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Preparation of highly reactive polyisobutenes

The present invention relates to a process for the preparation of
5 highly reactive polyisobutenes.

The highly reactive polyisobutenes discussed are those which have
a high content of, preferably, more than 60 mol % of terminal
vinylidene groups. Highly reactive polyisobutenes are desirable
10 intermediates for the production of additives for lubricants and
fuels.

Such highly reactive polyisobutenes are obtainable, for example,
by the process of EP 0 628 575, by cationic polymerization of
15 isobutene in the liquid phase with the aid of boron trifluoride
and a secondary alcohol at from 0 to -60°C.

The prior Patent Applications DE 199 48 947.5, DE 199 52 031.3,
DE 199 52 030.5, DE 100 28 585.6 and DE 100 35 298.7 relate to
20 improvements or advantageous embodiments of such a process.

After reaching the desired molecular weight, the polymerization
catalyst is deactivated and the polymerization is stopped in this
manner. EP 0 628 575 recommends for this purpose passing the
25 reaction discharge into a medium, such as water, an alcohol,
acetonitrile, ammonia or an aqueous solution of a mineral base,
such as an alkali metal or alkaline earth metal hydroxide
solution or a solution of a carbonate of one of these metals.

30 For the preparation of highly reactive polyisobutenes, it is
critical that the polymerization catalyst is deactivated as
rapidly and quantitatively as possible after the desired
molecular weight has been reached, in order to prevent
isomerization reactions giving polyisobutene molecules in which
35 the double bond assumes a thermodynamically more favorable
position in the interior of the molecule.

Organic chain-terminating agents, such as acetonitrile and
alcohols, have the advantage that they are miscible with the
40 organic reaction phase and can therefore be readily and uniformly
distributed in said phase. However, they have the disadvantage
that their affinity to the BF_3 molecule is comparatively low and
they therefore lead only to gradual catalyst deactivation. Since



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they can also act as phase mediators, they complicate the subsequent extraction with water for removal of the catalyst deactivation products.

5 Aqueous chain-terminating agents, in particular water itself, have the advantage that the catalyst deactivation and removal of the catalyst deactivation or hydrolysis products by extraction can take place simultaneously. The disadvantage however is that the aqueous phase is immiscible with the organic reaction phase
10 and the catalyst deactivation can take place only at the phase boundary. In continuous regions of the organic reaction phase, the polymerization reaction can still continue or undesired isomerizations can take place after the organic reaction phase has been brought into contact with an aqueous chain-terminating
15 agent.

JP-A 7196724 discloses a process for removing a Lewis acid catalyst, used for carrying out a cationic polymerization, from the organic reaction phase, in which the reaction phase is
20 treated with water or acidified water and separation into a polymer-containing organic phase and an aqueous phase containing the dissolved catalyst is effected. The water or acidified water is preferably preheated in order to promote the removal of the catalyst. The amount of water or acidified water is at least 5,
25 preferably at least 20, in particular at least 40, % by volume, based on the reaction phase. The preparation of highly reactive polyisobutenes is not discussed.

US 4,940,833 describes a process for working up a liquid
30 polymerization reaction mixture which contains olefin monomer, catalyst residues and catalyst deactivation products, in which the mixture is washed with water and the organic and aqueous phase are then separated. Oxygen-containing compounds, such as alcohols, dicarbonyl compounds and/or alkylene oxides, are
35 mentioned as preferred catalyst deactivators, methanol being most preferred.

It is an object of the present invention to provide a process for the preparation of highly reactive polyisobutenes which permits
40 rapid and substantially quantitative catalyst deactivation and simple extraction of the catalyst deactivation products.

We have found that this object is achieved, according to the invention, by a process for the preparation of highly reactive
45 polyisobutenes, in which

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- a) isobutene is polymerized in the presence of a complex of boron trifluoride and at least one cocatalyst in a liquid organic phase at a reaction temperature of from -60 to -4°C ,
- 5 b) the organic phase which is substantially at the reaction temperature is brought into intimate contact with a first portion of water whose temperature is at least 80°C , preferably at least 90°C , above the reaction temperature, with formation of an emulsion which contains finely dispersed
- 10 water droplets in the organic phase,
- c) a second portion of water is added to the emulsion with formation of a continuous, predominantly organic phase and a continuous, predominantly aqueous phase, and
- 15 d) the organic phase is separated from the aqueous phase.

