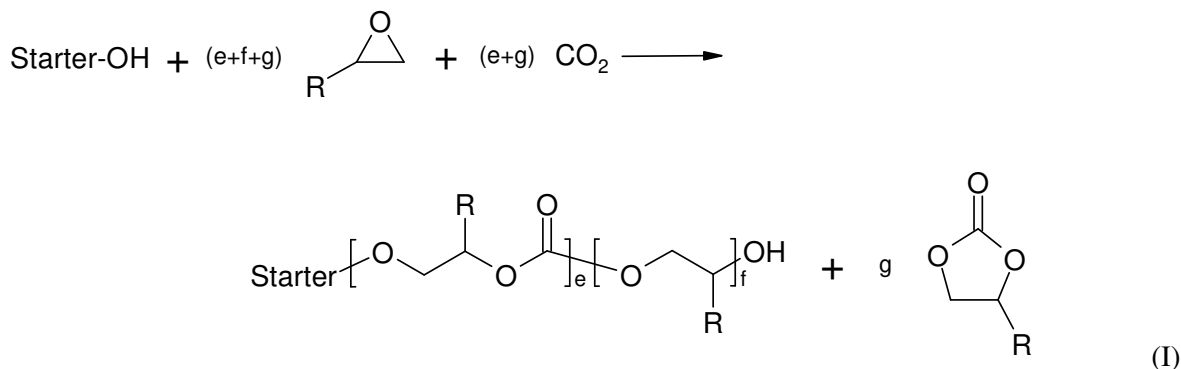


Process for producing polyether carbonate polyols

The present invention relates to a process for preparing polyethercarbonate polyols from H-functional starter compound, alkylene oxide and carbon dioxide in the presence of a double metal cyanide (DMC) catalyst. It further relates to polyethercarbonate polyols obtained by the process according to the invention.

The preparation of polyethercarbonate polyols by catalytic reaction of alkylene oxides (epoxides) and carbon dioxide in the presence of H-functional starter substances ("starters") has been the subject of intensive study for more than 40 years (e.g. Inoue et al, Copolymerization of Carbon Dioxide and Epoxide with Organometallic Compounds; Die Makromolekulare Chemie [Macromolecular Chemistry] 130, 210-220, 1969). This reaction is shown in schematic form in scheme (I), where R is an organic radical such as alkyl, alkylaryl or aryl, each of which may also contain heteroatoms, for example O, S, Si, etc., and where e, f and g are integers, and where the product shown here in scheme (I) for the polyethercarbonate polyol should merely be understood in such a way that blocks having the structure shown may in principle be present in the polyethercarbonate polyol obtained, but the sequence, number and length of the blocks and the OH functionality of the starter may vary and is not restricted to the polyethercarbonate polyol shown in scheme (I). This reaction (see scheme (I)) is highly advantageous from an environmental standpoint since this reaction is the conversion of a greenhouse gas such as CO₂ to a polymer. A further product formed, actually a by-product, is the cyclic carbonate shown in scheme (I) (for example, when R = CH₃, propylene carbonate).



EP 0 222 453 A2 discloses a process for preparing polycarbonates from alkylene oxides and carbon dioxide using a catalyst system composed of DMC catalyst and a cocatalyst such as zinc sulfate. This polymerization is initiated here by one-off contacting of a portion of the alkylene oxide with the catalyst system. Only thereafter are the remaining amount of alkylene oxide and the carbon dioxide metered in simultaneously. The amount of 60% by weight of alkylene oxide relative to the H-functional starter compound, as specified in EP 0 222 453 A2 for the activation step in examples 1 to 7, is high and has the disadvantage that this constitutes a safety risk for industrial scale applications because of the high exothermicity of the homopolymerization of alkylene oxides.

WO 2016/079065 A1 discloses a continuous process for preparing polyethercarbonate polyols, wherein a mixture of H-functional starter substances and activated DMC catalyst, alkylene oxide and carbon dioxide is metered in. However, no details of the free alkylene oxide concentration are given.

For the preparation of polyethercarbonate polyols on an industrial scale, there is a need for a method for performing the reaction in which product quality and safety are assured.

The object was therefore that of providing a process for preparing polyethercarbonate polyols which features a low concentration of free alkylene oxide in the process, a narrow molar mass distribution of the polyethercarbonate polyols obtained, and good selectivity. In addition, the process should lead to shorter dwell times, which enables a reduction in the reactor volume and lower capital costs.

It has been found that, surprisingly, the object of the invention is achieved by a process for preparing polyether carbonate polyols, comprising the step of reaction of alkylene oxide with carbon dioxide in the presence of an H-functional starter compound and double metal cyanide catalyst, **characterized in that**

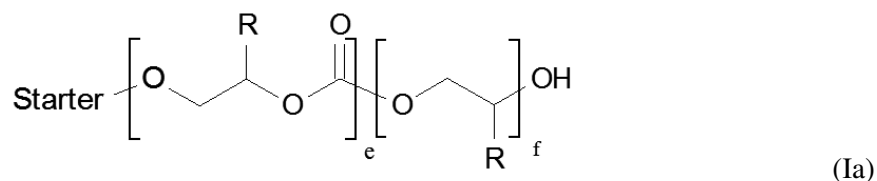
- (α) a portion of H-functional starter substance and/or suspension medium containing no H-functional groups is initially charged in a reactor, in each case together with DMC catalyst,
- (β) a portion of alkylene oxide is added to the mixture from step (α) at temperatures of 90 to 150°C, and then the addition of the alkylene oxide is stopped,
- (γ) alkylene oxide, carbon dioxide and a mixture comprising nonactivated double metal cyanide catalyst and an H-functional starter compound, where the H-functional starter compound is a polyol having a number-average molar mass according to DIN 55672-1 of 550 to 2000 g/mol, is metered continuously into the mixture resulting from (β).

