocarbyl ethers mentioned may be open-chain or cyclic, where the two variables R¹ and R² 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, diethyl ether, 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, 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, ditolyl ether, dixylyl ether and dibenzyl ether. Among the dihydrocarbyl ethers mentioned, di-n-butyl ether and diphenyl ether have been found to be particularly advantageous as donors for the aluminum trihalide-donor complexes or the alkylaluminum halide complexes, especially the aluminum trichloride-donor complexes.

In a further preferred embodiment of the present invention, as an alternative, an aluminum trihalide-donor complex or an alkylaluminum halide complex, especially an aluminum trichloride-donor complex, is used, which comprises, as the donor, a hydrocarbyl carboxylate of the general formula $R^3\text{-COOR}^4$ in which the variables R^3 and R^4 are each independently C_1 - to C_{20} -alkyl radicals, especially C_1 - to C_8 alkyl radicals, C_5 - to C_8 -cycloalkyl radicals, C_6 - to C_{20} -aryl radicals, especially C_6 - to C_{12} aryl radicals, or C_7 - to C_{20} -arylalkyl radicals, especially C_7 - to C_{12} -arylalkyl radicals.

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 aluminum trihalide-donor complexes or the alkylaluminum halide complexes, especially the aluminum trichloride-donor complexes.

In addition, particularly advantageous dihydrocarbyl ethers and hydrocarbyl carboxylates as donors for the aluminum trihalide-donor complexes or the

alkylaluminum halide complexes, especially the aluminum trichloride-donor 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 the specific case of the dihydrocarbyl ethers, preference is given in particular to those

- 5 having a total of 6 to 14 and especially 8 to 12 carbon atoms. In the specific case of the hydrocarbyl carboxylates, preference is given in particular to those having a total of 3 to 10 and especially 4 to 6 carbon atoms.

- 10 The molar ratio of the donor compounds mentioned to the aluminum trihalide or to the alkylaluminum halide, especially to the aluminum trichloride, in the donor complex generally varies within the range from 0.3:1 to 1.5:1, especially from 0.5:1 to 1.2:1, in particular 0.7:1 to 1.1:1; in most cases it is 1:1. However, it is also possible to work with a greater excess of the donor compounds, often up to a 10-fold and especially 3-fold molar excess; the excess amount of donor compounds then acts additionally as a
- 15 solvent or diluent.

- Typically, the aluminum trihalide-donor complex or the alkylaluminum halide complex, especially the aluminum trichloride-donor complex, is prepared separately prior to the polymerization from the aluminum trihalide or the alkylaluminum halide, especially from
- 20 anhydrous aluminum trichloride, and the donor compound, and is then - usually dissolved in an inert solvent such as a halogenated hydrocarbon, for example dichloromethane - added to the polymerization medium. However, the complex can also be prepared in situ prior to the polymerization.

- 25 In a preferred embodiment of the present invention, the polymerization is 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
- 30 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
- 35 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.

- 40 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 R^5-OH , in which R^5 denotes C_1 - to C_{20} -alkyl radicals, especially C_1 - to C_8 -alkyl radicals, C_5 - to C_8 -cycloalkyl radicals, C_6 - to C_{20} -aryl radicals, especially C_6 - to C_{12} -aryl radicals, or C_7 - to C_{20} -arylalkyl radicals, especially

C₇- to C₁₂-arylalkyl radicals. In addition, the R⁵ 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.

5

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-phenyl-ethanol, 1- and 2-(p-methoxyphenyl)ethanol, 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, 1-hydroxy-1,1-diphenylpropan-2-one, benzoic acid, 9-phenyl-9-fluorenone, 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, 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.

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- 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-fluorenone.

35

Organic halogen compounds which have one halogen atom in the molecule and are suitable as monofunctional initiators are in particular compounds of the general formula R⁶-Hal in which Hal is a halogen atom selected from fluorine, iodine and especially chlorine and bromine, and R⁶ denotes C₁- to C₂₀-alkyl radicals, especially C₁- to C₈-alkyl radicals, C₅- to C₈-cycloalkyl radicals or C₇- to C₂₀-arylalkyl radicals, especially C₇- to C₁₂-arylalkyl radicals. In addition, the R⁶ radicals may also comprise mixtures of the abovementioned structures and/or have other functional groups than those already

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mentioned, for example a keto function, a nitroxide or a carboxyl group, and/or heterocyclic structural elements.

Typical examples of such monohalogen compounds are methyl chloride, methyl
 5 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-chlorohexane, 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,
 10 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-bromopropane, 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-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 chloride).

The initiator is more preferably selected from organic hydroxyl compounds in which one or more hydroxyl groups are each bonded to an sp^3 -hybridized carbon atom, organic halogen compounds, in which one or more halogen atoms are each bonded to an sp^3 -hybridized carbon 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 sp^3 -hybridized carbon atom.

In the case of the organic halogen compounds as initiators, particular preference is further given to those in which the one or more halogen atoms are each bonded to a secondary or especially to a tertiary sp^3 -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^5 , R^6 and R^7 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^5 , R^6

and R⁷ is hydrogen and at least one of the variables R⁵, R⁶ and R⁷ is phenyl which may also bear one or more, preferably one or two, C₁- to C₄-alkyl, C₁- to C₄-alkoxy, C₁- to C₄-hydroxyalkyl or C₁- to C₄-haloalkyl radicals as substituents.

5 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,
 10 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.

15 The molar ratio of the initiators mentioned to the isobutene monomer used in the case of homopolymerization of isobutene, or to the total amount of the polymerizable monomers used in the case of copolymerization of isobutene, based on each individual functional site of the initiator, is generally 0.0005:1 to 0.1:1, especially 0.001:1 to 0.075:1, in particular 0.0025:1 to 0.05:1. When water is used as the sole initiator or in
 20 combination with organic hydroxyl compounds and/or organic halogen compounds as further initiators, the molar ratio of water to the isobutene monomer used in the case of homopolymerization of isobutene, or to the total amount of the polymerizable monomers used in the case of copolymerization of isobutene, is especially 0.0001:1 to 0.1:1, in particular 0.0002:1 to 0.05:1.

