

Preparation of polytetrahydrofuran

The present invention relates to processes for the preparation of polytetrahydrofuran or polytetrahydrofuran monoesters of C_1 - C_{10} monocarboxylic acids by the polymerization of tetrahydrofuran over a heterogeneous catalyst in the presence of one of the telogens water, 1,4-butanediol or polytetrahydrofuran having a molecular weight of from 200 to 700 dalton, of a C_1 - C_{20} monocarboxylic acid or of a carboxylic anhydride derived from C_2 - C_{20} monocarboxylic acids, or mixtures of these telogens.

Polytetrahydrofuran (PTHF), also called polyoxybutylene glycol, serves as intermediate for the preparation of polyurethane, polyester and polyamide elastomers, for the preparation of which it is employed as diol component. The inclusion of PTHF in these polymers causes the latter to become soft and flexible, for which reason PTHF is also referred to as a soft segment component for these polymers. Polytetrahydrofuran monoesters of monocarboxylic acids are used, for example, as plasticizers (US-A 4,482,411), impregnating agents (DE-A 2,932,216), monomers (EP-A 286,454), emulsifiers and dispersing aids (JP-A 138,452/1987) and are further employed for deinking in the regeneration of waste paper (JP-A-303,190/1988).

The cationic polymerization of tetrahydrofuran (THF) with the aid of catalysts has been described by Meerwein et al. (Angew. Chem. 72 (1960), 927). Either preformed catalysts are used as catalysts during this process, or the catalysts are produced in situ in the reaction mixture. This takes place by producing oxonium ions in the reaction medium with the aid of strong Lewis acids such as boron trichloride, aluminum chloride, tin tetrachloride, antimony pentachloride, iron(III) chloride or

phosphorus pentafluoride or by means of strong Brönsted acids, such as perchloric acid, tetrafluoroboric acid, fluorosulfonic acid, chlorosulfonic acid hexachlorostannic acid, iodic acid, hexachloroantimonic acid or tetrachloroferric acid and with the aid of reactive compounds designated as promoters, such as alkylene oxides, eg. ethylene oxide, propylene oxide, epichlorohydrin or butylene oxide, oxetanes, orthoesters, acetals, α -halo ethers, benzyl halides, triarylmethyl halides, acid chlorides, β -lactones, carboxylic anhydrides, thionyl chloride, phosphorus oxychloride or sulfonic halides, which oxonium ions initiate the polymerization of the THF. Of the large number of these catalyst systems only few have attained commercial significance however, since they are in some cases highly corrosive and/or in the preparation of PTHF lead to discolored PTHF products having only restricted usefulness. Moreover, many of these catalyst systems do not operate in a truly catalytic manner, but must be employed in stoichiometric amounts, based on the macromolecule to be prepared, and are consumed during the polymerization. For example, in the preparation of PTHF using fluorosulfonic acid as catalyst according to US-A 3,358,042, two molecules of fluorosulfonic acid must be used as catalyst per molecule of PTHF. A particular drawback of the use of halogen-containing catalysts is that these lead to the formation of halogenated by-products during the preparation of PTHF, which are very difficult to separate from pure PTHF and have a detrimental influence on its properties.

In the preparation of PTHF in the presence of the promoters cited these promoters are incorporated as telogens in the PTHF molecule so that the primary product of the THF polymerization is not PTHF but a PTHF derivative, for example a PTHF diester or sulfonate, from which the PTHF must be freed in a further reaction, eg. by saponification or transesterification (cf. US-A 2,499,725 and

DE-A 2,760,272). When using alkylene oxides as promoters these also act as comonomers and are incorporated in the polymer with the result that THF alkylene oxide copolymers are formed having properties which differ from those of PTHF, particularly as regards the application properties.

As described in US-A 5,149,862 sulfate-doped zirconium dioxide is used as an acidic, heterogeneous polymerization catalyst which is insoluble in the reaction medium. In order to accelerate the polymerization a mixture of acetic acid and acetic anhydride is added to the reaction medium, since the polymerization runs only very slowly in the absence of these promoters and a conversion of only 6% is achieved over a period of 19 hours. In this process PTHF diacetates are formed which must then be converted by saponification or transesterification to PTHF.

US-A 5,344,964 teaches the production of PTHF diesters by reaction of THF with a mixture of a monocarboxylic acid and a carboxylic anhydride. The reaction takes place in contact with metal oxides of metals of Groups III and IV of the Periodic Table of the Elements.

