

Preparation of highly reactive polyisobutenes

The present invention relates to a process for preparing highly reactive polyisobutenes having a terminal vinylidene group content of more than 80 mol% and an average molecular weight of from 500 to 5000 dalton by cationic polymerization of isobutene in the liquid phase in the presence of boron trifluoride complexes at from +40°C to -60°C.

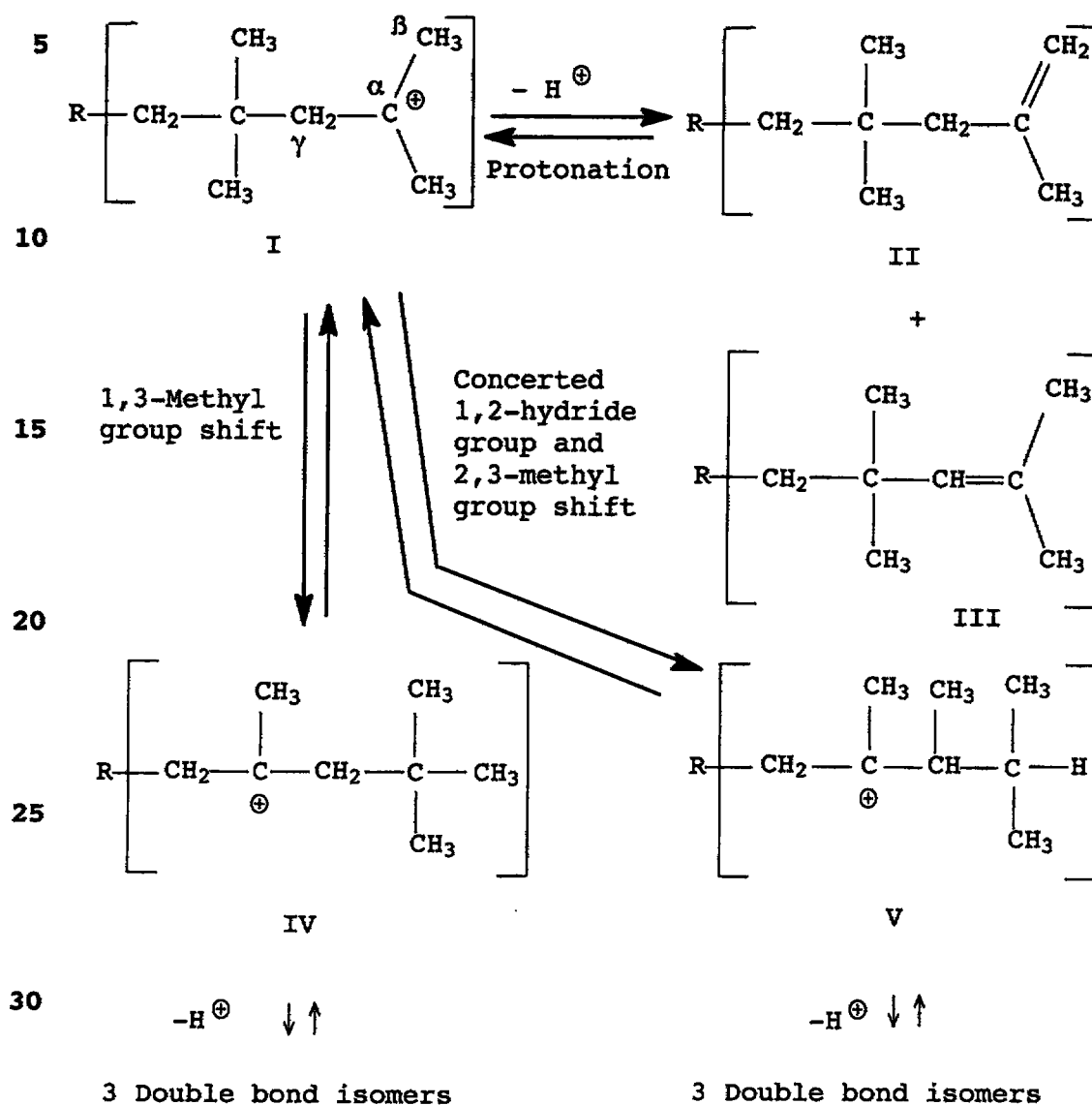
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High molecular weight polyisobutenes having molecular weights of up to several 100,000 dalton have long been known and their preparation is described, for example, in H. Güterbock: Polyisobutylen und Mischpolymerisate, pages 77 to 104, Springer, Berlin 1959. The currently available polyisobutenes having molecular weights of from 500 to 5000 dalton are prepared with the aid of Lewis acid catalysts, such as aluminum chloride, alkylaluminum chlorides or boron trifluoride, and generally have a terminal double bond (vinylidene group) content of less than 10 mol% and a molecular weight distribution (dispersity) between 2 and 5.