25 A proportion of the initiator molecules added as organic hydroxyl or halogen compounds is incorporated into the polymer chains. The proportion (I_{eff}) of polymer chains which are started by such an incorporated organic initiator molecule may be up to 100%, and is generally 5 to 90%. The remaining polymer chains arise either from
 30 water originating from traces of moisture as an initiator molecule, or from chain transfer reactions.

In a further preferred embodiment of the present invention, the polymerization is performed in the presence of 0.01 to 10 mmol, especially of 0.05 to 5.0 mmol, in
 35 particular of 0.1 to 1.0 mmol, based in each case on 1 mol of isobutene monomer used in the case of homopolymerization of isobutene, or on 1 mol of the total amount of the polymerizable monomers used in the case of copolymerization of isobutene, of a nitrogen-containing basic compound.

40 Such a nitrogen-containing basic compound used may be an aliphatic, cycloaliphatic or aromatic amine of the general formula R⁷-NR⁸R⁹, or else ammonia, in which the variables R⁷, R⁸ and R⁹ are each independently hydrogen, 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. When none of these variables is hydrogen, the amine is a tertiary amine. When one of these variables is hydrogen, the amine is a secondary amine. When two of these variables is hydrogen, the amine is a primary amine. When all these variables are hydrogen, the amine is ammonia.

Typical examples of such amines of the general formula R⁷-NR⁸R⁹ are methylamine, ethylamine, n-propylamine, isopropylamine, n-butylamine, tert-butylamine, sec-butylamine, isobutylamine, tert-amylamine, n-hexylamine, n-heptylamine, n-octylamine, 2-ethylhexylamine, cyclopentylamine, cyclohexylamine, aniline, dimethylamine, diethylamine, di-n-propylamine, diisopropylamine, di-n-butylamine, di-tert-butylamine, di-sec-butylamine, diisobutylamine, di-tert-amylamine, di-n-hexylamine, di-n-heptylamine, di-n-octylamine, di-(2-ethylhexyl)amine, dicyclopentylamine, dicyclohexylamine, diphenylamine, trimethylamine, triethylamine, tri-n-propylamine, tri-isopropylamine, tri-n-butylamine, tri-tert-butylamine, tri-sec-butylamine, tri-isobutylamine, tri-tert-amylamine, tri-n-hexylamine, tri-n-heptylamine, tri-n-octylamine, tri-(2-ethylhexyl)amine, tricyclopentylamine, tricyclohexylamine, triphenylamine, dimethylethylamine, methyl-n-butylamine, N-methyl-N-phenylamine, N,N-dimethyl-N-phenylamine, N-methyl-N,N-diphenylamine or N-methyl-N-ethyl-N-n-butylamine.

In addition, such a nitrogen-containing basic compound used may also be a compound having a plurality of, especially having two or three, nitrogen atoms and having 2 to 20 carbon atoms, where these nitrogens may each independently bear hydrogen atoms or aliphatic, cycloaliphatic or aromatic substituents. Examples of such polyamines are 1,2-ethylenediamine, 1,3-propylenediamine, 1,4-butylenediamine, diethylenetriamine, N-methyl-1,2-ethylenediamine, N,N-dimethyl-1,2-ethylenediamine, N,N'-dimethyl-1,2-ethylenediamine or N,N-dimethyl-1,3-propylenediamine.

However, a suitable nitrogen-containing basic compound of this kind is especially a saturated, partly unsaturated or unsaturated nitrogen-containing five-membered or six-membered heterocyclic ring which comprises one, two or three ring nitrogen atoms and may have one or two further ring heteroatoms from the group of oxygen and sulfur 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.

It is possible to use a single nitrogen-containing basic compound or mixtures of such
5 nitrogen-containing basic compounds.

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",
10 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
15 stream from a metathesis unit, which are generally used after customary purification and/or concentration. Suitable C₄ hydrocarbon streams generally comprise less than 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
20 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 the polymerization process according to the invention, the unbranched butenes in the raffinate 1 generally behave virtually inertly, and only the isobutene is polymerized.

25 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
30 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
35 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.

40 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.

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 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.

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 atoms, 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 1-[tri(methoxyethoxy)silyl]-2-methylpropene-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 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, diblock, 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 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 vinylaromatic 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.

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
 5 -70°C to -10°C, especially at -60°C to -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
 10 reactors.

The polymerization in the process according to the invention is preferably 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
 15 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,
 20 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
 25 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.

30 The inventive polymerization is preferably 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
 35 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.

40 In a further preferred embodiment, the inventive 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.

- 5 The polymerization in the process according to the invention 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
- 10 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
- 15 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
- 20 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
- 25 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.
- 30 The polymerization of the isobutene or of the isobutenic starting material generally proceeds spontaneously when the aluminum trihalide-donor complex or the alkylaluminum halide complex, especially the aluminum trichloride-donor complex, is contacted with the isobutene or the isobutenic monomer mixture at the desired reaction temperature. The procedure here may be to initially charge the monomers, optionally in
- 35 the diluent, to bring it to reaction temperature and then to add the aluminum trihalide-donor complex or the alkylaluminum halide complex, especially the aluminum trichloride-donor complex. The procedure may also be to initially charge the aluminum trihalide-donor complex or the alkylaluminum halide complex, especially the aluminum trichloride-donor complex, optionally in the diluent, and then to add the monomers. In
- 40 that case, the start of polymerization is considered to be that time at which all reactants are present in the reaction vessel.