PTHF diesters are formed likewise during the polymerization of THF using Fuller's earth catalysts according to EP-A 3,112.

In US-A 4,303,782 zeolites are employed for the preparation of PTHF. The THF polymers obtainable in this process have extremely high average molecular weights - M_n from 250,000 to 50,000 D - and could not be generally adopted for the aforementioned purposes. Accordingly this process has also not attained industrial significance. A further serious drawback of this process is the small space-time yield (about 4% of PTHF in 24 hours) which is

achieved with the zeolites used therein.

According to US-A 4,120,903 PTHF can be prepared from THF and water with the aid of super-acidic Nafion® ion exchanger resins. These special ion exchangers are difficult to manufacture and thus very expensive and cause an increase in the cost of the PTHF prepared with their assistance. A further drawback of these ion exchanger resins is their inadequate long-term stability and their lack of ability to be reactivated, which also has a negative influence on the economy of this process.

JP-A 83,028/1983 teaches the polymerization of THF in the presence of a carboxylic halide or carboxylic anhydride, a heteropolyacid being used as catalyst. PTHF diesters are again formed during this process, and these must be hydrolyzed to PTHF.

JP-A 91171/94 relates to a catalyst consisting of an oxidic support material which contains a salt of a heteropolyacid and which has been prepared by application of the heteropolyacid salt to the support material and drying at 300°C. At this drying temperature the chemical structure of the heteropolyacid remains unchanged. The use of these catalysts for the polymerization of tetrahydrofuran is proposed. These catalysts have, however, the drawback of a brief useful life since the heteropolyacid adsorbed on the support bleeds during execution of the process.

In US-A 4,568,775 and US-A 4,658,065 there is described a process for the preparation of PTHF in which heteropolyacids are employed as catalysts. The heteropolyacids are soluble to a certain extent in the polymerization mixture and in the polymer and must be removed therefrom, since they cause discoloration of the PTHF product, by the use of elaborate measures, viz the

addition of a hydrocarbon in order to precipitate the heteropolyacid, the separation of the precipitated heteropolyacid and the separation of the added hydrocarbon. EP-A 503,394 relates to a process for the preparation of polytetrahydrofuran monoesters of monocarboxylic acids by means of hetero polyacid catalysts.

All the aforementioned processes for the preparation of PTHF or PTHF diesters have the drawback of producing low or moderate space-time yields. It is thus the object of the present invention to provide a process which makes it possible to obtain PTHF and PTHF monoesters in high space-time yields, ie. with high selectivity at a high THF conversion.

Accordingly we have found a process for the preparation of polytetrahydrofuran or polytetrahydrofuran monoesters of C_1 - C_{10} monocarboxylic acids by the polymerization of tetrahydrofuran over a heterogeneous catalyst in the presence of one of the telogens water, 1,4-butanediol or polytetrahydrofuran having a molecular weight of from 200 to 700 dalton, or of a C_1 - C_{10} monocarboxylic acid or mixtures of these telogens, wherein the catalyst used is a supported catalyst which contains a catalytically active amount of an oxygen-containing tungsten or molybdenum compound or mixtures of these compounds on an oxidic support material which has been calcined at from 500 to 1000°C following the application of the precursor compounds of the oxygen-containing molybdenum and/or tungsten compounds to the support material precursor.

The polymerization catalysts used in processes according to the invention are supported catalysts consisting of an oxidic support material, which contain oxygen-containing molybdenum or tungsten compounds or mixtures of such compounds as catalytically active compounds and which

furthermore, if desired, can be additionally doped with sulfate or phosphate groups. In order to convert them to their catalytically active form the supported catalysts are subjected, following the application of the precursor compounds of the catalytically active, oxygen-containing molybdenum and/or tungsten compounds to the support material, to calcination at from 500 to 1000°C, the support material and the precursor compound experiencing conversion to the catalysts which can be used according to the invention.

Examples of suitable oxidic supports are zirconium dioxide, titanium dioxide, hafnium oxide, yttrium oxide, iron(III) oxide, aluminum oxide, tin(IV) oxide, silicon dioxide, zinc oxide or mixtures of these oxides. Zirconium dioxide and/or titanium dioxide are particularly preferred.

The catalysts which can be used according to the invention contain in general from 0.1 to 50% by weight, preferably from 1 to 30% by weight, particularly preferably from 5 to 20% by weight, of the catalytically active, oxygen-containing compounds of molybdenum or tungsten or the mixtures of the catalytically active, oxygen-containing compounds of these metals, in each case based on the total weight of the catalyst, and in each case calculated as MoO_3 or WO_3 respectively, since the chemical structure of the catalytically active, oxygen-containing compounds of molybdenum and/or tungsten is not yet exactly known but can only be postulated, for example from the data of the IR spectra of the catalysts which can be used according to the invention.