In a preferred embodiment, the invention relates to a process for preparing polyether carbonate polyols, comprising the step of reaction of alkylene oxide with carbon dioxide in the presence of an H-functional starter compound and double metal cyanide catalyst, **characterized in that**

- (α) a portion of H-functional starter substance and/or suspension medium containing no H-functional groups is initially charged in a reactor, in each case optionally together with DMC catalyst,
- (β) a portion of alkylene oxide is added to the mixture from step (α) at temperatures of 90 to 150°C, and then the addition of the alkylene oxide is stopped,
- (γ) alkylene oxide, carbon dioxide and a mixture comprising nonactivated double metal cyanide catalyst and an H-functional starter compound, where the H-functional starter compound is a polyol having a number-average molar mass according to DIN 55672-1 of 550 to 2000 g/mol, is metered continuously into the mixture resulting from (β),
- (δ) the reaction mixture obtained in step (γ) remains in the reactor or is transferred continuously into a postreactor, with reduction in the content of free alkylene oxide in the reaction mixture in each case by means of further reaction under the chosen process conditions (including temperature and dwell time).

A characteristic feature of the polyethercarbonate polyols prepared in the presence of a double metal cyanide (DMC) catalyst in accordance with the invention is that they also contain ether groups

between the carbonate groups. In relation to formula (Ia), this means that the ratio of e/f is preferably from 2:1 to 1:20, more preferably from 1.5:1 to 1:10.



5 Step (α):

The process of the invention for preparing polyethercarbonate polyols by adding alkylene oxide and carbon dioxide onto H-functional starter substance comprises a step (α) .

It is possible first to initially charge the reactor with H-functional starter substance and/or a suspension medium containing no H-functional groups, preference being given to initially charging a portion of the H-functional starter substance. Subsequently, an amount of DMC catalyst, preferably in unactivated form, can be added to the reactor. The sequence of addition is not critical. It is also possible to charge the reactor firstly with the DMC catalyst and subsequently with the suspension medium. Alternatively, it is also possible first to suspend the DMC catalyst in the inert suspension medium and then to introduce the suspension into the reactor. The suspension medium provides a sufficient heat transfer area with the reactor wall or cooling elements installed in the reactor, such that the heat of reaction released can be removed very efficiently. Moreover, the suspension medium, in the event of a cooling failure, provides heat capacity, such that the temperature in this case can be kept below the breakdown temperature of the reaction mixture.

The suspension media used do not contain any H-functional groups. Suitable suspension media are any polar aprotic, weakly polar aprotic and nonpolar aprotic solvents, none of which contain any H-functional groups. Suspension media used may also be mixtures of two or more of these suspension media. The following polar aprotic solvents are mentioned here by way of example: 4-methyl-2-oxo-1,3-dioxolane (also referred to hereinafter as cyclic propylene carbonate or cPC), 1,3-dioxolan-2-one (also referred to hereinafter as cyclic ethylene carbonate or cEC), acetone, methyl ethyl ketone, acetonitrile, nitromethane, dimethyl sulfoxide, sulfolane, dimethylformamide, dimethylacetamide and *N*-methylpyrrolidone. The group of the nonpolar aprotic and weakly polar aprotic solvents includes, for example, ethers, for example dioxane, diethyl ether, methyl tert-butyl ether and tetrahydrofuran, esters, for example ethyl acetate and butyl acetate, hydrocarbons, for example pentane, n-hexane, benzene and alkylated benzene derivatives (e.g. toluene, xylene, ethylbenzene) and chlorinated hydrocarbons, for example chloroform, chlorobenzene, dichlorobenzene and carbon tetrachloride. Preferred suspension media are 4-methyl-2-oxo-1,3-dioxolane, 1,3-dioxolan-2-one, toluene, xylene, ethylbenzene, chlorobenzene and dichlorobenzene, and mixtures of two or more of these suspension media; particular preference is given to 4-methyl-2-oxo-1,3-dioxolane and 1,3-dioxolan-2-one or a mixture of 4-methyl-2-oxo-1,3-dioxolane and 1,3-dioxolan-2-one.

Likewise suitable as suspension media are aliphatic lactones, aromatic lactones, lactides, cyclic carbonates having at least three optionally substituted methylene groups between the oxygen atoms of the carbonate group, aliphatic cyclic anhydrides and aromatic cyclic anhydrides.

Aliphatic or aromatic lactones in the context of the invention are cyclic compounds containing an ester bond in the ring, preferably

4-membered lactone rings such as β -propiolactone, β -butyrolactone, β -isovalerolactone, β -caprolactone, β -isocaprolactone, β -methyl- β -valerolactone,

5-membered lactone rings such as γ -butyrolactone, γ -valerolactone, 5-methylfuran-2(3H)-one, 5-methylidenedihydrofuran-2(3H)-one, 5-hydroxyfuran-2(5H)-one, 2-benzofuran-1(3H)-one and 6-methyl-2-benzofuran-1(3H)-one,

6-membered lactone rings such as δ -valerolactone, 1,4-dioxan-2-one, dihydrocoumarin, 1H-isochromen-1-one, 8H-pyrano[3,4-b]pyridin-8-one, 1,4-dihydro-3H-isochromen-3-one, 7,8-dihydro-5H-pyrano[4,3-b]pyridin-5-one, 4-methyl-3,4-dihydro-1H-pyrano[3,4-b]pyridin-1-one, 6-hydroxy-3,4-dihydro-1H-isochromen-1-one, 7-hydroxy-3,4-dihydro-2H-chromen-2-one, 3-ethyl-1H-isochromen-1-one, 3-(hydroxymethyl)-1H-isochromen-1-one, 9-hydroxy-1H,3H-benzo[de]isochromen-1-one, 6,7-dimethoxy-1,4-dihydro-3H-isochromen-3-one and 3-phenyl-3,4-dihydro-1H-isochromen-1-one,