The present invention is based on the finding that, for the substantially quantitative extraction of the boron trifluoride

20 cocatalyst complex or of the hydrolysis products thereof from the organic reaction phase, the amount of aqueous phase may not fall below a minimum amount, based on the organic reaction phase. If, however, the organic reaction phase and an amount of aqueous phase which corresponds to the required minimum amount or is

25 greater than this are brought into contact, it is found that the phases have a considerable tendency to phase separation with the formation of a continuous organic phase and a continuous aqueous phase. This situation makes it more difficult to disperse the aqueous phase finely in the organic reaction phase, which

30 dispersing is necessary for achieving rapid, quantitative and uniform catalyst deactivation. In an attempt to carry out the catalyst deactivation using a smaller amount of water, it was found that contact of the aqueous phase with the reaction phase, which has a temperature below the freezing point of water, can

35 result in the formation of ice crystals which lead to blockage of pipelines and/or valves and do not permit satisfactory catalyst deactivation.

The novel process avoids all of the problems described above. In

40 particular, it is surprising that no undesirable isomerization reactions occur when the reaction phase is brought into contact with the first portion of water whose temperature is at least 80°C above the reaction temperature.

45 Preferably, the sum of the first and second portions of water is from 5 to 100, in particular from 20 to 90, % by weight, based on the weight of the organic phase. The weight ratio of the first

portion to the second portion is preferably from 1:10 to 10:1, in particular from 1:5 to 5:1, particularly preferably from 1:5 to 1:1.5.

- 5 Preferably, the emulsion obtained by bringing the organic phase into contact with the first portion of water has a mixing temperature of from +5 to +50°C, in particular from +10 to +45°C.

- The first and/or second portions of water can contain dissolved
10 substances, such as mineral bases, e.g. alkali metal or alkaline earth metal hydroxides or carbonates, ammonia or acids, such as hydrochloric acid, etc. Since, however, no further advantage is generally associated therewith, the first and second portions of water preferably contain no significant amounts of dissolved
15 substances. Tap water or river water is suitable. In general, however, demineralized water is preferred. The pH of the first and second portions of water is in general from 6 to 10.

- The novel process is suitable for the preparation of
20 polyisobutenes having a number average molecular weight of from 500 to 5 000 and is particularly suitable for the preparation of polyisobutenes having a number average molecular weight of from 1 800 to 5 000. The polymerization in step a) of the novel process is therefore preferably carried out in such a way that
25 polyisobutene molecules having a weight average molecular weight of from 1 800 to 5 000 are obtained.

- At the time of being brought into contact with the first portion of water, the organic phase is substantially at the reaction
30 temperature, i.e. it is not significantly heated after reaching the desired degree of polymerization before the catalyst is deactivated by adding the first portion of water.

- The first portion of water is preferably added by means of a
35 nozzle into a pipeline through which the organic reaction phase is passed. The outlet orifice of the nozzle is preferably arranged in the direction of flow of the organic phase. The formation of the emulsion is assisted if the stream of the organic phase in the region of the addition of the first portion
40 of water has turbulent flow. Measures for generating turbulent flows are known to a person skilled in the art. The first portion of water typically has a temperature of from 80 to 160°C. Temperatures of more than 100°C necessitate keeping the water under a pressure which is higher than ambient pressure.

The addition of the second portion of water can likewise advantageously be effected via a nozzle into the stream of the emulsion obtained by bringing the organic phase into contact with the first portion of water. The nozzle for adding the second
5 portion of water is then arranged a distance downstream of the nozzle via which the first portion of water is added. A suitable spacing between the nozzles can readily be determined by a person skilled in the art by means of simple experiments. The optimum spacing is as a rule dependent on the flow rate of the organic
10 phase. As a rule, it is such that a time span of from 2 to 1 000, in particular from 2 to 200, seconds elapses from the bringing of a volume element of the organic phase into contact with the first portion of water to the addition of the second portion of water. The second portion of water typically has a temperature of from
15 40 to 80°C.

After the addition of the second portion of water, the mixture of organic phase and aqueous phase can be passed into a calming zone for separation of the two phases and separated. This is
20 expediently done in a horizontal, continuously operated phase separation vessel through which flow takes place with a low flow rate. Owing to the difference between the densities of the phases, the mixture of the organic phase and aqueous phase separates under the action of gravity so that the two phases are
25 present in continuous form and substantially free of foreign phases, as layers one on top of the other.

Whereas in general no problems at all are encountered when separating off the main amount of the aqueous phase, the organic
30 phase often also contains dispersed water droplets which do not coalesce spontaneously. Complete phase separation on the basis of the density difference requires a very long residence time, with the result that economical removal of the final amounts of aqueous phase is not possible. In order to remove the dispersed
35 droplets of the aqueous phase which are still present after the main amount of the aqueous phases has been separated off, the organic phase containing still dispersed water droplets is advantageously passed through an apparatus having coalescence-promoting internals, and the coalesced aqueous phase
40 is separated from the organic phase. The coalescence-promoting internals are as a rule packings, coalescence surfaces or fine-pored internals.