A distinction must be made between these conventional polyisobutenes and the highly reactive polyisobutenes, which have a high terminal vinylidene group content of preferably substantially more than 60 mol%. Such highly reactive polyisobutenes have achieved a 10% share of the market and are used as intermediates for the preparation of additives for lubricants and fuels, as described, for example, in DE-A 27 02 604. For the preparation of these additives, polyisobutene/maleic anhydride adducts, in particular polyisobutenylsuccinic anhydrides, are first produced by reacting predominantly terminal double bonds of the polyisobutene with maleic anhydride, and said adducts are then reacted with certain amines to give the finished additive. Since terminal vinylidene groups are the main reaction sites in the adduct formation with maleic anhydride (whereas, depending on their position in the macromolecule, the double bonds present further in the interior of the macromolecule lead to substantially lower, if any, conversion without the addition of halogens), the amount of terminal vinylidene groups in the molecule is the most important quality criterion for this type of polyisobutene.

The formation of terminal vinylidene groups and the isomerization of terminal double bonds in the isobutene macromolecules to internal double bonds are, according to Puskas et al., J. Polymer

Sci.: Symposium No. 56, (1976) 191, based on the concepts shown in the scheme below.



35 R: Polyisobutylene radical

The polyisobutene cation I formed in the course of the polymerization reaction may be converted into the corresponding polyisobutene by elimination of a proton. The proton may be
 40 eliminated either from one of the β -methyl groups or from the internal γ -methylene group. Depending on which of these two positions the proton is eliminated from, a polyisobutene having a terminal vinylidene group II or having a trisubstituted double bond III present close to the end of the molecule is formed.

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The polyisobutene cation I is relatively unstable and tries to achieve stability by rearrangement to form more highly substituted cations. Both 1,3-methyl group shifts to give the polyisobutene cation IV and successive or concerted 1,2-hydride
5 group and 2,3-methyl group shifts to give the polyisobutene cation V may take place. Depending on the position from which the proton is eliminated, in each case three different polyisobutene double bond isomers can form from the cations IV and V. However, it is also possible for the cations IV and V to undergo further
10 rearrangement, causing the double bond to migrate even further into the interior of the polyisobutene macromolecule.

All these deprotonations and rearrangements are equilibrium reactions and therefore reversible, but ultimately the formation
15 of more stable, more highly substituted cations and hence the formation of polyisobutenes having an internal double bond with establishment of a thermodynamic equilibrium is favored. These deprotonations, protonations and rearrangements are catalyzed by any traces of acid present in the reaction mixture, but in
20 particular by the actual Lewis acid catalyst required for catalyzing the polymerization. The loss of reactivity due to isomerization can therefore only be counteracted by short residence times or steric hindrance of the complex anion. Since only polyisobutenes having terminal vinylidene groups according
25 to formula II react really efficiently with the maleic anhydride with adduct formation, polyisobutenes of the formula III have by comparison substantially lower reactivity and other polyisobutenes having more highly substituted double bonds are virtually unreactive toward maleic anhydride, the continued
30 efforts of many research groups to find improved processes for the preparation of highly reactive polyisobutenes or polyisobutenes having higher and higher contents of terminal double bonds are understandable.

35 According to DE-A 27 02 604, reactive polyisobutenes having a terminal double bond content of up to 88% by weight are obtainable by boron trifluoride-catalyzed polymerization of isobutene at from -50 to +30°C and residence times of less than 10 minutes. The lowest dispersity found for the polyisobutenes
40 thus prepared is 1.8.

