polymerizing isobutene in the presence of an alkylaluminum halogenide an ether complex as a polymerization catalyst.

WO 18/015306 discloses a process for preparing high-reactivity isobutene homo- or copolymers in which certain Lewis Acids are used together with at least one donor and at least one ionic liquid.

Examples for such ionic liquids disclosed in WO 18/015306 are *inter alia* phosphor-containing compounds in which the cation is a permanent quaternary phosphonium salt.

It is, however, a disadvantage of such ionic liquids that they are expensive to prepare and dramatically attenuate the reactivity of the Lewis Acid used.

In Kostjuk et al., Polym. Chem., 2016, 7, 5615 – 5619 and Polymer, 145 (2018) 382-390 it is further pointed out that ionic liquids as catalyst for isobutene polymerization require quite long reaction time in order to achieve medium to high conversion of the monomers. Figure 2 shows a diagram taken from the latter document in which conversion of isobutene and exo-selectivity of the reaction in the presence of [emim]Cl–$AlCl_3$ (1), [emim]Cl-$FeCl_3$ (2), and [emim]Cl-$GaCl_3$ (3) are shown vs the reaction time.

CN 102399308 A (machine translation) discloses a cationic polymerization in emulsion of isobutene as monomer using aluminium trichloride and triphenyl phosphinoxide as catalyst. Sorbitol monooleate is used as an emulsifier in the polymerization mixture.

No information on double bond content is given, only polyisobutene with a high molecular weight of 240,000 is obtained.

It was an object of the present ~~invention~~disclosure to provide a process for preparing high-reactivity isobutene homo- or copolymers with an increased content of terminal vinylidene double bonds (α-double bonds) as well as β-double bonds per polyisobutene chain end of at least 60 mol% in acceptable yields and high reaction rates. The catalyst system should at the same time have sufficient activity and service life, the preparation thereof should be easy. It was further an object of the present ~~invention~~ disclosure to develop a catalyst system which leads to high conversion and keeps the selectivity of the reactive double bonds, especially the α-double bonds even at high conversion.

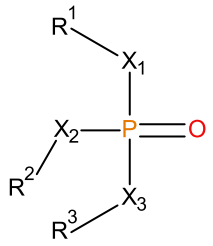
The object was achieved by a process for preparing high-reactivity isobutene homo- or copolymers with a content of α-double bonds and β-double bonds (in sum) per polyisobutene chain end of at least 60, preferably at least 70 and very preferably at least 75 mol%, which comprises polymerizing isobutene or an isobutene-comprising monomer mixture in the presence of at least one Lewis Acid effective as a polymerization catalyst, selected from the group consisting of an aluminum trihalide-donor complex, an alkylaluminum halide-donor complex, an iron trihalide-donor complex, a gallium trihalide-donor complex, a titanium tetrahalide-donor complex, a zinc

aromatic ring which may be interrupted by one or more oxygen and/or sulphur atoms and/or one or more substituted or unsubstituted imino groups, where the radicals mentioned may each be substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocyclesSince the complex formed from the at least one Lewis Acid and the at least one phosphorus-containing compound of formula (I) or (Ia) or (Ib) is liquid under these conditions it is also referred to as "Liquid Coordination Complex" or "LCC".

J. M. Hogg, L. C. Brown, K. Matuszek, P. Latos, A. Chrobok and M. Swadźba-Kwaśny, Dalton Transaction, 2017, 46, 11561 report the successful synthesis and liquid state at the room temperature for complexes formed from tri-n-octylphosphine oxide with $AlCl_3$ respectively $TiCl_4$. However, only Diels-Alder reactions of these complexes are disclosed, polymerization of isobutene is not rendered obvious.