7-membered lactone rings such as ϵ -caprolactone, 1,5-dioxepan-2-one, 5-methyloxepan-2-one, oxepane-2,7-dione, thiepan-2-one, 5-chlorooxepan-2-one, (4*S*)-4-(propan-2-yl)oxepan-2-one, 7-butyloxepan-2-one, 5-(4-aminobutyl)oxepan-2-one, 5-phenyloxepan-2-one, 7-hexyloxepan-2-one, (5*S*,7*S*)-5-methyl-7-(propan-2-yl)oxepan-2-one, 4-methyl-7-(propan-2-yl)oxepan-2-one,

lactone rings having higher numbers of members, such as (7*E*)-oxacycloheptadec-7-en-2-one.

Particular preference is given to ϵ -caprolactone and dihydrocoumarin.

Lactides in the context of the invention are cyclic compounds containing two or more ester bonds in the ring, preferably glycolide (1,4-dioxane-2,5-dione), L-lactide (L-3,6-dimethyl-1,4-dioxane-2,5-dione), D-lactide, DL-lactide, mesolactide and 3-methyl-1,4-dioxane-2,5-dione, 3-hexyl-6-methyl-1,4-dioxane-2,5-dione, 3,6-di(but-3-en-1-yl)-1,4-dioxane-2,5-dione (in each case including optically active forms). Particular preference is given to L-lactide.

Cyclic carbonates having at least three optionally substituted methylene groups between the oxygen atoms of the carbonate group are preferably trimethylene carbonate, neopentyl glycol carbonate (5,5-dimethyl-1,3-dioxan-2-one), 2,2,4-trimethylpentane-1,3-diol carbonate, 2,2-dimethylbutane-1,3-diol carbonate, butane-1,3-diol carbonate, 2-methylpropane-1,3-diol carbonate, pentane-2,4-diol carbonate, 2-methylbutane-1,3-diol carbonate, TMP monoallyl ether carbonate, pentaerythritol diallyl ether carbonate, 5-(2-hydroxyethyl)-1,3-dioxan-2-one, 5-[2-(benzyloxy)ethyl]-1,3-dioxan-2-one, 4-ethyl-1,3-dioxolan-2-one, 1,3-dioxolan-2-one, 5-ethyl-5-methyl-1,3-dioxan-2-one, 5,5-

diethyl-1,3-dioxan-2-one, 5-methyl-5-propyl-1,3-dioxan-2-one, 5-(phenylamino)-1,3-dioxan-2-one and 5,5-dipropyl-1,3-dioxan-2-one. Particular preference is given to trimethylene carbonate and neopentyl glycol carbonate.

Cyclic anhydrides are preferably maleic anhydride, phthalic anhydride, cyclohexane-1,2-dicarboxylic anhydride, diphenic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, norbornenedioic anhydride and chlorination products thereof, succinic anhydride, glutaric anhydride, diglycolic anhydride, 1,8-naphthalic anhydride, succinic anhydride, dodecenylsuccinic anhydride, tetradecenylsuccinic anhydride, hexadecenylsuccinic anhydride, octadecenylsuccinic anhydride, 3- and 4-nitrophthalic anhydride, tetrachlorophthalic anhydride, tetrabromophthalic anhydride, itaconic anhydride, dimethylmaleic anhydride, allylnorbornenedioic anhydride, 3-methylfuran-2,5-dione, 3-methyldihydrofuran-2,5-dione, dihydro-2H-pyran-2,6(3H)-dione, 1,4-dioxane-2,6-dione, 2H-pyran-2,4,6(3H,5H)-trione, 3-ethyldihydrofuran-2,5-dione, 3-methoxydihydrofuran-2,5-dione, 3-(prop-2-en-1-yl)dihydrofuran-2,5-dione, N-(2,5-dioxotetrahydrofuran-3-yl)formamide and 3[(2E)-but-2-en-1-yl]dihydrofuran-2,5-dione. Particular preference is given to succinic anhydride, maleic anhydride and phthalic anhydride.

The suspension medium used may also be a mixture of two or more of the suspension media mentioned. Most preferably, the suspension medium used in step (α) is at least one compound selected from the group consisting of 4-methyl-2-oxo-1,3-dioxolane, 1,3-dioxolan-2-one, acetone, methyl ethyl ketone, acetonitrile, nitromethane, dimethyl sulfoxide, sulfolane, dimethylformamide, dimethylacetamide, N-methylpyrrolidone, dioxane, diethyl ether, methyl tert-butyl ether, tetrahydrofuran, ethyl acetate, butyl acetate, pentane, n-hexane, benzene, toluene, xylene, ethylbenzene, chloroform, chlorobenzene, dichlorobenzene, carbon tetrachloride, ϵ -caprolactone, dihydrocoumarin, trimethylene carbonate, neopentyl glycol carbonate, 3,6-dimethyl-1,4-dioxane-2,5-dione, succinic anhydride, maleic anhydride and phthalic anhydride.

In one embodiment of the invention, in step (α), a suspension medium containing no H-functional groups is initially charged in the reactor, optionally together with DMC catalyst, without including any H-functional starter substance in the initial reactor charge. Alternatively, it is also possible in step (α) to initially charge the reactor with a suspension medium containing no H-functional groups, and additionally with a portion of the H-functional starter substance(s) and optionally with DMC catalyst.