In principle, the catalysts according to the invention, in addition to the catalytically active, oxygen-containing molybdenum and/or tungsten compounds can also be doped with from 0.05 to 10% by weight, preferably with

from 0.1 to 5% by weight, in particular with from 0.25 to 3% by weight, of oxygen-containing compounds containing sulfur or phosphorus or sulfur and phosphorus, in each case calculated on the total weight of the catalyst.

5 Since it is likewise not known in what chemical form these compounds containing sulfur or phosphorus are present in the finished catalyst, the contents of these groups in the catalyst are in all cases calculated as SO_4 or PO_4 , respectively.

10 For the preparation of the catalysts according to the invention it is usual to start from the hydroxides of the respective support components. If these hydroxides are commercially available, such commercially available hydroxides can be used as starting materials for the

15 preparation of the oxidic supports, but preferably freshly precipitated hydroxides are used for the preparation of the oxidic supports, which are dried after precipitation generally at from 20 to 350°C, preferably from 50 to 150°C, in particular from 100 to 120°C, under

20 atmospheric pressure or reduced pressure.

The water-soluble or hydrolyzable salts of the elements constituting the support material, for example their halides, preferably their nitrates or carboxylates, in particular their acetates, serve as starting compounds

25 for the preparation of these hydroxides. Suitable starting compounds for the precipitation of these hydroxides are, for example, zirconyl chloride, zirconyl nitrate, titanyl chloride, titanyl nitrate, yttrium nitrate, yttrium acetate, aluminum nitrate, aluminum acetate,

30 iron(III) nitrate, tin(IV) halides, in particular tin(IV) chloride, zinc nitrate or zinc acetate. From the solutions of these salts the corresponding hydroxides are precipitated preferably by means of aqueous ammonia solution. Alternatively the hydroxides can be obtained by

35 the addition of dilute or weak acids, such as acetic

acid, to water-soluble hydroxo complexes of the respective metals until precipitation of the respective hydroxide occurs. Likewise it is possible to obtain the hydroxides by the hydrolysis of organometallic compounds, for example the alcoholates of the respective metals, such as zirconium tetraethanolate, zirconium tetraisopropylate, titanium tetramethanolate, titanium tetraisopropylate, etc.

A gel-like precipitate generally forms during precipitation of these hydroxides, which after drying yields an X-ray amorphous powder. Possibly, these X-ray amorphous precipitates may comprise, in addition to the hydroxides of the respective metals, a large number of other hydroxyl-containing compounds, for example oxide hydrates, or polymeric, water-insoluble hydroxo complexes, etc. Since the exact chemical composition of these precipitates cannot be determined however, it is assumed for the purposes of this application, and for the sake of simplicity, that the compounds concerned are the hydroxides of the stated metals. The term "hydroxides" used in this application thus represents a collective term for the hydroxyl-containing precipitates obtained by the aforementioned methods of precipitation.

When using silicon dioxide as oxidic support material, preferably freshly precipitated silicic acid is employed as starting material for the preparation of the catalysts which can be used according to the invention, which can be obtained, for example, by acidification of a water-glass solution, and which is advantageously dried prior to further processing, as described above for the hydroxide precipitates.

To the resulting hydroxides of the support components or the silicic acid, which in this application are also termed support material precursors, the precursor com-