In an aspect, there is provided a bulk- or solution polymerisation process for preparing high-reactivity isobutene homo- or copolymers with a number-average molecular weight M_n (determined by gel permeation chromatography) of preferably of 500 to 100 000 and a content of α-double bonds and β-double bonds (in sum) per polyisobutene chain end of at least 60 mol%, which comprises polymerizing isobutene or an isobutene-comprising monomer mixture in the presence of at least one Lewis Acid effective as a polymerization catalyst, selected from the group consisting of an aluminum trihalide-donor complex, an alkylaluminum halide-donor complex, an iron trihalide-donor complex, a gallium trihalide-donor complex, a titanium tetrahalide-donor complex, a zinc dihalide-donor complex, a tin dihalide-donor complex, a tin tetrahalide-donor complex, and a boron trihalide-donor complex, said complex comprising, as the donor, a mixture of

- at least one organic compound (II) comprising at least one oxygen or nitrogen atom with at least one lone electron pair, preferably comprising at least one oxygen atom with at least one lone electron pair, very preferably 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, and
- at least one phosphorus-containing compound of formula (I)



or formula (Ia)

$P(OR^1)(OR^2)(OR^3)$

or formula (Ib)

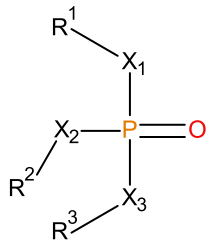
$P(OR^1)(OR^2)(OR^3)(OR^4)(OR^5)$

in which

X_1, X_2, and X_3 independently of another are oxygen, sulphur or a single bond, preferably oxygen or a single bond, and very preferably a single bond, and
R^1, R^2, R^3, R^4, and R^5 independently of another are an organic residue with up to 20 carbon atoms,
with the proviso that the complex formed from the at least one Lewis Acid and the at least one phosphorus-containing compound of formula (I) or (Ia) or (Ib) has a melting point of not more than 60 °C, preferably not more than 40 °C, and especially not more than 20 °C.

In another aspect, there is provided iron trihalide-donor complexes consisting of at least one iron trihalide,

- optionally at least one organic compound (II) comprising at least one oxygen or nitrogen atom with at least one lone electron pair, preferably comprising at least one oxygen atom with at least one lone electron pair, very preferably 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, and
- at least one phosphorus-containing compound of formula (I)



or formula (Ia)

$P(OR^1)(OR^2)(OR^3)$

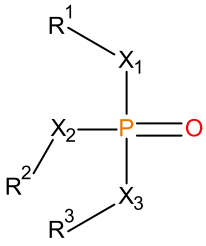
or formula (Ib)

$P(OR^1)(OR^2)(OR^3)(OR^4)(OR^5)$

in which

X_1, X_2, and X_3 independently of another are oxygen, sulphur or a single bond, preferably oxygen or a single bond, and very preferably a single bond, and
R^1, R^2, R^3, R^4, and R^5 independently of another are an organic residue with up to 20 carbon atoms,
wherein the complex formed from the at least one iron trihalide and the at least one phosphorus-containing compound of formula (I) or (Ia) or (Ib) have a melting point of not more than 60 °C.

In another aspect, there is provided boron trihalide-donor complexes consisting of at least one boron trihalide,
- optionally at least one organic compound (II) comprising at least one oxygen or nitrogen atom with at least one lone electron pair, preferably comprising at least one oxygen atom with at least one lone electron pair, very preferably 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, and
- at least one phosphorus-containing compound of formula (I)



or formula (Ia)

$P(OR^1)(OR^2)(OR^3)$

or formula (Ib)

$P(OR^1)(OR^2)(OR^3)(OR^4)(OR^5)$

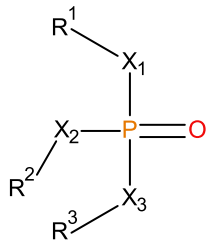
in which

X_1, X_2, and X_3 independently of another are oxygen, sulphur or a single bond, preferably oxygen

or a single bond, and very preferably a single bond, and
R^1, R^2, R^3, R^4, and R^5 independently of another are an organic residue with up to 20 carbon atoms,
wherein the complex formed from the at least one boron trihalide and the at least one phosphorus-containing compound of formula (I) or (Ia) or (Ib) have a melting point of not more than 60 °C.

In another aspect, there is provided a metal halide-donor complexes consisting of

- at least one metal halide, selected from the group consisting of aluminum trihalide, alkylaluminum halide, gallium trihalide, titanium tetrahalide, zinc dihalide, tin dihalide, tin tetrahalide, and boron trihalide,
- at least one organic compound (II) comprising at least one oxygen or nitrogen atom with at least one lone electron pair, preferably comprising at least one oxygen atom with at least one lone electron pair, very preferably 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, and
- at least one phosphorus-containing compound of formula (I)



or formula (Ia)

$P(OR^1)(OR^2)(OR^3)$

or formula (Ib)

$P(OR^1)(OR^2)(OR^3)(OR^4)(OR^5)$

in which

X_1, X_2, and X_3 independently of another are oxygen, sulphur or a single bond, preferably oxygen or a single bond, and very preferably a single bond, and
R^1, R^2, R^3, R^4, and R^5 independently of another are an organic residue with up to 20 carbon atoms.