To prepare isobutene copolymers, the procedure may be to initially charge the monomers, optionally in the diluent, and then to add the aluminum trihalide-donor complex or the alkylaluminum halide complex, especially the aluminum trichloride-donor complex. The reaction temperature can be established before or after the

5 addition of the aluminum trihalide-donor complex or the alkylaluminum halide complex, especially of the aluminum trichloride-donor complex. The procedure may also be first to initially charge only one of the monomers, optionally in the diluent, then to add the aluminum trihalide-donor complex or the alkylaluminum halide complex, especially the aluminum trichloride-donor complex, and to add the further monomer(s) only after a

10 certain time, for example when at least 60%, at least 80% or at least 90% of the monomer has been converted. Alternatively, the aluminum trihalide-donor complex or the alkylaluminum halide complex, especially the aluminum trichloride-donor complex, can be initially charged, optionally in the diluent, then the monomers can be added simultaneously or successively, and then the desired reaction temperature can be

15 established. In that case, the start of polymerization is considered to be that time at which the aluminum trihalide-donor complex or the alkylaluminum halide complex, especially the aluminum trichloride-donor complex, and at least one of the monomers are present in the reaction vessel.

20 In addition to the batchwise procedure described here, the polymerization in the process according to the invention can also be configured as a continuous process. In this case, the feedstocks, i.e. the monomer(s) to be polymerized, optionally the diluent and optionally the aluminum trihalide-donor complex or the alkylaluminum halide complex, especially the aluminum trichloride-donor complex, are supplied continuously

25 to the polymerization reaction, and reaction product is withdrawn continuously, such that more or less steady-state polymerization conditions are established in the reactor. The monomer(s) to be polymerized can be supplied as such, diluted with a diluent or solvent, or as a monomer-containing hydrocarbon stream.

30 The aluminum trihalide-donor complex effective as a polymerization catalyst or the alkylaluminum halide complex, especially the aluminum trichloride-donor complex, is generally present in dissolved, dispersed or suspended form in the polymerization medium. Supporting of the aluminum trihalide-donor complex or of the alkylaluminum halide complex, especially of the aluminum trichloride-donor complex, on customary

35 support materials is also possible. Suitable reactor types for the polymerization process of the present invention are typically stirred tank reactors, loop reactors and tubular reactors, but also fluidized bed reactors, stirred tank reactors with or without solvent, fluid bed reactors, continuous fixed bed reactors and batchwise fixed bed reactors (batchwise mode).

40 In the process according to the invention, the aluminum trihalide-donor complex effective as a polymerization catalyst or the alkylaluminum halide complex, especially the aluminum trichloride-donor complex, is generally used in such an amount that

the molar ratio of aluminum in the aluminum trihalide-donor complex or alkylaluminum halide complex, especially in the aluminum trichloride-donor complex, to isobutene in the case of homopolymerization of isobutene, or to the total amount of the polymerizable monomers used in the case of copolymerization of isobutene, is in the range from 1:5 to 1:5000, preferably from 1:10 to 1:5000, especially 1:15 to 1:1000, in particular 1:20 to 1:250.

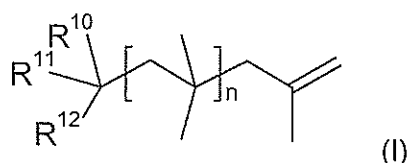
To stop the reaction, the reaction mixture is preferably deactivated, for example by adding a protic compound, especially by adding water, alcohols such as methanol, ethanol, n-propanol and isopropanol or mixtures thereof with water, or by adding an aqueous base, for example an aqueous solution of an alkali metal or alkaline earth metal hydroxide such as sodium hydroxide, potassium hydroxide, magnesium hydroxide or calcium hydroxide, an alkali metal or alkaline earth metal carbonate such as sodium, potassium, magnesium or calcium carbonate, or an alkali metal or alkaline earth metal hydrogencarbonate such as sodium, potassium, magnesium or calcium hydrogencarbonate.

The process according to the invention serves to prepare high-reactivity isobutene homo- or copolymers with a content of terminal vinylidene double bonds (α -double bonds) per polyisobutene chain end of at least 50 mol%, preferably of at least 60 mol%, preferably of at least 70 mol%, preferably of at least 80 mol%, preferably of at least 85 mol%, more preferably of at least 90 mol%, more preferably of more than 91 mol% and especially of at least 95 mol%, for example of virtually 100 mol%. More particularly, it also serves to prepare high-reactivity isobutene copolymers which are formed from isobutene and at least one vinylaromatic monomer, especially styrene, and have a content of terminal vinylidene double bonds (α -double bonds) per polyisobutene chain end of at least 50 mol%, preferably of at least 60 mol%, preferably of at least 70 mol%, preferably of at least 80 mol%, preferably of at least 80 mol%, preferably of at least 85 mol%, more preferably of at least 90 mol%, more preferably of more than 91 mol% and especially of at least 95 mol%, for example of virtually 100 mol%. To prepare such copolymers of isobutene and at least one vinylaromatic monomer, especially styrene, isobutene or an isobutenic hydrocarbon cut is copolymerized with the at least one vinylaromatic monomer in a weight ratio of isobutene to vinylaromatic of 5:95 to 95:5, especially of 30:70 to 70:30.

The high-reactivity isobutene homo- or copolymers prepared by the process according to the invention and specifically the isobutene homopolymers preferably have a polydispersity ($PDI = M_w/M_n$) of 1.05 to less than 3.5, preferably of 1.05 to less than 3.0, preferably of 1.05 to less than 2.5, preferably of 1.05 to 2.3, more preferably of 1.05 to 2.0 and especially of 1.1 to 1.85. Typical PDI values in the case of an optimal process regime are 1.2 to 1.7.

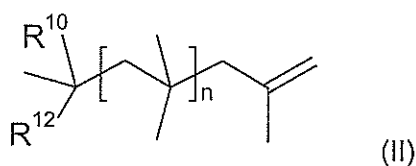
The high-reactivity isobutene homo- or copolymers prepared by the process according to the invention preferably possess a number-average molecular weight M_n (determined by gel permeation chromatography) of preferably 500 to 250 000, more preferably of 500 to 100 000, even more preferably of 500 to 25 000 and especially of 500 to 5000. Isobutene homopolymers even more preferably possess a number-average molecular weight M_n of 500 to 10 000 and especially of 500 to 5000, for example of about 1000 or of about 2300.

