

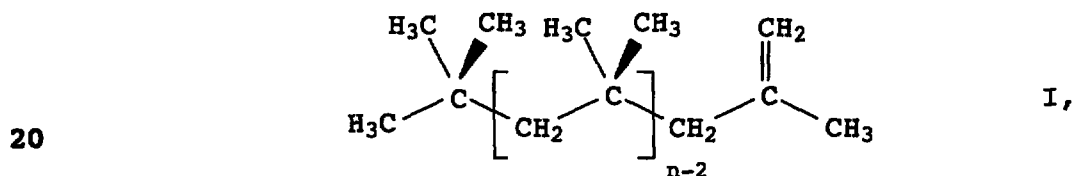
Preparation of halogen-free, reactive polyisobutene

Description

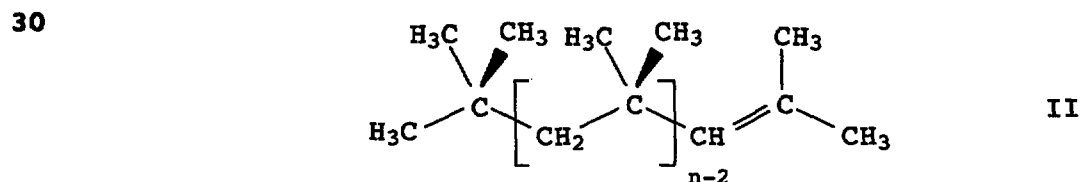
5

The present invention relates to a process for preparing halogen-free, reactive polyisobutene having a terminal double bond content of more than 50 mol% and an average molecular weight M_n of 500 - 5000 dalton by cationic polymerization in the liquid
10 phase of isobutene or hydrocarbon mixtures comprising isobutene in the presence of molybdo-heteropolyacids.

The polymerization of isobutene yields an inseparable mixture of polyisobutenes, in which the position of the double bond varies between the individual polyisobutenes. Polyisobutenes of formula I



wherein n is the degree of polymerization which in turn is derived from the average molecular weight M_n of the polyisobutene prepared, contain terminal C-C double bonds of the vinylidene type which are herein also referred to as α -olefinic double bonds owing to their position in the polyisobutene molecule. Accordingly, the double bonds in polyisobutenes of formula II



35

are referred to as β -olefinic. If the polymerization of isobutene is carried out without taking special measures, a random mixture is formed which comprises polyisobutenes having α -olefinic, ie. terminal, double bonds, β -olefinic double bonds and double bonds
40 located further toward the interior of the polyisobutene molecule. Both the terminal double bond content and the β -olefinic double bond content of a polyisobutene product prepared by a particular process are both reported in mol%.

45 Polyisobutenes having molecular weights of up to 100000 dalton are known. These olefins are usually prepared by Lewis acid-catalyzed isobutene polymerization employing aluminum

chloride, alkylaluminum chloride or boron trifluoride as Lewis acids, as described, for example, in H. Güterbock, Polyisobutylene und Mischpolymerisate, p. 77-104, Springer Verlag, Berlin, 1959. However, the resulting polymers have a relatively low vinylidene type terminal C-C double bond content of less than 10 mol%.

In contrast, reactive polyisobutene (PIB) having molecular weights of usually 500 - 5000 dalton has a high terminal vinylidene group content of, preferably, more than 50 mol%. These reactive polyisobutenes are used as intermediates in the preparation of additives for lubricants and fuels as described, for example, in DE-A 27 02 604. These additives are prepared by initially reacting polyisobutene with maleic anhydride. The preferred reactive sites for this reaction are the terminal double bonds of the vinylidene type, whereas double bonds located further toward the interior of the macromolecule react to a lesser extent if at all, depending on their position in the molecule. The polyisobutene/maleic anhydride adducts formed are then reacted with certain amines to give the corresponding additives. It is therefore absolutely necessary for polyisobutenes used as starting materials for the abovementioned additives to have a high terminal double bond content. The same applies to the preparation of the polyisobuteneamines of EP-A 244 616 which are also used as fuel additives and which are prepared by hydroformylation of the reactive polyisobutene and subsequent reductive amination of the resulting polyisobutene aldehyde. For this process, preference is likewise given to using polyisobutene having a high terminal double bond content, but β -olefinic polyisobutenes also give the desired product when the hydroformylation is carried out using cobalt catalysts, owing to their double bond isomerization activity.

