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 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% "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 and an aluminum trichloride/di-n-butyl ether complex for polymerization of styrene. 2-Phenyl-2-propanol acts as an initiator for the polymerization but does not significantly form alkoxyaluminum compounds. The polydispersities M_w/M_n of the styrene polymers thus prepared are "~2.5" (see summary) or "~3" (see page 230).

WO 11/101281 disclose the preparation of highly reactive polyisobutene polymers by polymerizing a monomer mixture containing isobutene in the presence of an aluminum trihalogenide donor complex acting as a polymerization catalyst. The donor complex comprises an organic compound having at least one ether function or a carboxylic acid function as the donor.

However, a disadvantage of $AlCl_3$ is its low solubility in organic aprotic solvents which requires the use of halogenated solvents such as methylene chloride or chloroform as solvent. Therefore, a catalyst is needed with improved solubility in organich solvents, especially halide-free solvents such as toluene or alkanes, such as pentane-, hexane- or heptane-isomers.

Dmitriy I. Shiman, Irina V. Vasilenko, Sergei V. Kostjuk, Journal of Polymer Science, Part A: Polymer Chemistry 2014, 52, 2386–2393 disclose the preparation of polyisobutene polymers by polymerizing isobutene in the presence of an alkylaluminum halogenide an ether complex as a polymerization catalyst.

Unpublished International Application PCT/EP2017/053098, filed February 13, 2017, discloses the preparation of highly reactive polyisobutene polymers with narrow polydispersity by polymerizing a monomer mixture containing isobutene in the presence of a alkylaluminum halide-donor complex, said complex comprising, as the donor, a mixture of at least two organic compounds with at least one ether function each.

It was an object of the present disclosure to provide a process for preparing high-reactivity isobutene homo- or copolymers with an increased content of terminal vinylidene double bonds per polyisobutene chain end of at least 70 mol% and simultaneously with a narrow molecular weight distribution (i.e. low polydispersities) in acceptable yields without the necessity to use mixtures

of different donors. 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.

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 70, preferably at least 75 and very preferably at least 80 mol%, which comprises polymerizing isobutene or an isobutene-comprising monomer mixture in the presence of a hydrocarbyloxy aluminum compound $Al(OR^a)_p(R^b)_qX_r$, or mixtures thereof,

wherein

R^a and R^b independently of another represent an organic residue of up to 20 carbon atoms, preferably C_1- to C_{20}-alkyl, C_5- to C_8-cycloalkyl radical, C_6- to C_{20}-aryl radical or C_7- to C_{20}-arylalkyl radical,
X independently of another represents halide,
p independently of another represents a rational number of greater than 0 (zero) and less than 3,
q independently of another represents a rational number of at least 0 (zero) and less than 3, and
r independently of another represents a rational number of at least 0 (zero) and less than 3,

with the proviso that the sum of (p + q + r) is always 3,

effective as a polymerization catalyst, optionally in the presence of at least one donor compound.

Therefore, in an aspect, there is provided 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 70, preferably at least 75 and very preferably at least 80 mol%, which comprises polymerizing isobutene or an isobutene-comprising monomer mixture in the presence of a hydrocarbyloxy aluminum compound $Al(OR^a)_p(R^b)_qX_r$, or mixtures thereof,

wherein

R^a and R^b independently of another represent an organic residue of up to 20 carbon atoms, preferably C_1- to C_{20}-alkyl, C_5- to C_8-cycloalkyl radical, C_6- to C_{20}-aryl radical or C_7- to C_{20}-arylalkyl radical,
X independently of another represents halide,
p independently of another represents a rational number of greater than 0 (zero) and less than 3,
q independently of another represents a rational number of at least 0 (zero) and less than 3, and
r independently of another represents a rational number of at least 0 (zero) and less than 3,

with the proviso that the sum of (p + q + r) is always 3,

effective as a polymerization catalyst, in the presence of at least one donor compound.

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 less than 2 mol%, preferably less than 1 mol%, very preferably less than 0.7 mol% and especially less than 0.5 mol% of copolymerized monomers other than isobutene, for example isoprene or linear butenes, preferably 1-butene, cis-2-butene, and trans-2-butene.

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

A C_1- to C_8-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-dimethyl-propyl, 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-

Claims

1. Process for preparing high-reactivity isobutene homo- or copolymers with a content of terminal vinylidene double bonds per polyisobutene chain end of at least 70, preferably at least 75 and very preferably at least 80 mol%, which comprises polymerizing isobutene or an isobutene-comprising monomer mixture in the presence of a hydrocarbyloxy aluminum compound $Al(OR^a)_p(R^b)_qX_r$, or mixtures thereof,

   wherein

   R^a and R^b independently of another represent an organic residue of up to 20 carbon atoms, preferably C_1- to C_{20}-alkyl, C_5- to C_8-cycloalkyl radical, C_6- to C_{20}-aryl radical or C_7- to C_{20}-arylalkyl radical,
   X independently of another represents halide,
   p independently of another represents a rational number of greater than 0 (zero) and less than 3,
   q independently of another represents a rational number of at least 0 (zero) and less than 3, and
   r independently of another represents a rational number of at least 0 (zero) and less than 3,

   with the proviso that the sum of (p + q + r) is always 3,

   effective as a polymerization catalyst, in the presence of at least one donor compound.

2. Process according to Claim 1, wherein R^a is a C_1- to C_4-alkyl radical.

3. Process according to Claim 1 or 2, wherein R^b is a C_1- to C_4-alkyl radical.

4. Process according to any of the preceding claims, wherein X is selected from the group consisting of chloride and bromide.

5. Process according to any of the preceding claims, wherein the at least one donor compound is selected from the group consisting of ethers, hydrocarbyl carboxylates, ethers, alcohols, aldehyde, ketones, and phenols.

6. Process according to Claim 6, wherein the donor is at least one 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, preferably C_1- to C_8 alkyl radicals especially C_1- to C_4 alkyl radicals, C_1- to C_8 haloalkyl radicals, C_5- to C_8-cycloalkyl radicals, preferably C_5- to C_6-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.

7. Process according to Claim 6, wherein the donor is at least one 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, 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.

8. The process according to any of the preceeding claims, 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.

9. The process according to Claim 8, 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.

10. The process according to Claim 8 or 9, wherein 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 from 0.0005:1 to 0.1:1, or when water is used as the sole initiator or in 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 from 0.0001:1 to 0.1:1.

11. The process according to any of the preceding claims, wherein the polymerization is performed at a temperature of -90°C to +30°C.

12. The process according to any of the preceding claims, wherein the polymerization is performed in a halogen-free solvent.

13. The process according to any of the preceding claims, wherein the hydrocarbyloxy aluminum compound is free of any additional Brønsted acids, preferably free of any hydrogen halide acids.