Some of the isobutene polymers which have terminal vinylidene double bonds and also comprise incorporated initiator molecules and occur as the predominant proportion in the isobutene homopolymers prepared in accordance with the invention are novel compounds. The present invention therefore also provides isobutene polymers of the general formula I



in which

R^{10} , R^{11} and R^{12} 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 C_1 - to C_4 -alkyl- or C_1 - to C_4 -alkoxy radicals or moieties of the general formula II



as substituents, where not more than one of the variables R^{10} , R^{11} or R^{12} is hydrogen and at least one of the variables R^{10} , R^{11} or R^{12} is phenyl which may also bear one or more C_1 - to C_4 -alkyl- or C_1 - to C_4 -alkoxy radicals or moieties of the general formula II as substituents, and

n is a number from 9 to 4500, preferably 9 to 180, especially 9 to 100, in particular 12 to 50.

In a preferred embodiment, R^5 , R^6 and R^7 are each independently hydrogen, C_1 - to C_4 -alkyl, especially methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, sec.-butyl or tert-butyl, or phenyl which may also bear one or two C_1 - to C_4 -alkyl- or C_1 - to C_4 -alkoxy radicals or moieties of the general formula II as substituents, where not more than one

of the variables R^5 , R^6 and R^7 is hydrogen and at least one of the variables R^5 , R^6 and R^7 is phenyl which may also bear one or two C_1 - to C_4 -alkyl or C_1 - to C_4 -alkoxy radicals or moieties of the general formula II as substituents, and n is a number from 9 to 4500, preferably 9 to 180, especially 9 to 90, in particular 15 to 45.

5

The process according to the invention successfully polymerizes isobutene or isobutene-comprising monomer mixtures under cationic conditions with satisfactory to high conversions of generally 20 to 100%, especially 35 to 90%, in short reaction times of generally 5 to 120 minutes, especially 30 to 120 minutes, to give high-reactivity
10 isobutene homo- or copolymers with a content of terminal vinylidene double bonds per polyisobutene chain end of at least 80 mol% and with a narrow molecular weight distribution.

The examples which follow are intended to illustrate the present invention in detail
15 without restricting it.

Example 1: Polymerization of isobutene with $AlCl_3 \cdot Bu_2O$ without initiator

1.43 g (25.5 mmol) of pure isobutene were polymerized in a mixture of 20 ml of
20 dichloromethane and 5 ml of n-hexane at $-20^\circ C$ with 0.62 mmol of the complex of aluminum trichloride and di-n-butyl ether in a molar ratio of 1:1 (in the form of a 1 molar solution in dichloromethane) within 30 minutes at a conversion of 71% to give a polyisobutene with a number-average molecular weight M_n of 2095, a polydispersity (PDI) of 2.27 and a content of terminal vinylidene double bonds of 91 mol%.

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Example 2: Polymerization of isobutene with $AlCl_3 \cdot EtOAc$ without initiator

1.43 g (25.5 mmol) of pure isobutene were polymerized in a mixture of 20 ml of
dichloromethane and 5 ml of n-hexane at $-20^\circ C$ with 0.62 mmol of the complex of
30 aluminum trichloride and ethyl acetate in a molar ratio of 1:1 (in the form of a 1 molar solution in dichloromethane) within 30 minutes at a conversion of 17% to give a polyisobutene with a number-average molecular weight M_n of 1930, a polydispersity (PDI) of 1.45 and a content of terminal vinylidene double bonds of 88 mol%.

35 Example 3: Polymerization of isobutene with $AlCl_3 \cdot Bu_2O$ with cumene as an initiator

1.43 g (25.5 mmol) of pure isobutene were polymerized in a mixture of 20 ml of
dichloromethane and 5 ml of n-hexane at $-40^\circ C$ with 0.62 mmol of the complex of
aluminum trichloride and di-n-butyl ether in a molar ratio of 1:1 (in the form of a 1 molar
40 solution in dichloromethane) in the presence of 0.5 mmol of 2-phenyl-2-propanol (cumene) as an initiator within 30 minutes at a conversion of 62% to give a polyisobutene with a number-average molecular weight M_n of 1515, a polydispersity

(PDI) of 1.45 and a content of terminal vinylidene double bonds of 90 mol%. The proportion of cumene-started polymer chains (I_{eff}) was 70%.

Example 4: Polymerization of isobutene with $\text{AlCl}_3 \cdot \text{Bu}_2\text{O}$ with cumene as an initiator

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1.43 g (25.5 mmol) of pure isobutene were polymerized in a mixture of 20 ml of dichloromethane and 5 ml of n-hexane at -40°C with 1.24 mmol of the complex of aluminum trichloride and di-n-butyl ether in a molar ratio of 1:1 (in the form of a 1 molar solution in dichloromethane) in the presence of 1.0 mmol of 2-phenyl-2-propanol (cumene) as an initiator within 30 minutes at a conversion of 76% to give a polyisobutene with a number-average molecular weight M_n of 1180, a polydispersity (PDI) of 1.21 and a content of terminal vinylidene double bonds of 88 mol%. The proportion of cumene-started polymer chains (I_{eff}) was 90%.

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Example 5: Polymerization of isobutene with $\text{AlCl}_3 \cdot \text{Bu}_2\text{O}$ with cumene as an initiator

1.43 g (25.5 mmol) of pure isobutene were polymerized in a mixture of 20 ml of dichloromethane and 5 ml of n-hexane at -60°C with 0.62 mmol of the complex of aluminum trichloride and di-n-butyl ether in a molar ratio of 1:1 (in the form of a 1 molar solution in dichloromethane) in the presence of 0.5 mmol of 2-phenyl-2-propanol (cumene) as an initiator within 31 minutes at a conversion of 91% to give a polyisobutene with a number-average molecular weight M_n of 2275, a polydispersity (PDI) of 1.83 and a content of terminal vinylidene double bonds of 85 mol%. The proportion of cumene-started polymer chains (I_{eff}) was 90%.