The preparation of reactive polyisobutene by homogeneously catalyzed polymerization of isobutene is already known. According to DE-A 27 02 604, for example, a polyisobutene product having a terminal double bond content of up to 88% is obtained by reacting isobutene in the presence of boron trifluoride. EP-A 145 235 teaches the polymerization of isobutene in the presence of a complex of boron trifluoride and a primary alcohol at from -100°C to +50°C to give products with similarly high vinylidene double bond contents. According to US-A 5 286 823, highly reactive polyisobutene can also be prepared using complexes of boron trifluoride and secondary alcohols as catalysts.

The disadvantages of this homogeneously catalyzed process are that the Lewis acid catalysts used are corrosive and that there is a risk that, apart from the desired reactive polyisobutene, halogenated polymeric byproducts are formed which are virtually
5 inseparable from PIB and adversely affect the product and processing characteristics of the PIB. In these processes, the homogeneous catalyst is usually separated by quenching with a nucleophile to destroy the catalyst and subsequently removing the PIB from the quenching mixture by extraction. These additional
10 work-up steps are a further disadvantage of the homogeneously catalyzed PIB preparation process.

WO 94/28036 discloses, inter alia, the preparation of polyisobutene using heterogeneous Lewis acid-like catalysts.
15 Catalysts used are salts of elements of transition groups III, IV, V and VI of the periodic table of the elements which are insoluble in the reaction medium, preferably halides, sulfates, perchlorates, trifluoromethanesulfonates, nitrates and fluorosulfonates thereof. In the examples of this application,
20 only the halides of these elements are used as catalysts for isobutene polymerization. No information is given about the properties of the polyisobutene obtained in these examples in terms of their molecular weight or their terminal double bond content. The polymerization is terminated by adding methanolic
25 ammonia solution to the reaction medium to destroy or at least substantially inactivate the catalysts in question.

The preparation of PIB using heterogeneous catalysts is also known. US-A 4 288 649 describes a process for producing
30 polyisobutene having an average molecular weight > 1250 dalton by polymerizing C₄ hydrocarbon mixtures comprising isobutene over halided alumina catalysts. These catalysts are prepared by treating the alumina with a haliding agent, preferably with a chloriding agent, in particular with carbon tetrachloride, at an
35 elevated temperature. The disadvantage of this process is that some of the chlorine is transferred from the catalyst to the polymer which forms. For example, the polymerization of a mixture of n-butane, isobutane and isobutene over a chlorided alumina catalyst prepared in this manner gives, after a reaction time of
40 2 hours, a polyisobutene product having a chlorine content of 46 ppm.

US-A 5 326 920 discloses a process for polymerizing isobutene employing as heterogeneous catalyst an oxidic support material,
45 preferably silica, which has been activated with a metal chloride attached thereto, preferably with an aluminum chloride. Particular preference is given therein to an SiO₂-AlCl₃ catalyst

in which AlCl_2 groups are anchored on the SiO_2 support via oxygen linkages. The disadvantages of this process are that the polyisobutene products obtained have an extremely broad molecular weight distribution D of from 8 to 14, a low terminal double bond content and a chlorine content in the ppm range. Furthermore, this process requires the presence of promoters such as water, alcohols, alkyl halides or hydrogen chloride to achieve a catalyst activity which is sufficient for industrial operation. Similar catalyst systems for the polymerization of isobutene are described in WO 95/26815, WO 95/26816, WO 95/26814 and WO 96/26818.

JP-A 139 429/1981 utilizes heterogeneous zirconium dioxide and molybdenum oxide catalysts to prepare isobutene oligomers having a molecular weight of less than 300 dalton. These catalysts can be mixed with aluminum fluoride to increase their activity. According to this publication, the reaction of an isobutene-comprising C_4 cut (composition: 46% of isobutene, 28% of 1-butene, 8% of 2-butenes, 12% of n-butane, 5% of isobutane, 1% of 1,3-butadiene) over an $\text{MoO}_3/\text{ZrO}_2$ catalyst having a molybdenum content, calculated as MoO_3 , of 13% by weight at 120°C yields an isobutene oligomer mixture comprising 29% of diisobutene, 49% of triisobutene and 19% of tetraisobutene.