The internals having coalescence surfaces are generally plate
45 packets having corrugated or inclined surfaces on which dispersed droplets accumulate and initially form a film. If this film encloses the individual plate and is sufficiently thick, large

drops of the dispersed phase form at the plate edge and fall down. They then form a layer which can be readily separated off mechanically. In the case of fine-pored internals, the inner structure of the internals forces the finely dispersed drops to
5 come into contact with the internal surface, which drops then form a film and leave the hollow structure of the fine-pored internals in the form of combined larger drops.

Suitable packings are the packings usually used in distillation.
10 Preferably, the organic phase containing dispersed droplets of the aqueous phase is passed through a bed of packings. Wetting of the large surface of the packing results in surface coalescence and simultaneously, as a result of drop movement, in drop-drop coalescence.

15 Coalescing filters in the form of filter cartridges which consist, for example, of polypropylene have proven particularly useful.

20 It has proven advantageous to mix the organic phase freed from the main amount of the aqueous phase with a third portion of water before the passage through the apparatus having coalescence-promoting internals. The third portion of water is, for example, from 0.5 to 10, in particular from 2 to 7, % by
25 weight, based on the organic phase. The temperature of the third portion is not critical and is usually from 20 to 60°C.

The polymerization of isobutene can be carried out continuously or batchwise but is preferably effected continuously. Processes
30 for continuous polymerization in the presence of a complex of boron trifluoride and at least one cocatalyst in a liquid organic phase are known per se. In a continuous process, a part of the reaction mixture formed in the polymerization reactor is discharged continuously. An amount of starting materials, in this
35 case isobutene or isobutene-containing feed, which correspond to the discharge is fed continuously to the polymerization reactor. The ratio of the amount of substances present in the polymerization reactor to the amount which is discharged is determined by the circulation/feed ratio which, in the case of
40 the continuous polymerization of isobutene to polyisobutene, is as a rule from 1 000:1 to 1:1, preferably from 500:1 to 5:1, in particular from 50:1 to 200:1. The average residence time of the isobutene to be polymerized in the polymerization reactor may be from five seconds to several hours. Residence times of from 1 to
45 30, in particular from 2 to 20, minutes are particularly preferred.

The polymerization of the isobutene is carried out in the conventional reactors, such as stirred kettles, tubular reactors, tube-bundle reactors and loop reactors, loop reactors, i.e. tubular reactors or tube-bundle reactors having the
5 characteristics of a stirred kettle, being preferred. Tubular reactors having tube cross-sections which lead to turbulence in segments are particularly advantageous.

The polymerization is carried out at a reaction temperature of
10 from -60 to -4°C, in particular from -25 to -5°C. The heat of polymerization is removed appropriately with the aid of a cooling apparatus. This may be operated, for example, with liquid ammonia as a coolant. Another possibility for removing the heat of polymerization is evaporative cooling. Here, the heat liberated
15 is removed by partial evaporation of the reaction mixture, for example of the isobutene and/or other readily volatile components of the isobutene feed or of a readily volatile diluent. Isothermal conditions are preferably employed, i.e. the temperature of the liquid organic reaction phase in the
20 polymerization reactor has a constant value and changes only slightly, if at all, during the operation of the reactor.

The concentration of the isobutene in the liquid reaction phase is as a rule from 0.2 to 50, preferably from 0.5 to 20, % by
25 weight, based on the liquid organic phase.

Suitable starting materials are both isobutene itself and isobutene-containing C₄-hydrocarbon streams, for example refined C₄ fractions, C₄ cuts from the dehydrogenation of isobutane and C₄
30 cuts from steam crackers or FCC crackers (fluid catalysed cracking), provided that they have been substantially freed from 1,3-butadiene contained therein. Suitable C₄-hydrocarbon streams contain, as a rule, less than 500 ppm, preferably less than 200 ppm, of butadiene. The presence of 1-butene and cis- and
35 trans-2-butene is substantially uncritical. The isobutene concentration in the C₄-hydrocarbon streams is typically from 40 to 60% by weight. When C₄ cuts are used as starting material, the hydrocarbons other than isobutene play the role of an inert diluent, as explained below. The isobutene-containing feed may
40 contain small amounts of contaminants, such as water, carboxylic acids or mineral acids, without there being any critical decreases in yield or selectivity. It is expedient to avoid an enrichment of these impurities by removing such pollutants from the isobutene-containing feed, for example by adsorption onto
45 solid adsorbents, such as active carbon, molecular sieves or ion exchangers.