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Example 6: Polymerization of isobutene with $\text{AlCl}_3 \cdot \text{Bu}_2\text{O}$ with cumene as an initiator

1.43 g (25.5 mmol) of pure isobutene were polymerized in a mixture of 15 ml of dichloromethane and 10 ml of n-hexane at -60°C with 0.36 mmol of the complex of aluminum trichloride and di-n-butyl ether in a molar ratio of 1:1 (in the form of a 1 molar solution in dichloromethane) in the presence of 0.29 mmol of 2-phenyl-2-propanol (cumene) as an initiator within 120 minutes at a conversion of 56% to give a polyisobutene with a number-average molecular weight M_n of 2690, a polydispersity (PDI) of 1.91 and a content of terminal vinylidene double bonds of 89 mol%. The proportion of cumene-started polymer chains (I_{eff}) was 88%.

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Example 7a: Polymerization of isobutene with $\text{AlCl}_3 \cdot \text{Bu}_2\text{O}$ with cumene as an initiator

1.43 g (25.5 mmol) of pure isobutene were polymerized in a mixture of 15 ml of dichloromethane and 10 ml of n-hexane at -60°C with 0.36 mmol of the complex of aluminum trichloride and di-n-butyl ether in a molar ratio of 1:1 (in the form of a 1 molar solution in dichloromethane) in the presence of 0.09 mmol of 2-phenyl-2-propanol (cumene) as an initiator within 30 minutes at a conversion of 47% to give a

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polyisobutene with a number-average molecular weight M_n of 3510, a polydispersity (PDI) of 2.17 and a content of terminal vinylidene double bonds of 95 mol%. The proportion of cumene-started polymer chains (I_{eff}) was 37%.

5 Example 7b: Polymerization of isobutene with $AlCl_3 \cdot Bu_2O$ with cumene as an initiator

Example 7a was repeated, except that the reaction time was quadrupled: after 120 minutes, at a conversion of 62%, a polyisobutene was obtained with a number-average molecular weight M_n of 3360, a polydispersity (PDI) of 1.93 and a content of terminal vinylidene double bonds of 91 mol% polymerized. The proportion of cumene-started polymer chains (I_{eff}) was 23%.

Example 8: Polymerization of isobutene with $AlCl_3 \cdot Bu_2O$ with cumene as an initiator

15 2.97 g (53.0 mmol) of pure isobutene were polymerized in 66 ml of dichloromethane at $-15^\circ C$ with 2.15 mmol of the complex of aluminum trichloride and di-n-butyl ether in a molar ratio of 1:1 (in the form of a 1 molar solution in dichloromethane) in the presence of 1.0 mmol of 2-phenyl-2-propanol (cumene) as an initiator within 60 minutes at a conversion of 40% to give a polyisobutene with a number-average molecular weight M_n of 1675, a polydispersity (PDI) of 1.75 and a content of terminal vinylidene double bonds of 96 mol%.

Example 9: Polymerization of isobutene with $AlCl_3 \cdot Bu_2O$ with cumene as an initiator

25 3.09 g (55.0 mmol) of pure isobutene were polymerized in 66 ml of dichloromethane at $-60^\circ C$ with 1.80 mmol of the complex of aluminum trichloride and di-n-butyl ether in a molar ratio of 1:1 (in the form of a 1 molar solution in dichloromethane) in the presence of 1.0 mmol of 2-phenyl-2-propanol (cumene) as an initiator within 60 minutes at a conversion of 99% to give a polyisobutene with a number-average molecular weight M_n of 1700, a polydispersity (PDI) of 1.82 and a content of terminal vinylidene double bonds of 96 mol%.

Example 10: Polymerization of isobutene with $AlCl_3 \cdot 0.8 Bu_2O$ with cumene as an initiator

35 1.43 g (25.5 mmol) of pure isobutene were polymerized in a mixture of 20 ml of dichloromethane and 5 ml of n-hexane at $-20^\circ C$ with 0.62 mmol of the complex of aluminum trichloride and di-n-butyl ether in a molar ratio of 1:0.8 (in the form of a 1 molar solution in dichloromethane) in the presence of 0.5 mmol of 2-phenyl-2-propanol (cumene) as an initiator within 30 minutes at a conversion of 44% to give a polyisobutene with a number-average molecular weight M_n of 1550, a polydispersity (PDI) of 1.74 and a content of terminal vinylidene double bonds of 87 mol%. The proportion of cumene-started polymer chains (I_{eff}) was 56%.

Example 11: Polymerization of "raffinate 1" with $\text{AlCl}_3 \cdot \text{Bu}_2\text{O}$ with cumene as an initiator

7.43 g of "raffinate 1", comprising 2.97 g (53.0 mmol) of pure isobutene, were
 5 polymerized in 66 ml of dichloromethane at -30°C with 2.15 mmol of the complex of
 aluminum trichloride and di-n-butyl ether in a molar ratio of 1:1 (in the form of a 1 molar
 solution in dichloromethane) in the presence of 1.0 mmol of 2-phenyl-2-propanol
 (cumene) as an initiator within 60 minutes at a conversion of 30% to give a
 polyisobutene with a number-average molecular weight M_n of 1720, a polydispersity
 10 (PDI) of 2.04 and a content of terminal vinylidene double bonds of 93 mol%.

Example 12a: Polymerization of isobutene with $\text{AlCl}_3 \cdot \text{Bu}_2\text{O}$ with cumene as an initiator

2.97 g (53.0 mmol) of pure isobutene were polymerized in 66 ml of dichloromethane at
 15 -60°C with 1.43 mmol of the complex of aluminum trichloride and di-n-butyl ether in
 a molar ratio of 1:1 (in the form of a 1 molar solution in dichloromethane) in the
 presence of 1.0 mmol of 2-phenyl-2-propanol (cumene) as an initiator within
 60 minutes at a conversion of 100% to give a polyisobutene with a number-average
 molecular weight M_n of 6005, a polydispersity (PDI) of 2.26 and a content of terminal
 20 vinylidene double bonds of 94 mol%.

Example 12b: Polymerization of isobutene with $\text{BF}_3 \cdot \text{MeOH}$ (for comparison against
 inventive example 12a)

25 2.97 g (53.0 mmol) of pure isobutene were polymerized in 66 ml of dichloromethane at
 -60°C with 1.34 mmol of the complex of boron trifluoride and methanol in a molar ratio
 of 1:1 within 60 minutes at a conversion of 43% to give a polyisobutene with a number-
 average molecular weight M_n of 4850, a polydispersity (PDI) of 4.05 and a content of
 terminal vinylidene double bonds of only 62.5 mol%.