NL-A 7 002 055 discloses a process for preparing isobutene oligomers in the gas phase using a tin oxide/molybdenum oxide on silica catalyst to give a mixture of isobutene dimers, trimers and tetramers.

EP-A 535 516 discloses a catalyst for the preparation of ethylene polymers comprising chromium trioxide on a particular SiO_2 support material. This publication does not teach the preparation of reactive, low molecular weight polyisobutene.

GB-A 1 115 521 discloses, inter alia, the polymerization of isobutene over a Na-X zeolite loaded with a platinum compound. This yields essentially dimers and trimers of isobutene along with minor amounts of tetramers and higher polymers. No information is given about the molecular weight of the higher polymers thus formed and their terminal double bond content.

DE-A 19528942 discloses a process for preparing low molecular weight, reactive and halogen-free polyisobutene utilizing, as catalyst, a support material comprising an oxygen-containing zirconium compound and doped with various promoters.

CAN 738019 describes a process for polymerizing isobutene by contacting supported heteropolyacid catalysts with isobutene at 20 - 200°C and space velocities of from 1 to 40 h⁻¹. In particular, a process for preparing triisobutene by
5 polymerization of isobutene at from 40 to 140°C is disclosed utilizing heteropolyacid catalysts supported on essentially alkali metal-free gels as support materials. It is possible to favor the formation of the isobutene trimers desired according to the patent cited by low reaction temperatures. Higher
10 temperatures lead to increased formation of dimers and tetramers. The isobutene is polymerized exclusively in the gas phase and the isobutene trimers obtained are mainly composed of 2,2,6,6-tetramethyl-4-methyleneheptane and 2,2,4,6,6-pentamethyl-3-heptene. The products obtained by this
15 process have only a low molecular weight (dimers 112, trimers 168, tetramers 224) and do not have the alpha- or beta-olefin structure of formulae I and II. The patent cited does not teach the preparation of reactive polyisobutene having a higher molecular weight.

20 JP-A 14538/1982 describes a process for preparing isobutene oligomers by selective oligomerization of isobutene in the presence of n-butene over dehydrated heteropolyacids and/or heteropolyacid salts at up to 120°C. The isobutene oligomers in
25 question are mainly isobutene dimers comprising minor amounts of isobutene trimers and the isobutene is polymerized exclusively under conditions under which the starting compounds are in the gas phase. This publication does not teach the preparation of reactive polyisobutene having a higher molecular weight and
30 present [sic] terminal double bonds.

Furthermore, JP-A 102825/1982 discloses a process for preparing isobutylene dimers and trimers over tungsten heteropolyacids. It is true that these heteropolyacids are calcined at 250 - 400°C,
35 but the oligomerization is carried out at from 50 to 150°C, in particular from 100 to 140°C, ie. always in the gas phase. Lowering the temperature is said to be undesirable since a reduction in the yield of the desired dimers and trimers was observed at below 50°C. Accordingly, the preparation of reactive
40 polyisobutene having higher molecular weight at low temperature in the liquid phase is not taught.

Finally, the oligomerization of i-butene over heteropolyacids and heteropolyacid salts is described by Cai-Tian-Xi et al. in Cuihua
45 Xuebao (1985), 6(4), 370. Here, too, the oligomerization is carried out under conditions under which i-butene is present as a gas phase. The authors state that the main product formed at

relatively low temperatures is a dimer and that it is possible to increase the proportion of tetrameric and higher polymers by raising the temperature to 120°C. It is further observed that the activity of 12-molybdophosphoric acid and 12-molybdosilicic acid is significantly lower than that of tungstophosphoric acids. No teaching is given in this publication with regard to the product, the reaction conditions or the particular catalyst required for the preparation of reactive polyisobutene having a certain molecular weight.

10

It is an object of the present invention to find a process for preparing halogen-free, reactive polyisobutene having a terminal double bond content of more than 50 mol%, in particular a terminal double bond and β -olefinic double bond content of more than 80 mol%, and an average molecular weight of 500 - 5000 dalton using a heterogeneous catalyst, which does not have the abovementioned disadvantages and which is technically easily feasible.