pounds of the catalytically active, oxygen-containing molybdenum and/or tungsten compounds are preferably applied by impregnation with an aqueous solution of these precursor compounds. Examples of water-soluble precursor compounds of the catalytically active, oxygen-containing tungsten or molybdenum compounds are, for example, the water-soluble salts of tungstic acid (H_2WO_4), as are formed, for example, by dissolving tungsten trioxide in aqueous ammonia, ie. the monotungstates, and the isopolytungstates formed therefrom by acidification, eg. the para-tungstates or meta-tungstates, the water-soluble salts or molybdic acid (H_2MoO_4), as are formed, for example, by dissolving molybdenum trioxide in aqueous ammonia, and the isopolymolybdates formed therefrom by acidification, in particular the meta-molybdates and para-molybdates. Preferably, the ammonia salts of these tungstic and molybdic acids are applied by impregnation, as precursor compounds, to the hydroxides of the support components or the silicic acid, respectively. For information on the nomenclature, composition and preparation of the molybdates, isopolymolybdates, tungstates or isopolytungstates reference is made to Römpps Chemie-Lexikon, 8th Edition, Vol. 4, pp. 2659-2660, Francksche Verlagsbuchhandlung, Stuttgart, 1985; Römpps Chemie-Lexikon, 8th Edition, Vol. 6, pp. 4641-4644, Stuttgart 1988 and Comprehensive Inorganic Chemistry, 1st Edition, Vol. 3, pp. 738-741 and 766-768, Pergamon Press, New York 1973. Instead of the abovementioned molybdenum or tungsten precursor compounds of the catalytically active molybdenum or tungsten compounds it is possible to use heteropolyacids of molybdenum or tungsten, such as 12-tungstosilicic acid ($\text{H}_4[\text{Si}\{\text{W}_{12}\text{O}_{40}\}]\cdot 26\text{H}_2\text{O}$) or 12-molybdatosilicic acid, or their water-soluble salts, preferably their ammonium salts, to effect application of the molybdenum or tungsten to the hydroxidic, ie. hydroxyl-containing, support material precursor. The thus impregnated hydroxides of the support components used in

each case or the impregnated silicic acid are in general dried at from 80 to 350°C, preferably from 90 to 150°C, under atmospheric pressure or reduced pressure.

5 There is also the possibility of incorporating the above precursor compounds of the catalytically active, oxygen-containing molybdenum or tungsten compounds in the subsequent catalyst by intimately mixing them with one or more of said hydroxides. Calcination of the support material precursor thus treated, to form the catalysts
10 which can be used according to the invention, takes place in the same manner as in the case of the support material precursors impregnated with these precursor compounds. However, the method of impregnation is preferably used for the preparation of the catalysts which can be used
15 according to the invention.

The catalyst precursors thus impregnated and dried are converted to the finished catalysts by calcination in air at from 500 to 1000°C, preferably from 550 to 900°C and particularly preferably at from 600 to 800°C. In the
20 course of calcination the hydroxides of the support components or the silicic acid is/are converted to the oxidic support material, and the precursor compounds of the catalytically active, oxygen-containing molybdenum or tungsten compounds applied to said support material by
25 impregnation are converted to these catalytically active components. Calcination at these high temperatures is important if the THF polymerization is to achieve a high conversion and thus a high space-time yield. At lower calcination temperatures the catalysts also cause THF
30 polymerization to take place but only with uneconomically low conversions. On account of IR analyses on catalysts produced in this manner Yinyan et al., Rare Metals 11 (1992), 185 suppose that, in the case of tungsten-doped supported zirconium oxide catalysts, the precursor
35 compound of the catalytically active, oxygen-containing

tungsten compound, applied by impregnation to the zirconium hydroxide, becomes chemically combined at the high calcining temperatures used, with the hydroxyl groups of the support material precursor, the catalytically active, oxygen-containing tungsten compound being formed, which as regards its chemical structure and chemical activity, particularly its catalytic properties, is distinctly different from oxygen-containing tungsten compounds which are merely adsorbed onto the support material zirconium dioxide. These facts are also assumed for the molybdenum-containing supported catalysts which can be used according to the invention.

As already mentioned, supported catalysts can also be used in the process of the invention to advantage when they are doped with compounds containing sulfur or phosphorus or sulfur and phosphorus in addition to compounds containing molybdenum and/or tungsten. The preparation of these catalysts takes place in a similar manner as that described above for the catalysts containing molybdenum and/or tungsten compounds only, compounds containing sulfur and/or phosphorus being additionally applied by impregnation to the hydroxides of the support components or the silicic acid produced in a similar way. The application of the sulfur and/or phosphorus compounds to the support material can take place concurrently with the application of the molybdenum and/or tungsten component or afterwards. Advantageously, the sulfur and/or phosphorus components are prepared by impregnation of the hydroxides of the support components or the silicic acid with an aqueous solution of a compound containing sulfate or phosphate groups, for example sulfuric acid or phosphoric acid. Advantageously, solutions of water-soluble sulfates or phosphates can also be used for the impregnation, ammonium sulfates or ammonium phosphates being particularly preferred. A further method of applying the phosphorus-containing

precursor compounds, together with the precursor compounds containing molybdenum or tungsten, to the hydroxidic support material precursor consists in impregnating the hydroxidic support material precursors, with phosphorus-containing heteropolyacids by the process described above. Examples of such heteropolyacids are 12-tungstatophosphoric acid ($H_3[P\{W_{12}O_{40}\} \cdot xH_2O]$ [sic] and 12-molybdatophosphoric acid ($H_7[P\{Mo_6O_{21}\}O_6] \cdot 28H_2O$). There can also be employed for this purpose heteropolyacids of molybdenum or tungsten with organic acids of phosphorus, for example phosphonic acids. Said heteropolyacids can also be used in the form of their salts, preferably as ammonium salts, for this purpose.