The DMC catalyst is preferably used in an amount such that the content of DMC catalyst in the reaction product resulting from step (γ) is 10 to 10 000 ppm, more preferably 20 to 5000 ppm, and most preferably 50 to 500 ppm.

In a preferred embodiment, in step (α), inert gas (for example argon or nitrogen), an inert gas/carbon dioxide mixture or carbon dioxide is introduced into the resulting mixture (i) of a portion of the H-functional starter substance and/or suspension medium and (ii) DMC catalyst at a temperature of

90°C to 150°C, more preferably of 100°C to 140°C, and at the same time a reduced pressure (absolute) of 10 mbar to 800 mbar, more preferably of 50 mbar to 200 mbar, is applied.

In an alternative preferred embodiment, in step (α), the resulting mixture (i) of a portion of the H-functional starter substance(s) and/or suspension medium and (ii) DMC catalyst is contacted at least once, preferably three times, at a temperature of 90°C to 150°C, more preferably of 100°C to 140°C, with 1.5 bar to 10 bar (absolute), more preferably 3 bar to 6 bar (absolute), of an inert gas (for example argon or nitrogen), an inert gas/carbon dioxide mixture or carbon dioxide and then the gauge pressure is reduced in each case to about 1 bar (absolute).

The DMC catalyst can be added in solid form or as a suspension in a suspension medium or in a mixture of at least two suspension media.

In a further preferred embodiment, in step (α),

(α -I) a portion of the H-functional starter substance and/or suspension medium is initially charged and

(α -II) the temperature of the portion of the H-functional starter substance and/or the suspension medium is brought to 50 to 200°C, preferably 80 to 160°C, more preferably 100 to 140°C, and/or the pressure in the reactor is lowered to less than 500 mbar, preferably 5 mbar to 100 mbar, in the course of which an inert gas stream (for example of argon or nitrogen), an inert gas/carbon dioxide stream or a carbon dioxide stream is optionally passed through the reactor,

wherein the double metal cyanide catalyst is added to the portion of the H-functional starter substance and/or suspension medium in step (α -I) or immediately thereafter in step (α -II), and

wherein the suspension medium contains no H-functional groups.

Step (β):

Step (β) serves to activate the DMC catalyst. This step (β) is preferably conducted under a carbon dioxide atmosphere. Activation in the context of this invention refers to a step wherein a portion of alkylene oxide is added to the DMC catalyst suspension at temperatures of 90°C to 150°C and the addition of the alkylene oxide is then interrupted, a subsequent exothermic chemical reaction causing an evolution of heat to be observed which can lead to a temperature spike ("hotspot") and the conversion of alkylene oxide and optionally CO₂ causing a pressure drop to be observed in the reactor. The process step of activation is the period of time from the addition of the portion of alkylene oxide, optionally in the presence of CO₂, to the DMC catalyst until the occurrence of the evolution of heat. Optionally, the portion of the alkylene oxide can be added to the DMC catalyst in a plurality of individual steps, optionally in the presence of CO₂, and then the addition of the alkylene oxide can be stopped in each case. In this case, the process step of activation comprises the period from the addition of the first portion of alkylene oxide, optionally in the presence of CO₂, to the DMC catalyst until the occurrence of the evolution of heat after addition of the last portion of alkylene

oxide. In general, the activation step may be preceded by a step for drying the DMC catalyst and optionally the H-functional starter substance at elevated temperature and/or reduced pressure, optionally with passage of an inert gas through the reaction mixture.

5 The alkylene oxide (and optionally the carbon dioxide) can in principle be metered in in different ways. The metered addition can be commenced from the vacuum or at a previously chosen supply pressure. The supply pressure is preferably established by introduction of carbon dioxide, where the pressure (in absolute terms) is 5 mbar to 100 bar, preferably 10 mbar to 50 bar and more preferably 20 mbar to 50 bar.

10 In a preferred embodiment, the amount of alkylene oxide used in the activation in step (β) is 0.1% to 25.0% by weight, preferably 1.0% to 20.0% by weight, more preferably 2.0% to 16.0% by weight (based on the amount of suspension medium used in step (α)). The alkylene oxide can be added in one step or in two or more portions. Preferably, addition of a portion of the alkylene oxide is followed by interruption of the addition of the alkylene oxide until the occurrence of evolution of heat, and only then is the next portion of alkylene oxide added.

15 Step (γ):

According to the invention, in step (γ), alkylene oxide, carbon dioxide and a mixture comprising nonactivated DMC catalyst and an H-functional starter compound, where the H-functional starter compound is a polyol having a number-average molar mass of 550 to 2000 g/mol, is metered continuously into a reactor.

20 The metered addition of the carbon dioxide, of the alkylene oxide, of the mixture comprising non-activated DMC catalyst and an H-functional starter compound, where the H-functional starter compound is a polyol having a number average molar mass of 550 to 2000 g/mol, and optionally also further H-functional starter compound, can be effected simultaneously or sequentially (in portions); for example, it is possible to add the entire amount of carbon dioxide, the entire amount of
25 mixture comprising nonactivated DMC catalyst and an H-functional starter compound, where the H-functional starter compound is a polyol having a number average molar mass of 550 to 2000 g/mol, the amount of further H-functional starter substances and/or the amount of alkylene oxide metered in in step (γ) all at once or continuously. The term "continuously" as used here can be defined as a mode of addition of a reactant such that a concentration of the reactant effective for the
30 copolymerization is maintained, meaning that, for example, the metered addition can be effected with a constant metering rate, with a varying metering rate or in portions.