20 We have found that this object is achieved according to the invention by a process for preparing halogen-free, reactive polyisobutene having a terminal double bond content of more than 50 mol% and an average molecular weight M_n of 500 - 5000 dalton by cationic polymerization in the liquid phase of isobutene or hydrocarbon mixtures comprising isobutene, which comprises polymerizing at from -40°C to +10°C in the presence of a dehydrated molybdo-heteropolyacid or tungsto-heteropolyacid.

Heteropolyacids to be used according to the invention contain, as essential element, tungsten or preferably molybdenum, although partial replacement by vanadium is possible. If vanadium is used, V : Mo atomic ratios of from 1 : 6 to 1 : 12 are preferred. Examples of central atoms are phosphorus, silicon, arsenic, germanium, boron, titanium, cerium, thorium, manganese, nickel, tellurium, iodine, cobalt, chromium, iron, gallium, vanadium, platinum, beryllium and zinc. Preference is given to phosphorus and silicon. A preferred ratio of molybdenum or tungsten atoms to the respective central atom is from 2.5 : 1 to 12 : 1, preferably from 11 : 1 to 12 : 1.

40

Specific examples of molybdenum-containing heteropolyacids are the following compounds:

dodecamolybdophosphoric acid ($H_3PMo_{12}O_{40} \cdot n H_2O$),
 45 dodecamolybdosilicic acid ($H_4SiMo_{12}O_{40} \cdot n H_2O$),
 dodecamolybdocerix(IV) acid ($H_8CeMo_{12}O_{42} \cdot n H_2O$),
 dodecamolybdoarsenic(V) acid ($H_3AsMo_{12}O_{42} \cdot n H_2O$),

- hexamolybdochromium(III) acid ($\text{H}_3\text{CrMo}_6\text{O}_{24}\text{H}_6 \cdot n \text{H}_2\text{O}$),
 hexamolybdonickel(II) acid ($\text{H}_4\text{NiMo}_6\text{O}_{24}\text{H}_6 \cdot 5 \text{H}_2\text{O}$),
 hexamolybdoiodic acid ($\text{H}_5\text{JMo}_6\text{O}_{24} \cdot n \text{H}_2\text{O}$),
 octadecamolybdodiphosphoric acid ($\text{H}_6\text{P}_2\text{Mo}_{18}\text{O}_{62} \cdot 11 \text{H}_2\text{O}$),
 5 octadecamolybdodiarsenic(V) acid ($\text{H}_6\text{As}_2\text{Mo}_{18}\text{O}_{62} \cdot 25 \text{H}_2\text{O}$),
 nonamolybdomanganic(IV) acid ($\text{H}_6\text{MnMo}_9\text{O}_{32} \cdot n \text{H}_2\text{O}$),
 undecamolybdovanadophosphoric acid ($\text{H}_4\text{PMo}_{11}\text{VO}_{40} \cdot n \text{H}_2\text{O}$),
 decamolybdodivanadophosphoric acid ($\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40} \cdot n \text{H}_2\text{O}$),
 hexamolybdohexatungstophosphoric acid ($\text{H}_3\text{PMo}_6\text{W}_6\text{O}_{40} \cdot n \text{H}_2\text{O}$).

10

It is of course also possible to use mixtures of heteropolyacids. Preference is given to using dodecamolybdophosphoric acid and dodecamolybdosilicic acid.

- 15 The heteropolyacids are known compounds and can be prepared by known processes, for example by the methods of Brauer (editor): Handbuch der Präparativen Anorganischen Chemie, Vol. III, Enke, Stuttgart, 1981, or by the processes of Top. Curr. Chem. 76 (1978), 1. Particular preference is given to preparation methods
 20 which do not use organic solvents and are carried out in aqueous solution instead.

- The heteropolyacids thus prepared are in general in hydrated form and, prior to use, are freed from coordinatively bound water
 25 present therein. This dehydration can advantageously be carried out thermally, for example by the method described in Makromol. Chem. 190, (1989) 929. Depending on the heteropolyacid used, another possible method of dehydrating it is to dissolve it in an organic solvent, for example in a dialkyl ether or alcohol,
 30 displace the water from its coordinate bond with the heteropolyacid using the organic solvent and remove the water azeotropically with the solvent.

- Anhydrous heteropolyacids prepared by these methods are then
 35 usually calcined at from 250 to 500°C, preferably from 280 to 400°C. Depending on the temperature and the pressure chosen, calcination is usually carried out over a period of 1-24 hours. The catalysts thus obtained may be directly used in the novel process.