During calcination under the aforementioned conditions the heteropolyacids dissociate to form the catalytically active, oxygen-containing molybdenum or tungsten compounds.

Some of the catalysts which can be used according to the invention are known and their preparation is described in JP-A 288,339/1989, JP-A 293,375/1993, J. Chem. Soc. Chem. Commun. 1259 (1988) and Rare Metals 11, (1992), 185. The catalysts have been used hitherto only in petrochemical processes, for example as catalysts for alkylations, isomerizations and the cracking of hydrocarbons, ie. processes which are not related to the process of the invention.

The catalysts which can be used according to the invention can be employed in the process of the invention in the form of powder, for example when carrying out the process by a suspension technique, or advantageously as shaped articles, eg. in the form of cylinders, balls, rings, coils or chips, particularly with the catalyst taking the form of a fixed bed, which is preferred when using, for example, loop reactors or when the process is

operated continuously.

5 C₁-C₁₀ monocarboxylic acids, preferably C₁-C₈ monocarboxylic acids and particularly preferably formic acid, acetic acid, propionic acid, 2-ethylhexanoic acid, acrylic acid and methacrylic acid, serve in general as telogens for the preparation of the PTHF monoesters of monocarboxylic acids.

10 Particularly surprising and particularly advantageous is the fact that when use is made of the telogens water and/or 1,4-butanediol PTHF can be obtained in the process of the invention in high space-time yields in one step. If desired, low molecular weight, open-chain PTHF having a molecular weight of from 200 to 700 dalton can also be recycled as telogen to the polymerization reaction, where
15 it is converted to PTHF of higher molecular weight. Since 1,4-butanediol and low molecular weight PTHF have two hydroxyl groups, they are not only incorporated as telogen at the chain ends of the PTHF chain, but are also incorporated into the PTHF chain as monomer.

20 The telogen is advantageously added to the polymerization in the form of a solution in THF. Since the telogen causes termination of the polymerization, the average molecular weight of the PTHF or PTHF diester can be controlled via the amount of telogen used. The more
25 telogen present in the reaction mixture, the lower the average molecular weight of the PTHF or the respective PTHF derivative. Depending on the telogen content of the polymerization mixture PTHF or the respective PTHF derivatives can be specifically prepared to have average
30 molecular weights of from 250 to 10,000 [lacuna]. Preferably the process of the invention produces PTHF or the respective PTHF derivatives with average molecular weights of from 500 to 10,000 dalton, particularly preferably from 650 to 3000 dalton. To this end the

telogen is, based on the THF amount employed, added in amounts of from 0.04 to 17 mol%, preferably from 0.2 to 8 mol% and particularly preferably from 0.4 to 4 mol%.

5 The polymerization is generally carried out at from 0 to 80°C, preferably from 25°C up to the boiling temperature of THF. The pressure used is usually not critical for the outcome of the polymerization, for which reason the process is generally carried out at atmospheric pressure or under the autogenous pressure of the polymerization
10 system.

To avoid the formation of ether peroxides the polymerization is advantageously carried out under an atmosphere of inert gas. Suitable inert gases are, for example, nitrogen, hydrogen, carbon dioxide or the noble gases,
15 with nitrogen being preferably used.

The process of the invention can be carried out batchwise or continuously, the continuous mode of operation usually being preferred for economic reasons.

20 When the process is carried out batchwise the reactants THF, the respective telogen, and the catalyst are generally caused to react in a stirred vessel or loop reactor at the temperatures stated until the desired conversion of THF is achieved. The reaction time can, depending on the amount of catalyst added, be from 0.5 to 40,
25 preferably from 1 to 30 hours. The catalysts are added, to effect polymerization, in general in an amount of from 1 to 90% by weight, preferably from 4 to 70% by weight and particularly preferably from 8 to 60% by weight of the THF employed.

30 To work up the reactor effluent from a batch process, said effluent is separated from the catalyst suspended therein, advantageously by filtration, decantation or

centrifugation.