It is possible, during the addition of the alkylene oxide, the mixture comprising nonactivated DMC catalyst and an H-functional starter compound, where the H-functional starter compound is a polyol having a number-average molar mass of 550 to 2000 g/mol, and/or of further H-functional starter
35 compounds, to increase or to lower the CO₂ pressure gradually or stepwise, or to leave it constant. The total pressure is preferably kept constant during the reaction by metered addition of further

carbon dioxide. The metered addition of alkylene oxide, the mixture comprising nonactivated DMC catalyst and an H-functional starter compound, where the H-functional starter compound is a polyol having a number-average molar mass of 550 to 2000 g/mol, and/or of further H-functional starter substance is effected simultaneously or sequentially with the metered addition of carbon dioxide. It is possible to meter in the alkylene oxide at a constant metering rate or to increase or lower the metering rate gradually or in steps or to add the alkylene oxide in portions. The alkylene oxide is preferably added to the reaction mixture at a constant addition rate. If two or more alkylene oxides are used for synthesis of the polyethercarbonate polyols, the alkylene oxides can be metered in individually or as a mixture. The metered addition of the alkylene oxides, of the mixture containing nonactivated DMC catalysts and an H-functional starter compound, where the H-functional starter compound is a polyol having a number-average molar mass of 550 to 2000 g/mol, or of further H-functional starter substances, can be effected simultaneously or sequentially (in portions) via respectively separate (metered) additions or via one or more metered additions, wherein the alkylene oxide or the further H-functional starter substances may be metered in individually or as a mixture. It is possible via the mode and/or sequence of metered addition of the further H-functional starter substances, the alkylene oxides, the mixture containing nonactivated DMC catalyst and an H-functional starter compound, where the H-functional starter compound is a polyol having a number-average molar mass of 550 to 2000 g/mol, and/or the carbon dioxide, to synthesize statistical, alternating, block or gradient polyethercarbonate polyols. In a preferred embodiment, the process is conducted as a semibatchwise process and in step (γ), the metered addition of the H-functional starter substance is ended at a juncture prior to the addition of the alkylene oxide.

Preferably, an excess of carbon dioxide is used, based on the calculated amount of carbon dioxide incorporated in the polyethercarbonate polyol, since an excess of carbon dioxide is advantageous because of the low reactivity of carbon dioxide. The amount of carbon dioxide can be fixed via the total pressure (in absolute terms) (in the context of the invention, the total pressure (in absolute terms) is defined as the sum total of the partial pressures of the alkylene oxide and carbon dioxide used) under the particular reaction conditions. An advantageous total pressure (absolute) for the copolymerization for preparing the polyether carbonate polyols has been found to be in the range from 5 to 120 bar, preferably 10 to 110 bar, more preferably from 20 to 100 bar. It is possible to feed in the carbon dioxide continuously or discontinuously. This depends on how quickly the alkylene oxides are consumed and on whether the product is to include any CO₂-free polyether blocks. The amount of the carbon dioxide (reported as pressure) can likewise be varied during addition of the alkylene oxides. CO₂ may be metered into the reactor in the gaseous state or in the liquid state. CO₂ can also be added to the reactor in solid form and then be converted to the gaseous, dissolved, liquid and/or supercritical state under the chosen reaction conditions. Carbon dioxide may be metered here into the gas phase or the liquid phase.

One feature of a preferred embodiment of the process of the invention is that in step (γ) the entire amount of the H-functional starter substance is added. This addition can be effected at a constant metering rate, with a varying metering rate, or in portions.

For the process of the invention, it has additionally been found that the copolymerization (step (γ))
5 for preparation of the polyethercarbonate polyols is conducted advantageously at 50°C to 150°C, preferably at 60°C to 145°C, more preferably at 70°C to 140°C and most preferably at 90°C to 130°C. If temperatures are set below 50°C, the reaction generally becomes very slow. At temperatures above 150°C, the amount of unwanted by-products rises significantly.

Steps (α), (β) and (γ) can be performed in the same reactor, or each can be performed separately in
10 different reactors. A particularly preferred reactor site is the stirred tank.

Polyethercarbonate polyols can be prepared in a stirred tank, in which case the stirred tank, according to the design and mode of operation, is cooled via the reactor jacket, internal cooling surfaces and/or cooling surfaces within a pumped circulation system. Both in semi-batchwise application, in which the product is not removed until after the end of the reaction, and in continuous application, in which
15 the product is removed continuously, particular attention should be paid to the metering rate of the alkylene oxide. Said rate should be adjusted such that despite the inhibiting effect of the carbon dioxide the alkylene oxides react sufficiently rapidly. The concentration of free alkylene oxides in the reaction mixture during the activation step (step β) is preferably > 0% to 100% by weight, more preferably > 0% to 50% by weight, most preferably > 0% to 20% by weight (in each case based on
20 the weight of the reaction mixture). The concentration of free alkylene oxides in the reaction mixture during the reaction (step γ) is preferably > 0% to 40% by weight, more preferably > 0% to 25% by weight, most preferably > 0% to 15% by weight (based in each case on the weight of the reaction mixture).

The polyethercarbonate polyols are preferably prepared in a continuous process.

The invention therefore also provides a process wherein, in step (γ), a mixture comprising an
25 activated DMC catalyst and an H-functional starter compound, where the H-functional starter compound is a polyol having a number-average molar mass of 550 to 2000 g/mol, and alkylene oxide are metered continuously into a reactor in the presence of carbon dioxide ("copolymerization"), and wherein the resulting reaction mixture (containing the reaction product) is removed continuously
30 from the reactor.