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Example 13: Polymerization of isobutene with $\text{AlCl}_3 \cdot \text{Bu}_2\text{O}$ with 1-phenyl-1-chloro-
 ethane as an initiator

1.43 g (25.5 mmol) of pure isobutene were polymerized in a mixture of 20 ml of
 35 dichloromethane and 5 ml of n-hexane at -40°C with 0.62 mmol of the complex of
 aluminum trichloride and di-n-butyl ether in a molar ratio of 1:1 (in the form of a 1 molar
 solution in dichloromethane) in the presence of 0.5 mmol of 1-phenyl-1-chloroethane
 as an initiator within 30 minutes at a conversion of 77% to give a polyisobutene with a
 number-average molecular weight M_n of 2170, a polydispersity (PDI) of 1.99 and a
 40 content of terminal vinylidene double bonds of 88 mol%. The proportion of 1-phenyl-1-
 chloroethane started polymer chains (I_{eff}) was 4%.

Example 14: Polymerization of isobutene with $\text{AlCl}_3 \cdot \text{Bu}_2\text{O}$ with 1-(p-methoxyphenyl)-ethanol as an initiator

1.43 g (25.5 mmol) of pure isobutene were polymerized in a mixture of 20 ml of dichloromethane and 5 ml of n-hexane at -20°C with 0.62 mmol of the complex of aluminum trichloride and di-n-butyl ether in a molar ratio of 1:1 (in the form of a 1 molar solution in dichloromethane) in the presence of 0.5 mmol of 1-(p-methoxyphenyl)-ethanol as an initiator within 10 minutes at a conversion of 26% to give a polyisobutene with a number-average molecular weight M_n of 960, a polydispersity (PDI) of 1.05 and a content of terminal vinylidene double bonds of 88 mol%.

Example 15a: Polymerization of isobutene with $\text{AlCl}_3 \cdot \text{Bu}_2\text{O}$ with cumene as an initiator in the presence of pyridine

1.43 g (25.5 mmol) of pure isobutene were polymerized in a mixture of 15 ml of dichloromethane and 10 ml of n-hexane at -60°C with 0.36 mmol of the complex of aluminum trichloride and di-n-butyl ether in a molar ratio of 1:1 (in the form of a 1 molar solution in dichloromethane) in the presence of 0.09 mmol of 2-phenyl-2-propanol (cumene) as an initiator and 0.0125 mol of pyridine as a nitrogen-containing basic compound within 30 minutes at a conversion of 44% to give a polyisobutene with a number-average molecular weight M_n of 2580, a polydispersity (PDI) of 1.86 and a content of terminal vinylidene double bonds of 90 mol%. The proportion of cumene-started polymer chains (I_{eff}) was 36%.

Example 15b: Polymerization of isobutene with $\text{AlCl}_3 \cdot \text{Bu}_2\text{O}$ and with cumene as an initiator in the presence of pyridine

Example 15a was repeated, except that the reaction time was quadrupled: after 120 minutes, at a conversion of 53%, a polyisobutene was obtained with a number-average molecular weight M_n of 2490, a polydispersity (PDI) of 1.84 and a content of terminal vinylidene double bonds of 91 mol% polymerized. The proportion of cumene-started polymer chains (I_{eff}) was 26%.

Example 16: Polymerization of isobutene with $\text{AlCl}_3 \cdot \text{Bu}_2\text{O}$ with cumene as an initiator in the presence of pyridine

1.43 g (25.5 mmol) of pure isobutene were polymerized in a mixture of 15 ml of dichloromethane and 10 ml of n-hexane at -20°C with 0.36 mmol of the complex of aluminum trichloride and di-n-butyl ether in a molar ratio of 1:1 (in the form of a 1 molar solution in dichloromethane) in the presence of 0.09 mmol of 2-phenyl-2-propanol (cumene) as an initiator and 0.0125 mol of pyridine as a nitrogen-containing basic compound within 120 minutes at a conversion of 21% to give a polyisobutene with a number-average molecular weight M_n of 1445, a polydispersity (PDI) of 1.69 and a

content of terminal vinylidene double bonds of 94 mol%. The proportion of cumene-started polymer chains (I_{eff}) was 27%.

5 Example 17: Polymerization of isobutene with $\text{AlCl}_3 \cdot \text{Bu}_2\text{O}$ with cumene as an initiator in the presence of pyridine

1.43 g (25.5 mmol) of pure isobutene were polymerized in a mixture of 20 ml of dichloromethane and 5 ml of n-hexane at -40°C with 0.62 mmol of the complex of aluminum trichloride and di-n-butyl ether in a molar ratio of 1:1 (in the form of a 1 molar solution in dichloromethane) in the presence of 0.5 mmol of 2-phenyl-2-propanol (cumene) as an initiator and 0.0125 mol of pyridine as a nitrogen-containing basic compound within 30 minutes at a conversion of 51% to give a polyisobutene with a number-average molecular weight M_n of 1270, a polydispersity (PDI) of 1.17 and a content of terminal vinylidene double bonds of 91 mol%. The proportion of cumene-started polymer chains (I_{eff}) was 48%.

Example 18: Polymerization of isobutene with $\text{AlCl}_3 \cdot \text{Bu}_2\text{O}$ and with 1-phenyl-1-chloroethane as an initiator

20 1.43 g (2.25 mmol) of pure isobutene were polymerized in a mixture of 20 ml of dichloromethane and 5 ml of n-hexane at -20°C with 0.62 mmol of the complex of aluminum trichloride and di-n-butyl ether in a molar ratio of 1:1 (in the form of a 1 molar solution in dichloromethane) in the presence of 0.5 mmol of 1-phenyl-1-chloroethane as an initiator within 3 minutes at a conversion of 37% to give a polyisobutene with a number-average molecular weight M_n of 3270, a polydispersity (PDI) of 1.76 and a content of terminal vinylidene double bonds of 97 mol%.