Polyisobutenes having similarly high terminal double bond contents, but a narrower molecular weight distribution, are obtainable by the process described in EP-A 145 235, by
45 polymerizing isobutene in the presence of a preformed complex of boron trifluoride and a primary alcohol at from -100 to +50°C and a contact time of the polymerization reaction of more than

8 minutes, the molar ratio of boron trifluoride to the alcohol being from 0.5:1 to 5:1. This process has the disadvantages that polyisobutenes having a high terminal double bond content of more than 80% can only be obtained at a low isobutene conversion and
5 that the resulting polyisobutenes are particularly costly to prepare.

Polyisobutenes having a terminal double bond content of up to 95 mol% are said to be available by the gas phase process
10 described in US-A 3 166 546 and also by the process described in US-A 3 024 226, in which the catalyst used is a boron trifluoride/sulfur dioxide gas mixture. These polyisobutenes are characterized on the basis of infrared spectroscopy results. However, when the polyisobutenes obtained by these processes were
15 analyzed by means of ^{13}C nuclear magnetic resonance (^{13}C NMR) spectroscopy, which is a much more specific and precise method for detecting terminal double bonds, yet not common at the time said patent was written, the terminal double bond content found was only up to 40 mol%.

20 US-A 4 227 027 teaches alkyl transfer reactions catalyzed by boron trifluoride, the catalysts used being adducts of boron trifluoride and diols or polyols at from 40 to 120°C. The polymerization of isobutane by this process using a boron
25 trifluoride/1,2-butanediol adduct catalyst gave diisobutylene as the only product. No polyisobutene was formed.

Further quality criteria for polyisobutenes useful for the abovementioned application are their average molecular weight and
30 the molecular weight distribution, also called dispersity, of the macromolecules contained in the polyisobutene. Generally, polyisobutenes having number average molecular weights (M_n) of from 500 to 5000 dalton are used as intermediates for the preparation of the abovementioned lubricant and fuel additives.
35 But polyisobutenes having molecular weights of from 800 to 3000 dalton, in particular from 1000 to 2500 dalton, are more effective for this purpose and thus preferred.

The polymerization of isobutene yields polyisobutene products
40 whose polyisobutene components, i.e. the polyisobutene macromolecules, have a more or less broad, random molecular weight distribution with the result that broadening the molecular weight distribution of these polyisobutenes would lead to an increasing proportion of polyisobutene macromolecules having
45 relatively low or relatively high molecular weights which are more or less unsuitable for the abovementioned purpose since they are relatively ineffective. It is therefore desirable to prepare

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highly reactive isobutenes having average molecular weights inside the preferred molecular weight ranges and preferably a very narrow molecular weight distribution so as to reduce the proportion of undesired, relatively high molecular weight or
5 relatively low molecular weight polyisobutenes in the resulting product and thus to improve the quality of the product.

It was attempted to solve this problem by a process described in US 5,408,018 in which highly reactive polyisobutenes having a
10 terminal vinylidene group content of more than 80 mol% and an average molecular weight of from 500 to 5000 dalton by cationic polymerization of isobutene in the liquid phase with the aid of boron trifluoride as catalyst at from 0°C to -60°C are produced by polymerizing in the presence of secondary alcohols having 3-20
15 carbon atoms and/or dialkyl ethers having 2-20 carbon atoms. The dialkyl ethers used are preferably ethers containing at least one tertiary alkyl group. This process yields very good results, according to Example 6 of the cited patent, in the presence of a complex of BF₃ with 2-butanol and 2-butyl t-butyl ether.

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It is an object of the present invention to simplify the process and in particular to reduce the formation of by-products in the form of tertiary butanol and tertiary organic fluorides, which increase the solvent purification costs and reduce the polymer
25 yield.