40

- The heteropolyacid catalysts can also be used in supported form. For this purpose, the heteropolyacid is applied to a support which is inert under the reaction conditions, such as activated carbon, silica, titanium dioxide or zirconium dioxide, by
 45 conventional methods, for example by impregnating the relevant support material with a solution of the heteropolyacid in a solvent, preferably water, and then drying at from 100 to 250°C,

preferably from 130 to 250°C, under reduced pressure until water can no longer be detected in the catalyst. Anhydrous heteropolyacids prepared by these methods are subsequently calcined at from 250 to 500°C, preferably from 280 to 400°C.

5

Prior to use, the catalysts to be employed according to the invention are advantageously shaped to give shaped articles such as tablets, spheres, cylinders, rings or spirals or comminuted to give granules in a conventional manner and preferably used in
10 this form in a fixed bed in the reactor or milled to give a powder and used in this form, for example as suspension catalysts.

The catalysts to be used according to the invention can be stored
15 over a virtually unlimited period of time, in particular with exclusion of moisture. Catalysts which have become moist are advantageously dried under atmospheric pressure or reduced pressure, under atmospheric pressure in general at temperatures above 150°C, preferably at from 180 to 250°C, under reduced
20 pressure also at lower temperatures, prior to use.

Feed materials that may be used in the novel process are pure isobutene and hydrocarbon mixtures comprising isobutene such as C₄ raffinate or isobutane/isobutene mixtures derived from the
25 dehydrogenation of isobutane. C₄ raffinate refers to hydrocarbon mixtures obtained by substantial removal of 1,3-butadiene, ie. removal down to trace amounts, for example by extractive distillation, from the C₄ cut from steam crackers or fluid catalyzed crackers (cf. Weissermel, Arpe: Industrielle Organische
30 Chemie, p. 69, 102-103, 2nd ed., Verlag Chemie 1978).

The process of the invention can be carried out batchwise or continuously at generally from -40°C to +10°C, preferably from -30 to +10°C, particularly preferably from -20°C to +10°C, under
35 atmospheric pressure or superatmospheric pressure, especially under the autogenous pressure of the reaction system, so that the isobutene remains in liquid form. It is possible to use conventional reactors such as stirred reactors or loop reactors in batchwise operation of the process or loop reactors or reactor
40 batteries in continuous operation of the process. It is also advantageous to use, in continuous operation of the process of the invention, tubular reactors or tubular reactor batteries operated in upflow or downflow mode. It is possible for the catalysts to be used according to the invention, preferably when
45 using loop reactors or tubular reactors, to be arranged in a fixed bed or to be suspended in the reaction medium in powder form. Typical space velocities are from 10 kg isobutene/kg cat.

*h to 0.1 kg/kg *h, preferably from 7 to 0.2 kg/kg *h, particularly preferably from 5 to 0.3 kg/kg *h. Depending on the design, typical residence times are from 0.05 to 30 h, preferably from 0.1 to 20 h, particularly preferably from 0.2 to 10 h.

5

The isobutene polymerization can be carried out with or without preferably apolar, halogen-free solvents, preferably hydrocarbons. When hydrocarbon mixtures comprising isobutene are used as starting material, the hydrocarbons which are present
10 therein in addition to the isobutene act as solvents or diluents. Preference is given to butanes, pentanes, hexanes, heptanes and octanes which can be linear or branched. Particular preference is given to butanes, pentanes and hexanes. Because of the exothermic nature of the isobutene polymerization it may be advantageous to
15 provide the reactors used with internal or external cooling means.

The desired average molecular weight M_n of the polyisobutene can be adjusted by variation of the reaction parameters, in
20 particular by variation of temperature, residence time and space velocity.

In the batch process, the average molecular weight M_n is generally adjusted by variation of the amount of catalyst used, the
25 reaction time and the reaction temperature. Depending on the amount of catalyst used, the reaction time is generally from 0.01 to 10 hours, preferably from 0.1 to 8 hours. In the discontinuous embodiment of the process of the invention, the catalyst is generally added in an amount of 0.1 - 50% by weight, preferably
30 0.5 - 20% by weight, particularly preferably 1 - 10% by weight, in each case based on the weight of the isobutane present in the starting material used. Depending on the catalyst and starting material used, the optimum polymerization conditions for the preparation of polyisobutene having a desired average molecular
35 weight M_n are advantageously determined in preliminary experiments. In continuous operation of the process of the invention, the average molecular weight M_n is adjusted correspondingly, but here the reaction parameters space velocity and residence time are varied instead of the amount of catalyst
40 used.