Example 19: Polymerization of isobutene with $\text{AlCl}_3 \cdot \text{Bu}_2\text{O}$ and with 1,4-bis(1-hydroxy-1-methylethyl)benzene as an initiator

30 1.43 g (25.5 mmol) of pure isobutene were polymerized in a mixture of 20 ml of dichloromethane and 5 ml of n-hexane at -20°C with 0.62 mmol of the complex of aluminum trichloride and di-n-butyl ether in a molar ratio of 1:1 (in the form of a 1 molar solution in dichloromethane) in the presence of 0.25 mmol of 1,4-bis(1-hydroxy-1-methylethyl)benzene as an initiator within 3 minutes at a conversion of 36% to give a polyisobutene with a number-average molecular weight M_n of 2750, a polydispersity (PDI) of 1.99 and a content of terminal vinylidene double bonds of 94 mol%.

Example 20: Polymerization of isobutene with $\text{AlCl}_3 \cdot \text{Bu}_2\text{O}$ without initiator

40 1.43 g (25.5 mmol) of pure isobutene were polymerized in a mixture of 15 ml of dichloromethane and 10 ml of n-hexane at -60°C with 0.36 mmol of the complex of aluminum trichloride and di-n-butyl ether in a molar ratio of 1:1 (in the form of a 1 molar

solution in dichloromethane) within 120 minutes at a conversion of 46% to give a polyisobutene with a number-average molecular weight M_n of 7895, a polydispersity (PDI) of 2.23 and a content of terminal vinylidene double bonds of 94 mol%.

5 Example 21: Polymerization of isobutene with $AlCl_3 \cdot Bu_2O$ and with water as an initiator

1.43 g (25.5 mmol) of pure isobutene were polymerized in 25 ml of dichloromethane at -20°C with 0.62 mmol of the complex of aluminum trichloride and di-n-butyl ether in a molar ratio of 1:1 (in the form of a 1 molar solution in dichloromethane) in the
10 presence of 0.07 mmol of water as an initiator within 3 minutes at a conversion of 65% to give a polyisobutene with a number-average molecular weight M_n of 2500, a polydispersity (PDI) of 1.92 and a content of terminal vinylidene double bonds of 92 mol%.

15 Example 22: Polymerization of isobutene with $AlCl_3 \cdot Bu_2O$ and with cumene as an initiator

1.43 g (25.5 mmol) of pure isobutene were polymerized in 25 ml of toluene at -20°C with 0.62 mmol of the complex of aluminum trichloride and di-n-butyl ether in a molar
20 ratio of 1:1 (in the form of a 1 molar solution in dichloromethane) in the presence of 0.5 mmol of 2-phenyl-2-propanol (cumene) as an initiator within 10 minutes at a conversion of 19% to give a polyisobutene with a number-average molecular weight M_n of 1030, a polydispersity (PDI) of 2.65 and a content of terminal vinylidene double bonds of 89 mol%. The proportion of cumene-started polymer chains (I_{eff}) was 98%.

25 Example 23: Polymerization of isobutene with $AlCl_3 \cdot Bu_2O$ and with cumene as an initiator

1.43 g (25.5 mmol) of pure isobutene were polymerized in a mixture of 15 ml of toluene
30 and 10 ml of trifluoromethylbenzene at -20°C with 0.62 mmol of the complex of aluminum trichloride and di-n-butyl ether in a molar ratio of 1:1 (in the form of a 1 molar solution in dichloromethane) in the presence of 0.5 mmol of 2-phenyl-2-propanol (cumene) as an initiator within 3 minutes at a conversion of 24% to give a polyisobutene with a number-average molecular weight M_n of 1095, a polydispersity
35 (PDI) of 1.93 and a content of terminal vinylidene double bonds of 78 mol%. The proportion of cumene-started polymer chains (I_{eff}) was 94%.

40 Example 24: Polymerization of isobutene with $AlCl_3 \cdot Bu_2O$ and with cumene as an initiator

3.00 g (53 mmol) of pure isobutene were polymerized in 50 ml of dichloromethane at -60°C with 187.2 mg of the complex of aluminum trichloride and di-n-butyl ether in a molar ratio of 1:1 (in the form of a 1 molar solution in dichloromethane) in the

presence of 24.5 mg of 2-phenyl-2-propanol (cumene) as an initiator within 120 minutes at a conversion of 23% to give a polyisobutene with a number-average molecular weight M_n of 3210, a polydispersity (PDI) of 1.90 and a content of terminal vinylidene double bonds of > 99 mol%.

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Example 25: Polymerization of isobutene with $AlCl_3 \cdot Bu_2O$ and with cumene as an initiator

3.00 g (53 mmol) of pure isobutene were polymerized in 50 ml of dichloromethane at
10 -60°C with 1140 mg of the complex of aluminum trichloride and di-n-butyl ether in
a molar ratio of 1:1 (in the form of a 1 molar solution in dichloromethane) in the
presence of 24.5 mg of 2-phenyl-2-propanol (cumene) as an initiator within
120 minutes at a conversion of 100% to give a polyisobutene with a number-average
molecular weight M_n of 4220, a polydispersity (PDI) of 2.05 and a content of terminal
15 vinylidene double bonds of > 99 mol%.

Example 26: Polymerization of "raffinate 1" with $AlCl_3 \cdot Bu_2O$ and with cumene as an initiator

20 7.50 g of "raffinate 1", comprising 3.00 g (53 mmol) of pure isobutene, were
polymerized in 50 ml of dichloromethane at -60°C with 566.8 mg of the complex of
aluminum trichloride and di-n-butyl ether in a molar ratio of 1:1 (in the form of a 1 molar
solution in dichloromethane) in the presence of 24.5 mg of 2-phenyl-2-propanol
(cumene) as an initiator within 60 minutes at a conversion of 80% to give a
25 polyisobutene with a number-average molecular weight M_n of 4770, a polydispersity
(PDI) of 2.67 and a content of terminal vinylidene double bonds of 96 mol%.