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Owing to the high viscosity of polyisobutene, it is advantageous to carry out the polymerization 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 is to be observed during the polymerization reaction, to such an extent that removal of the resulting heat of reaction can be ensured. Suitable diluents are those solvents or solvent mixtures which are inert to the reagents used. Suitable diluents are, for example, saturated hydrocarbons, such as butane, pentane, hexane, heptane or octane, e.g. n-hexane, isooctane or cyclopentane, halogenated hydrocarbons, such as methyl chloride, dichloromethane or trichloromethane, and mixtures of the abovementioned diluents, among which n-hexane is particularly preferred. Before they are used, the diluents are preferably freed from impurities, such as water, carboxylic acids or mineral acids, for example by adsorption onto solid adsorbents, such as active carbon, molecular sieves or ion exchangers.

Boron trifluoride is expediently used in the form of gaseous boron trifluoride, it being possible to use technical-grade boron trifluoride still containing small amounts of sulfur dioxide and SF₄, but highly pure boron trifluoride having a purity of about 99.5% by weight is preferably used.

Suitable cocatalysts are as a rule oxygen-containing compounds which preferably contain at least one divalent oxygen atom. Suitable oxygen-containing compounds in addition to water are organic compounds of up to 30 carbon atoms. Examples of these are C₁-C₃₀-alkanols, C₁-C₃₀-cycloalkanols, C₂-C₁₀-diols, C₁-C₂₀-carboxylic acids, C₄-C₁₂-carboxylic anhydrides and C₂-C₂₀-dialkyl ethers. Preferred among these are monohydric alkanols of 1 to 20, in particular 1 to 4, carbon atoms, which, if required, can be used together with the C₁-C₂₀-dialkyl ethers. Particularly preferred cocatalysts are monohydric secondary C₃-C₂₀-alkanols. Examples are isopropanol, 2-butanol, sec-pentanol, sec-hexanol, sec-heptanol, sec-octanol and the like. 2-Butanol and in particular isopropanol are particularly preferably used.

The molar ratio of boron trifluoride to cocatalyst is preferably from 1:1 to 1:10, in particular from 1:1.1 to 1:5, particularly preferably from 1:1.2 to 1:2.5.

The concentration of the complex of boron trifluoride and cocatalyst in the reactor is as a rule from 0.01 to 1, in particular from 0.02 to 0.7, particularly preferably from 0.03 to 0.5, % by weight, based on the liquid organic phase.

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After the desired degree of polymerization has been reached, a first portion of water is added, as described, to the organic phase which is substantially at the reaction temperature, and a second portion of water is then added to the emulsion obtained.

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The isobutene polymer contains, as a rule, more than 60, in particular more than 80, mol % of terminal vinylidene groups. The dispersity M_w/M_n is preferably not more than 1.8, in particular not more than 1.6.

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The working-up of the organic phase freed from the aqueous phase, for isolation of the desired polyisobutene, is carried out in a conventional manner. The polyisobutene is freed, as a rule by distillation, from unconverted isobutene, inert diluent and any

20 isobutene oligomers and is obtained as a distillation residue, for example as a bottom product of a distillation column.

The examples and comparative examples which follow illustrate the invention.

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Examples

For the preparation of a polyisobutene, the procedure according to EP-A 628 575, example 1, was followed: The

30 isobutene-containing feed used corresponded to the following composition:

Isobutane	< 1% by weight
n-Butane	< 1% by weight
35 1-Butene	< 1% by weight
trans-2-butene	< 1% by weight
cis-2-butene	< 1% by weight
Isobutene	about 45% by weight
Hexane	about 54% by weight
40 Butadiene	< 50 ppm
Water	about 2 ppm

In the course of one hour, 6 000 g of the above feed was fed to the suction side of a loop reactor which was equipped with an
45 integrated circulation pump whose tube diameter was 30 mm and whose volume was 1 000 ml. 1.6 times the molar amount, based on the boron trichloride (7.1 mmol/l), of isopropanol was added. The

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reactor was cooled so that the temperature in the reaction medium was -17°C . The average residence time of the reaction medium in the reactor was 6.6 minutes.