5 The polymerization reactor effluent freed from catalyst is generally worked up by distillation, unconverted THF being advantageously removed, by distillation, in a first stage. In a second purification stage, if desired, low molecular weight PTHF can then be separated from the polymer by distillation under reduced pressure and recycled to the reaction. Alternatively, volatile THF oligomers can be depolymerized, for example by the process described in DE-A 3,042,960, and recycled to the reaction in this form.

Examples

Preparation of the catalysts:

15 Catalyst A was prepared by the addition of 2600 g of zirconium hydroxide to a solution of 640 g of tungstic acid (H_2WO_4) in 3470 g of 25% strength ammonia solution. This mixture was kneaded for 30 min and thereafter dried for 2 h at 120°C. The powder resulting after a sifting operation was pelletized, the resulting pellets 20 (3 x 3 mm) then calcined at 450°C over a period of 2 h. The catalyst had a tungsten content, calculated as tungsten trioxide, of 20% by weight, based on the total weight of the catalyst.

Catalysts B and C:

25 Catalysts B and C were prepared analogously to catalyst A, but calcined at 600°C (cat. B) and 700°C (cat. C) respectively.

Catalyst D

Catalyst D was prepared by the addition of 1600 g of

zirconium hydroxide to a solution of 425 g of tungstic acid and 200 g of ammonium sulfate in 3470 g of 25% strength ammonia solution. This mixture was kneaded for 30 min and thereafter dried for 2 h at 120°C. The powder
5 resulting after a sifting operation was pelletized and the resulting pellets then calcined at 600°C over a period of 2 h. The catalyst had a tungsten content, calculated as tungsten trioxide, of 18% by weight and a sulfur content, calculated as SO_4 , of 7% by weight, based
10 on the total weight of the catalyst.

Catalyst E

Catalyst E was prepared by the addition of 2600 g of zirconium hydroxide to 2260 g of 26.5% strength by weight MoO_3 solution in 12% strength aqueous ammonia. This
15 mixture was kneaded for 30 min and then dried for 16 h at 120°C. The dried material was kneaded with 40 g of 75% strength phosphoric acid and 1.4 l of water over a period of 30 min, after which it was dried for 2 h at 120°C. The powder resulting after a sifting operation was pelletized
20 and the resulting pellets then calcined at 600°C over a period of 2 h. The catalyst had a molybdenum content, calculated as molybdenum trioxide, of 20% by weight and a phosphorus content, calculated as PO_4 , of 1% by weight, based on the total weight of the catalyst.

25 Catalyst F

Catalyst F was prepared analogously to catalyst A, but was calcined at 675°C.

Catalyst G

Catalyst G was prepared by adding 75 g of TiO_2 (P25, from Degussa) to a solution of 20 g of tungstic acid (H_2WO_4)
30 in 100 g of a 32% strength aqueous NH_3 solution. This

5 mixture was kneaded for 2 h and then dried for 12 h at 120°C. The powder obtained after trituration was calcined at 620°C for 2 hours. The pulverulent catalyst had a tungsten content, calculated at WO_3 , of 20% by weight, based on the total weight of the catalyst.

Catalyst H

10 16.58 kg of TiOCl_2 dissolved in 43.5 l of distilled water were combined with 45 kg of a 10% strength by weight aqueous NH_3 solution by adding both solutions at 50°C and while stirring at a constant pH of 6.5 to 30 l of distilled water over a period of 1 h. The mixture was stirred for a further hour. The resulting precipitate was then filtered off, washed and dried for 24 h at 120°C. 2.4 kg of this precipitated TiO_2 were added to a solution
15 of 638 g of tungstic acid in 3.65 kg of 25% strength aqueous NH_3 solution. The mixture was kneaded and then shaped into 1.5 mm pellets. The pellets were first calcined for 2 h at 450°C and then for 2 h at 610°C. The catalyst had a tungsten content, calculated as WO_3 , of
20 18.6% by weight, based on the total weight of the catalyst.

Batch THF polymerizations:

25 In a glass flask having a capacity of 100 ml and equipped with a reflux condenser 10 g of catalyst pellets (3 × 3 mm), which had been dried prior to use over a period of 18 hours at 180°C/0.3 mbar, for the removal of adsorbed water, were suspended under a blanket of nitrogen in 20 g of telogen-containing THF and left at 50°C for 24 hours. After this time the reaction mixture
30 was diluted with a further 20 g of THF. The catalyst pellets were removed by filtration and washed three times with 20 g of THF each time. The filtrates were combined, concentrated at 70°C/20 mbar in a rotary evaporator, and

weighed. To determine the average molecular weight M_n a portion of the PTHF obtained was subjected to bulb tube distillation (150°C/0.1 mbar).