The isolation of the polyisobutene from the polymerization mixture generally does not include any special technical features and may be effected by distillation, which, if a suspended
45 catalyst is used, is preceded by the removal of the suspended catalyst, for example by filtration, centrifugation or decanting. The distillation advantageously initially removes volatile

components of the polymerization mixture such as unconverted isobutene, hydrocarbons present in the starting material or added as solvents and then higher-boiling byproducts, for example low molecular weight isobutene oligomers from the polyisobutene.

5

The process of the invention provides a particularly economical way to prepare reactive, halogen-free polyisobutene having an average molecular weight M_n of generally 500 - 5000 dalton and a terminal double bond content of more than 50 mol%. Compared with
10 the nearest process of DE-A 19528942, the present process provides yet further improved yields.

Examples

15 I. Catalyst preparation

The catalyst was prepared and used in powder form. The Mo and P contents of the catalyst were determined by X-ray fluorescence analysis (Lit. R. Bock: Methoden der
20 Analytischen Chemie; Vol. 2: Nachweis- und Bestimmungsmethoden Teil 1, Verlag Chemie, Weinheim 1980).

Preparation:

125 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ are dissolved in 150 ml of water
25 at 40°C, and 8 g of H_3PO_4 (76%) are added. HNO_3 is added to this solution with stirring until pH 2 is reached. The mixture is evaporated to give a solid which is heated at 300°C for 16 h under nitrogen.

30 Analysis:

Mo: 61.0 g/100 g

P: 1.8 g/100 g

II. Polymerization of isobutene

35

The number average molecular weight M_n which is also referred to herein as average molecular weight M_n was determined by gel permeation chromatography using standardized polyisobutenes for calibration. The number average molecular
40 weight M_n was calculated from the resulting GPC chromatograms using the equation

$$M_n = \sum c_i / \sum (c_i / M_i)$$

45

where c_i is the concentration of the single polymer species in the resulting polymer mixture and M_i is the molecular weight of the single polymer species i . The molecular weight

distribution, also called dispersity (D), was calculated from the ratio of the weight average molecular weight (M_w) and number average molecular weight (M_n) using the equation

$$D = M_w / M_n$$

where the weight average molecular weight M_w was determined from the resulting GPC chromatograms using the equation:

$$M_w = \sum c_i M_i / \sum c_i$$

the α - and β -olefin content (formulae I and II) were determined by ^{13}C NMR spectroscopy. In the ^{13}C NMR spectrum, the C atoms of the terminal double bond of the α -olefins I show peaks at a chemical shift of 114.4 ppm (CH_2) and 143.6 ppm (C), whereas the signals of the C atoms of the trisubstituted double bond of the β -olefins II are at 127.9 (= CH-R) and 135.4 ppm (= C(CH_3) $_2$). The α - [sic] and β -olefin content can be determined by evaluation of the peak areas and comparison with the peak areas of the other olefinic c [sic] atoms. Deuterated chloroform (CDCl_3) was used as solvent and tetramethylsilane was used as internal standard.

Example 1

10 g of isobutene were condensed into a 25 ml glass pressure vessel under argon at -70°C . 1 g of catalyst A which had been predried at $180^\circ\text{C}/0.3$ mbar was added, the vessel was sealed and the suspension was stirred at 0°C for 2 h under the autogenous pressure of the reaction system. The polymerization mixture was then diluted with 10 g of n-hexane at 0°C . Unconverted isobutene was evaporated at room temperature, the catalyst was filtered off and the solvent added was removed from the filtrate by distillation at room temperature, slowly reducing the pressure to 0.3 mbar. Low molecular weight isobutene oligomers were removed from the resulting polyisobutene by Kugelrohr distillation at $120^\circ\text{C}/0.3$ mbar. The colorless polyisobutene which was obtained in a yield of 60% had an average molecular weight M_n of 760, a molecular weight distribution D of 3.0 and a terminal double bond content (= α -olefin content) of 85 mol%. The β -olefin content was 4%.