- 5 Thereafter, the reaction discharge was first mixed, with the aid of a nozzle, continuously and thoroughly with X g per hour of water at 90°C and thus brought to a temperature of $A^{\circ}\text{C}$. An average temperature of the reaction discharge/water mixture of $B^{\circ}\text{C}$ was then reached in the reaction discharge/water mixture after about
10 12 hours by continuous addition of a further amount of Y g per hour of water at 60°C .

- In a continuous 500 ml phase separation vessel, the aqueous phase was then separated from the organic phase and a third portion of
15 water amounting to Z g per hour and having a temperature of 40°C was added continuously to the latter, once again by means of a nozzle.

- The mixture thus obtained was passed continuously through a
20 100 ml cartridge filter and a further 500 ml phase separation vessel, in which aqueous and organic phases were once again separated.

- After the cartridge filter and the final phase separation
25 described, the organic phase was completely clear.

Analyses of the reaction discharge treated in this manner were carried out for assessing the separation of fluorine from the reaction discharge.

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Furthermore, those analytical data of the polyisobutene obtained after removal of the volatile components by distillation which are relevant for assessing the product quality were determined and are listed below in the form of a table.

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Table

Ex.	A $^{\circ}\text{C}$	B $^{\circ}\text{C}$	X g/h	Y g/h	Z g/h	F ppm	Mn	D	Vin. %
40 1	4	32	700	1700	0	38	2236	1.766	86.2
2	4	35	700	1900	0	37	2229	1.763	86.5
3	6	38	800	1900	0	34	2270	1.756	85.9
4	4	32	700	1700	50	26	2287	1.759	86.3
5	4	32	700	1700	100	21	2281	1.773	86.9
45 6	4	32	700	1700	150	17	2278	1.698	87.1

5	Comp. Ex.									
	7	4	4	2600 ¹⁾	0	0	121 ⁶⁾	2132	1.811	69.2
	8	-17	32	0	2600 ²⁾	0	42	2118	1.809	82.3
	9	5)	32	700 ³⁾	1900 ⁴⁾	0	-	-	-	-

where

- 10 A = Temperature of the reaction discharge/water mixture after the first addition of water
 B = Temperature of the reaction discharge/water mixture after the second addition of water
 X = Amount of first addition of water
 15 Y = Amount of second addition of water
 Z = Amount of third addition of water
 Mn = Number average molecular weight
 D = Dispersity
 Vin. = Vinylidene content
 20 1) 2600 g/h of water at 23°C
 2) 2600 g/h of water at 54°C
 3) 700 g/h of water at 50°C
 4) 1900 g/h of water at 65°C
 5) The pipe between the first and second water metering became
 25 blocked with ice in the course of 4 hours. The plant could not be further operated at these feed rates and temperatures.
 6) Substantial turbidity detectable in the organic phase.

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We claim:-

1. A process for the preparation of highly reactive polyisobutenes, in which
 - a) isobutene is polymerized in the presence of a complex of boron trifluoride and at least one cocatalyst in a liquid organic phase at a reaction temperature of from -60 to -4°C,
 - b) the organic phase which is substantially at the reaction temperature is brought into intimate contact with a first portion of water whose temperature is at least 80°C above the reaction temperature, with formation of an emulsion which contains finely dispersed water droplets in the organic phase,
 - c) a second portion of water is added to the emulsion with formation of a continuous, predominantly organic phase and a continuous, predominantly aqueous phase, and
 - d) the organic phase is separated from the aqueous phase.
2. A process as claimed in claim 1, in which the sum of the first and second portions of water is from 5 to 100% by weight, based on the weight of the organic phase, and the weight ratio of the first portion to the second portion is from 1:10 to 10:1.
3. A process as claimed in claim 1 or 2, in which the emulsion obtained by bringing the organic phase into contact with the first portion of water has a mixing temperature of from +5 to +50°C.
4. A process as claimed in any of the preceding claims, in which the cocatalyst used is a secondary alcohol of 3 to 20 carbon atoms.
5. A process as claimed in any of the preceding claims, in which polymerization is effected in step a) until polyisobutene molecules having a number average molecular weight of from 1 800 to 5 000 are obtained.
6. A process as claimed in any of the preceding claims, in which, in order to separate the organic phase from the aqueous phase, first the main amount of the aqueous phase is

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removed, the organic phase containing still dispersed water droplets is passed through an apparatus having coalescence-promoting internals and the coalesced aqueous phase is separated from the organic phase.

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7. A process as claimed in claim 6, in which the organic phase freed from the main amount of the aqueous phase is mixed with a third portion of water before the passage through the apparatus having coalescence-promoting internals.

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8. A process as claimed in claim 7, in which the third portion of water is from 0.5 to 10% by weight, based on the organic phase.

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