5 The average molecular weight (M_n) of the PTHF thus obtained was determined by gel permeation chromatography (GPC). M_n is defined by the equation

$$M_n = \frac{\sum c_i}{\sum \frac{c_i}{M_i}}$$

10 in which c_i stands for the concentration of the individual polymer species i in the polymer mixture obtained and in which M_i is the molecular weight of the individual polymer species i .

PTHF yields obtained batchwise using different catalysts and telogens and the average molecular weights M_n are listed in Table 1.

15 Table 2 lists the results of the batchwise polymerization of THF to PTHF over catalysts calcined at different temperatures under otherwise identical reaction conditions.

Table 1: Batch polymerization of THF using different catalysts and telogens

Example No.	Catalyst	Telogen	Amount of telogen ¹⁾ [ppm by weight]	THF conversion ²⁾ [%]	Average molecular weight [M _n]
1	WO ₃ /ZrO ₂ C	Butanediol	2000	56.8	7200
2	MoO ₃ /ZrO ₂ /PO ₄ E	Butanediol	2000	60.9	6900
3	WO ₃ /ZrO ₂ C	Water	400	48.0	9700
4	WO ₃ /ZrO ₂ C	Water	1000	12	2600
5	WO ₃ /ZrO ₂ C	Formic acid ³⁾	1020	35.5	6600

- 1) based on THF
 2) to PTHF or PTHF monoformate
 the selectivity of the reaction was in each case approximately 100%
 3) preparation of PTHF monoformate

Table 2: Batch polymerization of THF using WO_3/ZrO_2 catalysts calcined at different temperatures

Example No.	Catalyst	Calcining temperature [°C]	Telogen	Amount of telogen ¹⁾ [ppm]	Conversion of THF ²⁾ [%]
6	A	450	1,4-butanediol	2000	0.3
7	B	600			31.2
8	C	700			56.8

1) based on THF

2) selectivity toward PTHF approximately 100%

Continuous polymerization of THF

Example 9

A fixed-bed reactor having a capacity of 250 ml was filled under argon with 220 ml (372 g) of the
5 $\text{MoO}_3/\text{ZrO}_2/\text{PO}_4^{3-}$ catalyst E which had been dried for 20 hours at 180°C/0.3 mbar. When placed in the reactor the catalyst was covered with THF (<0.01% by weight of water). A circulating pump was provided to effect circulation of the reaction mixture. When the reactor,
10 pump and conduits had all been completely filled with THF the reaction mixture was pumped over the catalyst for 24 hours at a reactor temperature of 50°C, without THF feed. 8.1 g/hour of THF containing 0.2% by weight of 1,4-butanediol were then continuously metered into the
15 circuit over a period of 120 hours. The circulation/feed ratio was approximately 60 [lacuna]. The average THF yield over the reaction time of 120 hours was 48.9%. The average molecular weight M_n of the PTHF obtained was 2400 dalton as determined by GPC.

20 Example 10

The continuous THF polymerization described in Example 9 over catalyst E was continued with the same rate of feed of THF, which contained 0.4% by weight of 1,4-butanediol, but without recycling of the product (circulating pump
25 switched off), using otherwise identical reaction conditions. Once the PTHF yield had reached a steady value, the reactor effluent formed was collected over a period of 72 h. Following concentration of the reaction solution, as described for the batch tests, PTHF was
30 obtained with an average molecular weight of 900 dalton (as determined by GPC) at a THF conversion of 6.8%.

Batch polymerization of THF

The batch polymerization experiments with catalysts F to H were carried out as described in Example 1 or 2. Table 3 shows the experimental results obtained.