Example 27: Polymerization of "raffinate 1" with $AlCl_3 \cdot Bu_2O$ without solvent and with water as an initiator

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69.25 g of "raffinate 1", comprising 27.7 g (494 mmol) of pure isobutene, were
polymerized in an autoclave with 6.54 g of the complex of aluminum trichloride and di-
n-butyl ether prepared *in situ* in a molar ratio of 1:1, in the presence of 0.43 g
(23.8 mmol) of water as an initiator without solvent at 0°C within 60 minutes at a
35 conversion of 76% to give a polyisobutene with a number-average molecular weight M_n
of 965, a polydispersity (PDI) of 2.86 and a content of terminal vinylidene double bonds
of 76 mol%.

Example 28: Polymerization of "raffinate 1" with $AlCl_3 \cdot Bu_2O$ without solvent and with
40 water as an initiator

72.75 g of "raffinate 1", comprising 29.1 g (519 mmol) of pure isobutene, were
polymerized in an autoclave with 6.79 g of the complex of aluminum trichloride and di-

n-butyl ether prepared *in situ* in a molar ratio of 1:1, in the presence of 0.46 g (25.4 mmol) of water as an initiator without solvent at +20°C within 60 minutes at a conversion of 69% to give a polyisobutene with a number-average molecular weight M_n of 800, a polydispersity (PDI) of 2.69 and a content of terminal vinylidene double bonds of 70 mol%.

Example 29: Polymerization of "raffinate 1" with $AlCl_3 \cdot Bu_2O$ without solvent and without initiator

56.75 g of "raffinate 1", comprising 22.7 g (405 mmol) of pure isobutene, were polymerized in an autoclave with 6.57 g of the complex of aluminum trichloride and di-n-butyl ether prepared *in situ* in a molar ratio of 1:1 without solvent at +20°C within 60 minutes at a conversion of 93% to give a polyisobutene with a number-average molecular weight M_n of 1000, a polydispersity (PDI) of 2.90 and a content of terminal vinylidene double bonds of 76 mol%.

Example 30: Polymerization of "raffinate 1" with $AlCl_3 \cdot Bu_2O$ without solvent and without initiator

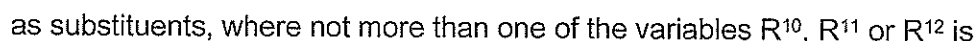
62.25 g of "raffinate 1", comprising 24.9 g (444 mmol) of pure isobutene, were polymerized in an autoclave with 6.56 g of the complex of aluminum trichloride and di-n-butyl ether prepared *in situ* in a molar ratio of 1:1 without solvent at 0°C within 60 minutes at a conversion of 88% to give a polyisobutene with a number-average molecular weight M_n of 1375, a polydispersity (PDI) of 2.94 and a content of terminal vinylidene double bonds of 69 mol%.

Claims

1. A process for preparing high-reactivity isobutene homo- or copolymers with a content of terminal vinylidene double bonds per polyisobutene chain end of at least 50 mol%, which comprises polymerizing isobutene or an isobutene-comprising monomer mixture in the presence of an aluminum trihalide-donor complex effective as a polymerization catalyst or of an alkylaluminum halide-donor complex, said complex comprising, as the donor, an organic compound with at least one ether function or a carboxylic ester function.
2. The process according to claim 1, wherein isobutene or an isobutene-comprising monomer mixture is polymerized in the presence of an aluminum trichloride-donor complex effective as a polymerization catalyst.
3. The process according to claim 1 or 2, wherein an aluminum trihalide-donor complex or an alkylaluminum halide-donor complex comprising, as the donor, a dihydrocarbyl ether of the general formula R^1-O-R^2 in which the variables R^1 and R^2 are each independently C_1 - to C_{20} -alkyl radicals, C_5 - to C_8 -cycloalkyl radicals, C_6 - to C_{20} -aryl radicals or C_7 - to C_{20} -arylalkyl radicals is used.
4. The process according to claim 1 or 2, wherein an aluminum trihalide-donor complex or an alkylaluminum halide-donor complex comprising, as the donor, a hydrocarbyl carboxylate of the general formula R^3-COOR^4 in which the variables R^3 and R^4 are each independently C_1 - to C_{20} -alkyl radicals, C_5 - to C_8 -cycloalkyl radicals, C_6 - to C_{20} -aryl radicals or C_7 - to C_{20} -arylalkyl radicals is used.
5. The process according to claims 1 to 4, wherein an aluminum trihalide-donor complex or an alkylaluminum halide-donor complex is used, in which the donor compound has a total carbon number of 3 to 16.
6. The process according to claims 1 to 5, wherein the polymerization is performed with additional use of a mono- or polyfunctional initiator which is selected from organic hydroxyl compounds in which one or more hydroxyl groups are each bonded to an sp^3 -hybridized carbon atom, organic halogen compounds in which one or more halogen atoms are each bonded to an sp^3 -hybridized carbon atom and water.
7. The process according to claim 6, wherein the initiator is selected from water, methanol, ethanol, 1-phenylethanol, 1-(p-methoxyphenyl)ethanol, n-propanol, isopropanol, 2-phenyl-2-propanol, n-butanol, isobutanol, sec.-butanol, tert-butanol, 1-phenyl-1-chloroethane, 2-phenyl-2-chloropropane, tert-butyl chloride and 1,3- or 1,4-bis(1-hydroxy-1-methylethyl)benzene.



R¹⁰, R¹¹ and R¹² are each independently hydrogen, C₁- to C₂₀-alkyl, C₅- to C₈-cycloalkyl, C₆- to C₂₀-aryl, C₇- to C₂₀-alkylaryl or phenyl, where any aromatic ring may also bear one or more C₁- to C₄-alkyl- or C₁- to C₄-alkoxy radicals or moieties of the general formula II



hydrogen and at least one of the variables R^{10} , R^{11} or R^{12} is phenyl which may also bear one or more C_1 - to C_4 -alkyl- or C_1 - to C_4 -alkoxy radicals or moieties of the general formula II as substituents, and

- 5 n is a number from 9 to 4500.