We have found that this object is achieved by a process for preparing highly reactive polyisobutenes having a terminal vinylidene group content of more than 80 mol% and an average
30 molecular weight of from 500 to 5000 dalton by cationic polymerization of isobutene in the liquid phase in the presence of a complex comprising boron trifluoride at from +40°C to -60°C, which comprises polymerizing in the presence of a complex comprising boron trifluoride and

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- a) a primary alcohol having 1-20 carbon atoms or a secondary alcohol having 3-20 carbon atoms, or a mixture of these alcohols, and
40 b) an ether containing no tertiary alkyl groups and having the formula I



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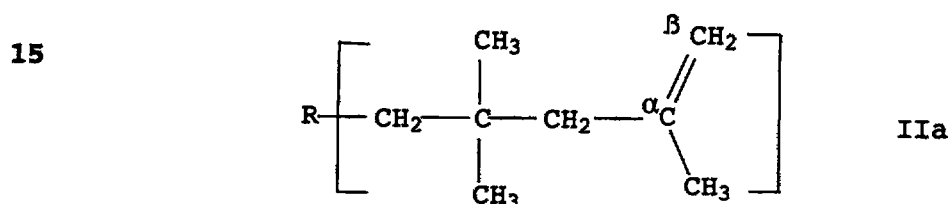
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where R¹ and R² are primary or secondary alkyl groups having 3-10 carbon atoms, with the proviso that at least one of R¹ and R² is a secondary alkyl group.

5 Preferred secondary alcohols used are 2-butanol and especially isopropanol, and preferred ethers used are diisopropyl ether or di-sec-butyl ether.

For the purposes of the present invention, terminal vinylidene
10 groups or terminal double bonds are those double bonds whose
position in the polyisobutene macromolecule is described by the
general formula IIa



where R is the polyisobutylene radical in question. The type and proportion of the double bonds present in the polyisobutene prepared according to the invention is determined by ^{13}C NMR spectroscopy. In the ^{13}C NMR spectrum, the two terminal double bond carbon atoms indicated by α and β in formula IIa can be identified by their peaks at a chemical shift of 114.4 and 143.6 ppm, respectively, and the proportion of terminal double bonds with regard to other types of double bonds is calculated by an evaluation of the peak areas in relation to the overall integral of the olefin peaks.

The number average molecular weight or number average molar mass used herein is the number average molecular weight M_n which can be determined, for example, by gel permeation chromatography, 35 ozonolysis or vapor-pressure osmometry.

The process according to the invention makes it possible to prepare polyisobutenes having a terminal vinylidene group content of more than 80 mol%, especially more than 90 mol%, by cationic
40 polymerization in the liquid phase of isobutene at from +40 to -60°C, preferably from -4 to -30°C, more preferably from -10 to -20°C.

Useful protic complex constituents, which are also referred to as
45 initiators, include virtually all primary alcohols having 1-20
carbon atoms as well as all secondary alcohols having 3-20 carbon

atoms, i.e. the primary or secondary alcohols may be linear or branched.

Examples of primary alcohols which can be used according to the invention are methanol, ethanol, n-propanol, n-butanol, n-pentanol, n-hexanol, n-heptanol, n-octanol, n-nonanol, n-decanol, 2-ethylhexanol, 2-propylheptanol, n-undecanol, n-dodecanol, n-tridecanol, ethylene glycol and n-eicosanol.

Examples of suitable secondary alcohols are: isopropanol, 2-butanol, and also sec-pentanol, sec-hexanol, sec-heptanol, sec-octanol, sec-nonanol, sec-decanol or sec-tridecanol.

In addition to monohydric, primary and/or secondary alcohols, (poly)etherols of ethylene oxide, propene oxide and butene oxide as well as polytetrahydrofuran may also be used according to the invention.

Preference is given to using 2-butanol and especially isopropanol.

The ether containing no tertiary alkyl groups and having the formula I

$$R^1-O-R^2,$$

may be any ether in which the groups R^1 and/or R^2 are derived from a secondary alcohol and are primary or secondary alkyl groups having 3-10 carbon atoms, i.e. alkyl groups which are attached to the ether oxygen atom either as $-CH_2-R$ or $-CH-(R)_2$ group, but not as $-C(R)_3$ group. Specific examples of R^1 and R^2 include the following groups:

isopropyl, 2-butyl, sec-pentyl, hexyl, heptyl and octyl, and for R^2 also methyl, ethyl, propyl, butyl, pentyl and hexyl groups.

Particular preference is given to diisopropyl ether, isopropyl 2-butyl ether and di-2-butyl ether.