The amount of DMC catalyst used is preferably chosen such that the content of DMC catalyst in the reaction product resulting from step (γ) is 10 to 10 000 ppm, more preferably 20 to 5000 ppm, and most preferably 50 to 500 ppm.

It is preferable when steps (α) and (β) are performed in a first reactor, and the resulting reaction
35 mixture is then transferred into a second reactor for the copolymerization of step (γ). However, it is also possible to perform steps (α), (β) and (γ) in one reactor.

- The term "continuously" used here can be defined as the mode of addition of a relevant catalyst or reactant such that an essentially continuous effective concentration of the DMC catalyst or the reactant is maintained. Catalyst feeding may be effected in a truly continuous manner or in relatively tightly spaced increments. Equally, continuous starter addition may be effected in a truly continuous manner or in increments. There would be no departure from the present process in adding a DMC catalyst or reactants incrementally such that the concentration of the materials added drops essentially to zero for a period of time before the next incremental addition. However, it is preferable for the DMC catalyst concentration to be kept substantially at the same concentration during the main portion of the course of the continuous reaction, and for starter substance to be present during the main portion of the copolymerization process. Incremental addition of DMC catalyst and/or reactant that does not significantly affect the characteristics of the product is nevertheless "continuous" in the sense in which the term is used here. It is possible, for example, to provide a recycling loop in which a portion of the reacting mixture is recycled to a prior point in the process, thus smoothing out discontinuities caused by incremental additions.
- The dwell time of the reaction mixture in the reactor is preferably 0.5 to 5.0 hours, more preferably 1.0 to 4.0 hours, especially preferably 1.5 to 3.5 hours. The dwell time is the average dwell time in an ideally mixed reactor.

Step (δ)

- In the optional step (δ), the reaction mixture resulting from step (γ), generally containing a content of 0.05% by weight to 10% by weight of alkylene oxide, can be subjected to a postreaction in the reactor or can be continuously transferred into a postreactor for postreaction, with reduction of the free alkylene oxide content by way of postreaction. In step (δ), by way of postreaction, the free alkylene oxide content is preferably reduced to less than 0.5% by weight, more preferably to less than 0.1% by weight, in the reaction mixture.
- When the reaction mixture resulting from step (γ) remains in the reactor, the reaction mixture is preferably kept at a temperature of 60°C to 140°C for 10 min to 24 h, more preferably at a temperature of 80°C to 130°C for 1 h to 12 h, for postreaction. The reaction mixture is preferably stirred for this period until the free alkylene oxide content has fallen to less than 0.5% by weight, more preferably to less than 0.1% by weight, in the reaction mixture. The consumption of free alkylene oxide and optionally carbon dioxide generally causes the pressure in the reactor to fall during the postreaction in step (δ) until a constant value has been achieved.

- The postreactor used may, for example, be a tubular reactor, a loop reactor or a stirred tank. The pressure in this postreactor is preferably at the same pressure as in the reaction apparatus in which reaction step (γ) is performed. The pressure in the downstream reactor can, however, also be selected at a higher or lower level. In a further preferred embodiment, the carbon dioxide, after reaction step (γ), is fully or partly released and the downstream reactor is operated at standard pressure or a slightly

elevated pressure. The temperature in the downstream reactor is preferably 50°C to 150°C and more preferably 80°C to 140°C.

The postreactor used is preferably a tubular reactor, it being possible to use, for example, a single tubular reactor or else a cascade of a plurality of tubular reactors arranged in parallel or in a linear series arrangement. The dwell time in the tubular reactor is preferably between 5 min and 10 h, more preferably between 10 min and 5 h.

DMC catalyst

DMC catalysts for use in the homopolymerization of alkylene oxides are known in principle from the prior art (see, for example, US-A 3 404 109, US-A 3 829 505, US-A 3 941 849 and US-A 5 158 922). DMC catalysts, which are described, for example, in US-A 5 470 813, EP-A 700 949, EP-A 743 093, EP-A 761 708, WO 97/40086, WO 98/16310 and WO 00/47649, have a very high activity and enable the preparation of polyethercarbonate polyols at very low catalyst concentrations, such that there is generally no need to separate the catalyst from the finished product. A typical example is that of the highly active DMC catalysts which are described in EP-A 700 949 and contain not only a double metal cyanide compound (e.g. zinc hexacyanocobaltate(III)) and an organic complex ligand (e.g. tert-butanol) but also a polyether having a number-average molecular weight greater than 500 g/mol.

The DMC catalysts are preferably obtained by

- (i) reacting an aqueous solution of a metal salt with the aqueous solution of a metal cyanide salt in the presence of one or more organic complex ligands, e.g. an ether or alcohol, in a first step,
 - (ii) removing the solid from the suspension obtained from (i) by known techniques (such as centrifugation or filtration) in a second step,
 - (iii) optionally washing the isolated solid with an aqueous solution of an organic complex ligand (for example by resuspending and subsequent reisolating by filtration or centrifugation) in a third step,
 - (iv) subsequently drying the solid obtained at temperatures of in general 20-120°C and at pressures of in general 0.1 mbar to atmospheric pressure (1013 mbar), optionally after pulverizing,
- and wherein, in the first step or immediately after the precipitation of the double metal cyanide compound (second step), one or more organic complex ligands, preferably in excess (based on the double metal cyanide compound), and optionally further complex-forming components are added.

The double metal cyanide compounds present in the DMC catalysts are the reaction products of water-soluble metal salts and water-soluble metal cyanide salts.