5 Table 3

Example No.	Catalyst	Telogen	Amount of telogen [ppm by weight]	THF conversion [%]	Average molecular weight [M_n]
11	WO ₃ /ZrO ₂ F	Butanediol	2000	36.2	5500
12	WO ₃ /TiO ₂ G	Butanediol	2000	47.9	7900
10 13	WO ₃ /TiO ₂ H	Butanediol	2000	37.2	5300

Continuous THF polymerization in the presence of butane-1,4-diol

Example 14

15 A fixed-bed reactor having a capacity of 250 ml was filled under argon with 322 g (250 ml) of the WO₃/ZrO₂ catalyst F which had been dried for 72 h at 180°C/0.3 mbar. The polymerization equipment was filled with THF containing butane-1,4-diol (0.5% by weight butane-1,4-diol). The reaction mixture was initially
20 pumped over the catalyst for 24 h and at a reactor temperature of 50°C. Subsequently, THF containing butane-1,4-diol (0.5% by weight butane-1,4-diol) was continuously added at a space velocity of 0.166 kg of THF/l of catalyst*h. The polymerization reactor effluent
25 obtained over a period of 72 h (3.00 kg) was worked up by distilling off the unreacted THF under reduced pressure,

followed by short-path distillation at 150°C/0.3 mbar. 290 g of PTHF were obtained which had, according to the ¹H-NMR spectrum, an average molecular weight M_n of 2100 dalton. The yield was 9.7%. The space-time yield was 16 g of PTHF 2100/l of catalyst*h.



We claim:

1. A process for the preparation of polytetrahydrofuran or polytetrahydrofuran monoesters of C_1 - C_{10} monocarboxylic acids by the polymerization of tetrahydrofuran over a heterogeneous catalyst in the presence of one of the telogens water, 1,4-butanediol or polytetrahydrofuran having a molecular weight of from 200 to 700 dalton, or mixtures of these telogens, wherein the catalyst used is a supported catalyst which contains a catalytically active amount of an oxygen-containing tungsten or molybdenum compound or mixtures of these compounds on an oxidic support material and which has been calcined at from 500 to 1000°C following the application of the precursor compounds of the oxygen-containing molybdenum and/or tungsten compounds to the support material precursor.
2. A process as claimed in claim 1, wherein the oxidic support material used is zirconium dioxide, titanium dioxide, hafnium oxide, yttrium oxide, iron oxide, aluminum oxide, tin oxide, silicon dioxide, zinc oxide or mixtures of these oxides.
3. A process as claimed in claims 1 and 2, wherein a catalyst is used which is additionally doped with oxygen-containing sulfur and/or phosphorus compounds.
4. A process as claimed in any of claims 1 to 3, wherein the supported catalyst contains from 0.1 to 50% by weight of molybdenum and/or tungsten, calculated as molybdenum trioxide or tungsten trioxide and based on the total weight of the catalyst.
5. A process as claimed in any of claims 1 to 4, where-



in a supported catalyst is used which contains from 0.05 to 10% by weight of sulfur and/or phosphorus, calculated as sulfate or phosphate and based on the total weight of the catalyst.

- 5 6. A process as claimed in any of claims 1 to 5, where-
 in zirconium dioxide is used as support material.
7. A process as claimed in any of claims 1 to 5, where-
 in titanium dioxide or mixtures of titanium dioxide
 with zirconium dioxide are used as support material.
- 10 8. A process as claimed in any of claims 1 to 7, where-
 in water or 1,4-butanediol or 1,4-butanediol/water
 mixtures are used as telogen.
9. A process as claimed in any of claims 1 to 8, where-
 in tetrahydrofuran having a telogen content of from
15 0.04 to 17 mol%, based on tetrahydrofuran, is used
 for the polymerization.
10. A process as claimed in any of claims 1 to 9, where-
 in supported catalysts are used which have been
20 prepared by impregnation of the freshly precipitated
 and dried hydroxides of zirconium, titanium,
 hafnium, yttrium, iron, aluminum, tin or zinc or
 freshly precipitated and dried silicic acid or mix-
 tures of these compounds with a solution of the
25 precursor compounds of the catalytically active
 molybdenum and/or tungsten compounds and optionally
 with sulfate-containing and/or phosphate-containing
 solutions, followed by drying and calcination at
 from 500 to 1000°C.

Preparation of polytetrahydrofuran

Abstract

A process for the preparation of polytetrahydrofuran or polytetrahydrofuran monoesters of C_1 - C_{10} monocarboxylic acids by the polymerization of tetrahydrofuran over a heterogeneous catalyst in the presence of one of the telomers water, 1,4-butanediol or polytetrahydrofuran having a molecular weight of from 200 to 700 dalton, or of a C_1 - C_{10} monocarboxylic acid or mixtures of these telomers, wherein the catalyst used is a supported catalyst which contains a catalytically active amount of an oxygen-containing tungsten or molybdenum compound or mixtures of these compounds on an oxidic support material and which has been calcined at from 500 to 1000°C following the application of the precursor compounds of the oxygen-containing molybdenum and/or tungsten compounds to the support material precursor.