The boron trifluoride/ether/alcohol complexes are advantageously prepared by introducing gaseous boron trifluoride into the ether and the alcohol in question or preferably into a solution in a solvent of the ether and the alcohol in question. These complexes are usually prepared at from -60 to $+40^\circ\text{C}$, preferably at from -20 to $+40^\circ\text{C}$. Although it is also possible to work at lower temperatures, it is technically more difficult to achieve such low temperatures. Since the complexing of boron trifluoride with

secondary alcohols is exothermic, the reaction mixture is preferably cooled to maintain it at the desired temperature.

At low temperatures, many of the boron trifluoride complexes to
5 be used according to the invention are highly viscous liquids or even solids. In these cases it is advantageous to generate the boron trifluoride complexes in a solvent. Examples of suitable solvents are hydrocarbons, such as pentane, hexane, isooctane, or halogenated hydrocarbons, such as methylene chloride or
10 chloroform. It is of course also possible to use solvent mixtures. Usually, the solubility of boron trifluoride complexes increases with increasing solvent polarity.

Therefore, when the boron trifluoride complexes to be used
15 according to the invention are prepared in apolar solvents, such as the abovementioned hydrocarbons or a polyisobutene solution, the boron trifluoride complex may exceed the solubility product and separate out to form an emulsion or suspension. Since the process according to the invention is catalyzed not only by
20 catalyst complexes dissolved homogeneously in the reaction medium but also by catalyst complexes dispersed heterogeneously in the reaction medium, such catalyst separations are usually not critical.

25 The boron trifluoride complexes may be preformed in separate reactors prior to use in the process according to the invention, temporarily stored after their formation and metered into the polymerization reactor as required.

30 For temporary storage, the solutions of the preformed boron trifluoride complexes, if desired after dilution with further solvent, are preferably filled into coolable containers and stored at generally below 0°C until used.

35 Another, preferred variation comprises generating the boron trifluoride complexes in situ in the polymerization reactor. This procedure comprises introducing the alcohol in question and the ether, if desired together with a solvent and together with the isobutene, into the polymerization reactor and dispersing the
40 boron trifluoride in the required amount in this reactant mixture in which the boron trifluoride reacts with the alcohol and the ether to give the boron trifluoride complex. The in situ generation of the boron trifluoride catalyst complex can advantageously be conducted using isobutene or the reaction
45 mixture comprising unconverted isobutene and polyisobutene as solvent instead of an additional solvent. If the reaction mixture of isobutene comprising polyisobutene is used as a solvent, the

isobutene is of course usually not converted completely, and it is advantageous to choose a partial isobutene conversion of in general up to 80%, preferably of up to 70%.

- 5 The in situ generation of the boron trifluoride complexes in the preparation of highly reactive polyisobutenes represents (as in the case of the process of US 5,408,018) a substantial simplification of the process for their preparation. Among other things, the investment in terms of equipment is reduced, since
10 neither reactors for preparing preformed complexes nor storage tanks for the preformed complex solutions are required.

- It is advantageous to prepare the catalysts comprising boron trifluoride, secondary alcohol and ether in the molar ratio
15 intended for the complex to be used in the process according to the invention, i.e. the molar boron trifluoride/sec-alcohol/ether ratio is usually not altered after generation of the complex in question.

- 20 The molar ratio of alcohol to ether may vary from 0.01 to 10. Particular preference is given to a ratio of from 0.02 to 2 and particularly preferably from 0.2 to 1.0.

- The BF_3 concentration in the reactor may be significantly higher
25 than the concentrations customary to date and should be in general in the range from 0.01 to 1% by weight, more preferably from 0.05 to 0.5% by weight. The molar concentration of the complexing agents alcohol and ether depends on the BF_3 concentration; the molar ratio of the sum of alcohol and ether to
30 BF_3 is more than 1 and less than 2 and is preferably from 1.4 to 2.

- The isobutene concentration in the reactor is generally from 0.5 to 60% by weight, for polyisobutene up to $M_N = 3000$ preferably
35 from 0.5 to 20% by weight more preferably below 5% by weight. The polymer concentration ranges from 10 to 60% by weight.

- In a preferred embodiment, the BF_3 /ether complex is first prepared separately or in the solvent feed to the reactor and then
40 combined with the alcohol in the complex or solvent feed to the reactor or in the reactor itself. This makes it possible to dissipate the energy of complex formation without detrimental by-product formation during the generation of the alcohol complex.