For example, an aqueous solution of zinc chloride (preferably in excess based on the metal cyanide salt, for example potassium hexacyanocobaltate) and potassium hexacyanocobaltate are mixed and then dimethoxyethane (glyme) or tert-butanol (preferably in excess, based on zinc hexacyanocobaltate) is added to the suspension formed.

Metal salts suitable for preparation of the double metal cyanide compounds preferably have the general formula (II)



5 where

M is selected from the metal cations Zn^{2+} , Fe^{2+} , Ni^{2+} , Mn^{2+} , Co^{2+} , Sr^{2+} , Sn^{2+} , Pb^{2+} and Cu^{2+} ; M is preferably Zn^{2+} , Fe^{2+} , Co^{2+} or Ni^{2+} ,

X are one or more (i.e. different) anions, preferably an anion selected from the group of halides (i.e. fluoride, chloride, bromide, iodide), hydroxide, sulfate, carbonate, cyanate, thiocyanate, isocyanate, isothiocyanate, carboxylate, oxalate and nitrate;

n is 1 when X = sulfate, carbonate or oxalate and

n is 2 when X = halide, hydroxide, carboxylate, cyanate, thiocyanate, isocyanate, isothiocyanate or nitrate,

15 or suitable metal salts have the general formula (III)



where

M is selected from the metal cations Fe^{3+} , Al^{3+} , Co^{3+} and Cr^{3+} ,

20 X are one or more (i.e. different) anions, preferably an anion selected from the group of halides (i.e. fluoride, chloride, bromide, iodide), hydroxide, sulfate, carbonate, cyanate, thiocyanate, isocyanate, isothiocyanate, carboxylate, oxalate and nitrate;

r is 2 when X = sulfate, carbonate or oxalate and

r is 1 when X = halide, hydroxide, carboxylate, cyanate, thiocyanate, isocyanate, isothiocyanate or nitrate,

or suitable metal salts have the general formula (IV)



30 where

M is selected from the metal cations Mo^{4+} , V^{4+} and W^{4+} ,

X are one or more (i.e. different) anions, preferably an anion selected from the group of halides (i.e. fluoride, chloride, bromide, iodide), hydroxide, sulfate, carbonate, cyanate, thiocyanate, isocyanate, isothiocyanate, carboxylate, oxalate and nitrate;

35 s is 2 when X = sulfate, carbonate or oxalate and

s is 4 when X = halide, hydroxide, carboxylate, cyanate, thiocyanate, isocyanate, isothiocyanate or nitrate,

or suitable metal salts have the general formula (V)



where

5 M is selected from the metal cations Mo^{6+} and W^{6+} ,

X are one or more (i.e. different) anions, preferably an anion selected from the group of halides (i.e. fluoride, chloride, bromide, iodide), hydroxide, sulfate, carbonate, cyanate, thiocyanate, isocyanate, isothiocyanate, carboxylate, oxalate and nitrate;

t is 3 when X = sulfate, carbonate or oxalate and

10 t is 6 when X = halide, hydroxide, carboxylate, cyanate, thiocyanate, isocyanate, isothiocyanate or nitrate.

Examples of suitable metal salts are zinc chloride, zinc bromide, zinc iodide, zinc acetate, zinc acetylacetonate, zinc benzoate, zinc nitrate, iron(II) sulfate, iron(II) bromide, iron(II) chloride,
15 iron(III) chloride, cobalt(II) chloride, cobalt(II) thiocyanate, nickel(II) chloride and nickel(II) nitrate. It is also possible to use mixtures of different metal salts.

Metal cyanide salts suitable for preparation of the double metal cyanide compounds preferably have the general formula (VI)

20



where

M' is selected from one or more metal cations from the group consisting of Fe(II), Fe(III), Co(II), Co(III), Cr(II), Cr(III), Mn(II), Mn(III), Ir(III), Ni(II), Rh(III), Ru(II), V(IV) and V(V); M' is
25 preferably one or more metal cations from the group consisting of Co(II), Co(III), Fe(II), Fe(III), Cr(III), Ir(III) and Ni(II),

Y is selected from one or more metal cations from the group consisting of alkali metal (i.e. Li^+ , Na^+ , K^+ , Rb^+) and alkaline earth metal (i.e. Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}),

A is selected from one or more anions from the group consisting of halides (i.e. fluoride, chloride, bromide, iodide), hydroxide, sulfate, carbonate, cyanate, thiocyanate, isocyanate, isothiocyanate,
30 carboxylate, azide, oxalate or nitrate, and

a, b and c are integers, the values for a, b and c being selected such as to ensure the electronic neutrality of the metal cyanide salt; a is preferably 1, 2, 3 or 4; b is preferably 4, 5 or 6; c preferably has the value 0.

35

Examples of suitable metal cyanide salts are sodium hexacyanocobaltate(III), potassium hexacyanocobaltate(III), potassium hexacyanoferrate(II), potassium hexacyanoferrate(III), calcium hexacyanocobaltate(III) and lithium hexacyanocobaltate(III).

Preferred double metal cyanide compounds present in the DMC catalysts are compounds of the general formula (VII)



where M is as defined in formula (II) to (V) and

M' is as defined in formula (VI), and

x, x', y and z are integers and are selected such as to ensure the electroneutrality of the double metal cyanide compound.

10

It is preferable when

x = 3, x' = 1, y = 6 and z = 2,

M = Zn(II), Fe(II), Co(II) or Ni(II) and

M' = Co(III), Fe(III), Cr(III) or Ir(III).

15

Examples of suitable double metal cyanide compounds a) are zinc hexacyanocobaltate(III), zinc hexacyanoiridate(III), zinc hexacyanoferrate(III) and cobalt(II) hexacyanocobaltate(III). Further examples of suitable double metal cyanide compounds can be found, for example, in US 5 158 922 (column 8, lines 29-66). Particular preference is given to using zinc hexacyanocobaltate(III).