Comparative Example (as described in Working Example 2 of JP-A 57-14538)

10 g of raffinate I (45.4% of isobutene, 28.5% of butene-1, 15.1%
5 of 2-butene, 11.0% of butane) were reacted with 10 g of
12-molybdophosphoric acid (Merck, powder dried at 180°C/0.3 mbar)
at 80°C and an autogenous pressure of 8 bar for 1 h in a glass
autoclave with stirring. The polymerization mixture was then
diluted at -10°C with about 20 ml of n-hexane, and the volatile C₄
10 compounds were evaporated under atmospheric pressure at room
temperature. The catalyst was filtered off, and the filtrate was
freed from the solvent added at room temperature, slowly reducing
the pressure to 0.3 mbar. Low molecular weight isobutene
oligomers were separated from the yellow polyisobutene obtained
15 by Kugelrohr distillation at 120°C/0.3 mbar. The yellow
polyisobutene obtained in a yield of 32% (based on isobutene
used) had an average molecular weight M_n of 310, a molecular
weight distribution D of 1.9 and a terminal double bond content
(= α -olefin content) of only 14 mol%. The β -olefin content was
20 15%.

25

30

35

40

45



We claim:

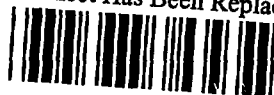
1. A process for preparing halogen-free, reactive polyisobutene
5 having a terminal double bond content of more than 50 mol%
and an average molecular weight M_n of 500 - 5000 dalton by
cationic polymerization in the liquid phase of isobutene or
hydrocarbon mixtures comprising isobutene, which comprises
10 polymerizing at from -40°C to $+10^{\circ}\text{C}$ in the presence of a
dehydrated molybdo-heteropolyacid or tungsto-heteropolyacid.
2. A process as claimed in claim 1, wherein a dehydrated
molybdo-heteropolyacid is used.
- 15 3. A process as claimed in claim 1, wherein the heteropolyacid
used has been calcined at from 250 to 500°C .
4. A process as claimed in claim 1, wherein the heteropolyacid
used has been calcined at from 280 to 400°C .
- 20 5. A process as claimed in claim 1, wherein the heteropolyacid
used is supported.
6. A process as claimed in claim 1, wherein the reaction is
25 carried out in the presence of molybdophosphoric acid,
vanadomolybdophosphoric acid.
7. A process as claimed in claim 1, wherein the reaction is
30 carried out in the presence of supported molybdophosphoric
acid or vanadomolybdophosphoric acid.

35

40

45

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

Preparation of halogen-free, reactive polyisobutene

Abstract

5

A process for preparing halogen-free, reactive polyisobutene having a terminal double bond content of more than 50 mol% and an average molecular weight M_n of 500 - 5000 Dalton by cationic polymerization of isobutene or hydrocarbon mixtures comprising

10 isobutene in the liquid phase comprises polymerizing at from -40°C to +10°C in the presence of a molybdo-heteropolyacid or tungsto-heteropolyacid.

15

20

25

30

35

40

45



We claim:

1. A process for preparing halogen-free, reactive polyisobutene
5 having a terminal double bond content of more than 50 mol% and an average molecular weight M_n of 500 - 5000 dalton by cationic polymerization in the liquid phase of isobutene or hydrocarbon mixtures comprising isobutene, which comprises polymerizing at from -40°C to $+10^{\circ}\text{C}$ in the presence of a
10 dehydrated molybdo-heteropolyacid or tungsto-heteropolyacid.
2. A process as claimed in claim 1, wherein a dehydrated molybdo-heteropolyacid is used.
- 15 3. A process as claimed in claim 1, wherein the heteropolyacid used has been calcined at from 250 to 500°C .
4. A process as claimed in claim 1, wherein the heteropolyacid used has been calcined at from 280 to 400°C .
- 20 5. A process as claimed in claim 1, wherein the heteropolyacid used is supported.
6. A process as claimed in claim 1, wherein the reaction is
25 carried out in the presence of molybdophosphoric acid or vanadomolybdophosphoric acid.
7. A process as claimed in claim 1, wherein the reaction is
30 carried out in the presence of supported molybdophosphoric acid or vanadomolybdophosphoric acid.

35

40

45