The starting material used for the preparation of the boron trifluoride complexes is advantageously gaseous boron trifluoride. Although it is possible to use technical grade boron trifluoride comprising minor amounts of sulfur dioxide and SiF_4 (purity: 96.5% by weight), it is preferable to use high purity boron trifluoride (purity: 99.5% by weight).

Thus, the preparation of highly reactive polyisobutenes according to the invention comprises disbursing the preformed boron trifluoride complex solution or suspension in the isobutene according to the catalyst requirement or alternatively generating the catalyst in the isobutene stream comprising alcohol and ether by introducing gaseous boron trifluoride in situ. Isobutene feedstocks which may be used in the process of the invention include pure isobutene and mixtures of isobutene and other hydrocarbons whose isobutene content should advantageously not be less than 6% by weight. Preference is given to using hydrocarbon mixtures having a high isobutene content and a low butadiene content, particular preference being given to a pure isobutene feedstock. This feedstock is convertible as such into polyisobutene with the aid of the catalyst system according to the invention in the presence of inert solvents, such as saturated hydrocarbons, for example butane, pentane, hexane, isooctane, cyclobutane or cyclopentane, halogenated hydrocarbons, such as methylene chloride or chloroform, or halocarbons having suitable melting and boiling points. The isobutene feedstock may comprise minor amounts of impurities such as water, carboxylic acids or mineral acids without causing critical yield or selectivity losses during polymerization. This results in a lower alcohol/ether consumption which alters the abovementioned molar ratios in favor of BF_3 . It is, however, convenient and advantageous to avoid an accumulation of these impurities in the system by removing such substances from the isobutene feedstock, for example by adsorption on solid adsorbents, such as activated carbon, molecular sieves or ion exchangers.

The isobutene polymerization can be carried out batchwise, semicontinuously or continuously. It is possible to use conventional reactors such as tubular reactors, tube bundle reactors or stirred tanks, but the process according to the invention is preferably carried out in a loop reactor, i.e. a tubular or tube bundle reactor with continuous circulation of the reacting material, where the feed/circulation ratio may generally vary from 1:1 to 1:1000, preferably from 1:50 to 1:200 v/v. It will be appreciated that the amount of feed equals the amount of

reaction effluent after equilibration of the polymerization reaction.

To avoid high local and steady-state catalyst concentrations in the polymerization reactor which may give rise to double bond shifts, it is advantageous to provide for good mixing of all reactants during their introduction into the reactor both in the case of preformed catalyst complexes being introduced into the reactor and in the case of generating the boron trifluoride complexes in the reactor in situ. It is also advantageous to generate a turbulent flow of the reaction mixture in the reactor, which can be achieved, for example, by providing the reactor with suitable internals such as baffles or by dimensioning the tube cross sections such that a suitable flow rate is achieved.

The residence time in the reactor of the isobutene to be polymerized may range from 5 sec to several hours, preference being given to choosing a residence time of from 1 to 30 minutes, more preferably from 2 to 20 minutes. The overall reaction rate depends on the amount, but in particular on the molar ratio, of the complex used. Virtually any overall reaction rate may be chosen by varying this ratio. The optimum reaction rate is a function of the equipment and depends on the dissipation of heat. Short reaction times are preferred. The boron trifluoride/alcohol/ether catalyst is usually introduced in an amount of from 0.05 to 1% by weight, based on the isobutene or isobutene/hydrocarbon mixture used.

The polymerization is advantageously carried out at below 20°C, preferably below 0°C. Although isobutene can be polymerized to give highly reactive polyisobutene at substantially lower temperatures, the polymerization is generally carried out at from +40 to -60°C, in particular from -4 to -30°C, particularly preferably from -10 to -20°C. The polymerization is generally conducted under atmospheric pressure, although it is also possible to work under elevated pressure, in particular under the autogeneous pressure of the reaction system, although this is usually immaterial to the result of the polymerization. The polymerization reaction is advantageously conducted under isothermal conditions and at a constant, steady-state monomer concentration in the reaction medium. Any steady-state isobutene concentration may be chosen in principle, but it is advantageous to choose a monomer concentration of in general from 0.2 to 50% by weight, preferably from 0.2 to 5% by weight, based on the total polymerization mixture.