In these definitions

C_1–C_{20}-alkyl which may be substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocycles is, for example, methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, pentyl, hexyl, heptyl, octyl, 2-ethylhexyl, 2,4,4-trimethylpentyl, decyl, dodecyl, tetradecyl, heptadecyl, octadecyl, eicosyl, 1,1-dimethylpropyl, 1,1-dimethylbutyl, 1,1,3,3-tetramethylbutyl, benzyl, 1-phenylethyl, 2-phenylethyl, α,α-dimethylbenzyl, benzhydryl, p-tolylmethyl,1-(p-butylphenyl)ethyl, p-chlorobenzyl, 2,4-dichlorobenzyl, p-methoxybenzyl, m-ethoxybenzyl, 2-cyanoethyl, 2-cyanopropyl, 2-methoxycarbonylethyl, 2-ethoxycarbonylethyl, 2-butoxycarbonylpropyl, 1,2-di-(methoxycarbonyl)ethyl, 2-methoxyethyl, 2-ethoxyethyl, 2-butoxyethyl, diethoxymethyl, diethoxyethyl, 1,3-dioxolan-2-yl, 1,3-dioxan-2-yl, 2-methyl-1,3-dioxolan-2-yl, 4-methyl-1,3-dioxolan-2-yl, 2-isopropoxyethyl, 2-butoxypropyl, 2-octyloxyethyl, chloromethyl, 2-chloroethyl, trichloromethyl, trifluoromethyl, 1,1-dimethyl-2-chloroethyl, 2-methoxyisopropyl, 2-ethoxyethyl, butylthiomethyl, 2-dodecylthioethyl, 2-phenylthioethyl, 2,2,2-trifluoroethyl, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 4-hydroxybutyl, 6-hydroxyhexyl, 2-aminoethyl, 2-aminopropyl, 3-aminopropyl, 4-aminobutyl, 6-aminohexyl, 2-methylaminoethyl, 2-methylaminopropyl, 3-methylaminopropyl, 4-methylaminobutyl, 6-methylaminohexyl, 2-dimethyl-aminoethyl, 2-dimethylaminopropyl, 3-dimethylaminopropyl, 4-dimethylaminobutyl, 6-dimethylaminohexyl, 2-hydroxy-2,2-dimethylethyl, 2-phenoxyethyl, 2-phenoxypropyl, 3-phenoxypropyl, 4-phenoxybutyl, 6-phenoxyhexyl, 2-methoxyethyl, 2-methoxypropyl, 3-methoxypropyl, 4-methoxybutyl, 6-methoxyhexyl, 2-ethoxyethyl, 2-ethoxypropyl, 3-ethoxypropyl, 4-ethoxybutyl or 6-ethoxyhexyl, and

C_2–C_{20}-alkyl interrupted by one or more oxygen and/or sulphur atoms and/or one or more substituted or unsubstituted imino groups is, for example, 5-hydroxy-3-oxa-pentyl, 8-hydroxy-3,6-dioxaoctyl, 11-hydroxy-3,6,9-trioxaundecyl, 7-hydroxy-4-oxaheptyl, 11-hydroxy-4,8-dioxaundecyl, 15-hydroxy-4,8,12-trioxapentadecyl, 9-hydroxy-5-oxanonyl, 14-hydroxy-5,10-oxatetradecyl, 5-methoxy-3-oxapentyl, 8-methoxy-3,6-dioxaoctyl, 11-methoxy-3,6,9-trioxaundecyl, 7-methoxy-4-oxaheptyl, 11-methoxy-4,8-dioxa-undecyl, 15-methoxy-4,8,12-trioxapentadecyl, 9-methoxy-5-oxanonyl, 14-methoxy-5,10-oxatetradecyl, 5-ethoxy-3-oxapentyl, 8-ethoxy-3,6-dioxaoctyl, 11-