Since the polymerization reaction is exothermic, the heat of polymerization is usually dissipated by a cooling means, which may be operated, for example, using liquid ammonia as coolant. Another way to dissipate the heat of polymerization is
5 evaporative cooling. In this case, the heat evolved is consumed by evaporation of the isobutene and/or other volatile constituents of the isobutene feedstock or the possibly volatile solvent such as ethane, propane or butane, keeping the temperature constant. However, a disadvantage is the volatility
10 of the BF_3 complexes which may result in side reactions occurring in the gas phase.

Any isobutene conversion may be chosen in principle. It will be appreciated, however, that very low isobutene conversions
15 jeopardize the economic viability of the process, whereas very high isobutene conversions of more than 99% increase the risk of double bond shifts which makes shorter reaction times, i.e. an improved dissipation of heat, absolutely necessary. For these reasons, the isobutene conversion is usually from 20 to 99%, more
20 preferably from 90 to 98%. Surprisingly, these high isobutene conversions, when achieved using the catalyst system according to the invention, result only to a minor extent in double bond shifts, and the resulting polymer still has a terminal vinylidene group content of more than 80 mol%. For the preparation of a
25 polyisobutene having a terminal double bond content of more than 90 mol%, preference is given (at a 50% strength by weight isobutene content of the feed) to an isobutene conversion of up to 99%, preferably from 90 to 99%, especially from 94 to 99%, particularly preferably from 96 to 98%.

30 The reaction effluent is advantageously worked up by introducing it into a medium which deactivates the polymerization catalyst and thus terminates the polymerization. Examples of suitable media include water, alcohols, acetonitrile, ammonia or aqueous
35 solutions of mineral bases, such as solutions of alkali metal and alkaline earth metal hydroxides, solutions of carbonates of these metals and the like.

As part of the continued workup, the polyisobutene is
40 advantageously subjected to one or more extractions to remove residual complex - usually washes with methanol or water - followed by separation by distillation into unconverted isobutene, solvent, oligomers and polyisobutene. The isobutene, the solvent and the oligomers may be returned to the
45 polymerization reactor. The desired polyisobutene is obtained as bottom product.

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The process of the invention provides an economical way to prepare highly reactive polyisobutenes which have a terminal double bond content of more than 80 mol%, often even more than 90 mol%, at very high selectivities and very high conversions, and moreover provides polyisobutenes in the preferred molecular weight range having narrow molecular weight distributions.

Alternatively, the process of the invention makes it possible to conduct the polymerization at an elevated temperature or to increase the reactivity of the polyisobutene produced even further as compared to the process of US 5,408,018, and it is easier to separate off the complex owing to its lower solubility.

Example 1

The reactor used was a recycle reactor consisting of a Teflon tube which had a length of 7.1 m and an internal diameter of 6 mm and via which 100 l/h of reactor content were circulated by means of a gear pump. The tube and pump had a capacity of 200 ml. The Teflon tube and pump head were immersed in a cold bath at -23.8°C (cryostat). A mixture of 300 g/h of isobutene and 300 g/h of hexane was dried over a 3 A molecular sieve to a water content of less than 3 ppm and fed to the recycle reactor through a capillary which had an internal diameter of 2 mm and was precooled to -23.8°C . BF_3 and isopropanol/diisopropyl ether as complexing agents were directly introduced into the hexane feed to the reactor. The BF_3 feed was set to 23.5 mmol, and the total amount of the feed of the mixture of hexane, isopropanol and diisopropyl ether (15:1:4 ml) was varied until an isobutene conversion of 92.0% was obtained. The isopropanol feed was 13.6 mmol, and the diisopropyl ether feed was 27.2 mmol, at a reactor temperature of -18°C . The reactor effluent was washed with water and worked up by distillation at $230^{\circ}\text{C}/2$ mbar. The molecular weight M_n of the polymer was 1070; the reactivity (vinylidene double bond content) was 97.0%.

Examples 2 - 6:

Example 1 was repeated, except that increasing molar ratios of ether to alcohol were used. At an isobutene conversion of from 92 to 98%, the amount of BF_3 was increased until a molecular weight of about 1000 as determined by GPC was obtained after workup. The ether used in Example 7 was di-sec-butyl ether. The results are summarized in Table 1.

Table 1: Polymerization using different molar ratios of sec-alcohol to ether at an isobutene conversion of from 92 to 98% and a polyisobutene molecular weight M_n of 1000.

Example	BF ₃	Isopropanol	Ether	Molar ratios*)		[Isobutene]	Mol. weight M_n	Reactivity [%]
	[mmol]	[mmol]	[mmol]	B : I	(I+B):S	[%]		
1	23.5	13.6	27.2	2	1.76	4.0	1070	97.0
2	10.8	5.0	10.0	2	1.39	4.0	1120	93.7
3	11.1	10.0	10.0	1	1.81	4.0	1040	94.0
4	12.2	10.0	10.0	1	1.63	2.0	990	94.2
5	23.7	25	12.5	0.5	1.58	4.0	1040	91.7
6	18.1	5.0	25.0	4	1.66	2.0	1070	92.9
7	21.4	10.0	25.0	2.5	1.64	1.0	890	95.9

*) I = Initiator = isopropanol, B = Lewis base = diisopropyl ether
S = Lewis acid = BF₃



We claim:

1. A process for preparing highly reactive polyisobutenes having
a terminal vinylidene group content of more than 80 mol% and
an average molecular weight of from 500 to 5000 dalton by
cationic polymerization of isobutene in the liquid phase in
the presence of a complex comprising boron trifluoride at
from +40°C to -60°C, which comprises polymerizing in the
presence of a complex comprising boron trifluoride and
 - a) a primary alcohol having 1-20 carbon atoms or a secondary alcohol having 3-20 carbon atoms, or a mixture of these alcohols, and
 - b) an ether containing no tertiary alkyl groups and having the formula I
$$R^1-O-R^2 \quad I,$$
where R^1 and R^2 are primary or secondary alkyl groups having 3-10 carbon atoms, with the proviso that at least one of R^1 and R^2 is a secondary alkyl group.
2. A process as claimed in claim 1, wherein the secondary alcohol a) used is isopropyl alcohol and/or 2-butanol.
3. A process as claimed in claim 1, wherein the ether b) used is diisopropyl ether, di-sec-butyl ether and/or isopropyl sec-butyl ether.
4. A process as claimed in claim 1, wherein the primary and/or secondary alcohol a) and the ether b) are used in a molar ratio of from 0.01:1 to 10:1.
5. A process as claimed in claim 1, wherein the primary and/or secondary alcohol a) and the ether b) are used in a molar ratio of from 0.02:1 to 2:1.
6. A process as claimed in claim 1, wherein boron trifluoride, primary and/or secondary alcohol and ether are combined in the polymerization reactor to generate the complex in situ in the polymerization mixture.
7. A process as claimed in claim 1, wherein the boron trifluoride/ether complex is preformulated and is introduced, together with the primary and/or secondary alcohol or



separately, into the solvent or monomer feed to the reactor or directly into the reactor.

8. A process as claimed in claim 1, wherein polyisobutenes
5 having a terminal vinylidene group content of more than 90 mol% are polymerized at an isobutene conversion of up to 95% using a preformed boron trifluoride/isopropanol/diisopropyl ether complex, a molar secondary alcohol/ether ratio of from 2:1 to 1:5 and a boron
10 trifluoride/diisopropyl ether ratio of from 0.6:1 to 0.9:1.
9. A process as claimed in claim 1, wherein the isobutene source is a C₄ cut comprising isobutene in an amount of at least 6% by weight.
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10. A polyisobutene having an average molecular weight of from 500 to 5000 dalton and a terminal vinylidene group content of more than 90%, obtainable by cationic polymerization of isobutene in the liquid phase with the aid of boron
20 trifluoride as catalyst at from 40 to -60°C in the presence of a boron trifluoride complex with
- a) a primary alcohol having 1-20 carbon atoms or a secondary alcohol having 3-20 carbon atoms, or a mixture of these
25 alcohols, and
- b) an ether containing no tertiary alkyl groups and having the formula I



where R¹ and R² are primary or secondary alkyl groups having 3-10 carbon atoms, with the proviso that at least one of the radicals R¹ and R² is a secondary alkyl group.

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