20

The organic complex ligands added in the preparation of the DMC catalysts are disclosed, for example, in US 5 158 922 (see especially column 6, lines 9 to 65), US 3 404 109, US 3 829 505, US 3 941 849, EP-A 700 949, EP-A 761 708, JP 4 145 123, US 5 470 813, EP-A 743 093 and WO-A 97/40086). The organic complex ligands used are, for example, water-soluble organic compounds containing heteroatoms such as oxygen, nitrogen, phosphorus or sulfur, which can form complexes with the double metal cyanide compound. Preferred organic complex ligands are alcohols, aldehydes, ketones, ethers, esters, amides, ureas, nitriles, sulfides and mixtures thereof. Particularly preferred organic complex ligands are aliphatic ethers (such as dimethoxyethane), water-soluble aliphatic alcohols (such as ethanol, isopropanol, n-butanol, isobutanol, sec-butanol, tert-butanol, 2-methyl-3-buten-2-ol and 2-methyl-3-butyne-2-ol), compounds containing both aliphatic or cycloaliphatic ether groups and aliphatic hydroxyl groups (for example ethylene glycol mono-tert-butyl ether, diethylene glycol mono-tert-butyl ether, tripropylene glycol monomethyl ether and 3-methyl-3-oxetanemethanol). Most preferred organic complex ligands are selected from one or more compounds of the group consisting of dimethoxyethane, tert-butanol, 2-methyl-3-buten-2-ol, 2-methyl-3-butyne-2-ol, ethylene glycol mono-tert-butyl ether and 3-methyl-3-oxetanemethanol.

25

30

35

Optionally used in the preparation of the DMC catalysts are one or more complex-forming component(s) from the compound classes of the polyethers, polyesters, polycarbonates, polyalkylene

glycol sorbitan esters, polyalkylene glycol glycidyl ethers, polyacrylamide, poly(acrylamide-co-acrylic acid), polyacrylic acid, poly(acrylic acid-co-maleic acid), polyacrylonitrile, polyalkylacrylates, polyalkylmethacrylates, polyvinyl methyl ether, polyvinyl ethyl ether, polyvinyl acetate, polyvinyl alcohol, poly-N-vinylpyrrolidone, poly(N-vinylpyrrolidone-co-acrylic acid),
5 polyvinyl methyl ketone, poly(4-vinylphenol), poly(acrylic acid-co-styrene), oxazoline polymers, polyalkyleneimines, maleic acid and maleic anhydride copolymers, hydroxyethyl cellulose and polyacetals, or of the glycidyl ethers, glycosides, carboxylic esters of polyhydric alcohols, gallic acid or the salts, esters or amides thereof, cyclodextrins, phosphorus compounds, α,β -unsaturated carboxylic esters or ionic surface- or interface-active compounds.

10

Preferably, in the preparation of the DMC catalysts, in the first step, the aqueous solutions of the metal salt (e.g. zinc chloride), used in a stoichiometric excess (at least 50 mol%) based on metal cyanide salt (i.e. at least a molar ratio of metal salt to metal cyanide salt of 2.25:1.00), and of the metal cyanide salt (e.g. potassium hexacyanocobaltate) are converted in the presence of the organic
15 complex ligand (e.g. tert-butanol), forming a suspension containing the double metal cyanide compound (e.g. zinc hexacyanocobaltate), water, excess metal salt and the organic complex ligand.

20

The organic complex ligand may be present in the aqueous solution of the metal salt and/or of the metal cyanide salt or it is added directly to the suspension obtained after precipitation of the double
20 metal cyanide compound. It has been found to be advantageous to mix the metal salt and the metal cyanide salt aqueous solutions and the organic complex ligand by stirring vigorously. Optionally, the suspension formed in the first step is subsequently treated with a further complex-forming component. This complex-forming component is preferably used in a mixture with water and organic complex ligand. A preferred process for performing the first step (i.e. the preparation of the
25 suspension) is effected using a mixing nozzle, more preferably using a jet disperser as described in WO-A 01/39883.

30

In the second step, the solid (i.e. the precursor of the catalyst) is isolated from the suspension by known techniques, such as centrifugation or filtration.
30
In a preferred execution variant, the isolated solid is subsequently washed in a third process step with an aqueous solution of the organic complex ligand (for example by resuspension and subsequent reisolation by filtration or centrifugation). In this way, it is possible to remove, for example, water-soluble by-products such as potassium chloride from the catalyst. The amount of the organic complex
35 ligand in the aqueous wash solution is preferably between 40% and 80% by weight, based on the overall solution.

A further complex-forming component is optionally added to the aqueous wash solution in the third step, preferably in the range between 0.5% and 5% by weight, based on the overall solution.

It is also advantageous to wash the isolated solids more than once. It is preferable when said solids
5 are washed with an aqueous solution of the organic complex ligand (for example with an aqueous solution of tert-butanol) in a first washing step (iii-1) (for example by resuspension and subsequent reisolation by filtration or centrifugation), in order thus to remove, for example, water-soluble by-products such as potassium chloride from the catalyst. More preferably, the amount of the organic complex ligand (for example tert-butanol) in the aqueous wash solution is between 40% and 80% by
10 weight, based on the overall solution for the first washing step. In the further washing steps (iii-2), either the first washing step is repeated one or more times, preferably one to three times, or, preferably, a nonaqueous solution, for example a mixture or solution of organic complex ligands (for example tert-butanol) and further complex-forming component (preferably in the range between 0.5% and 5% by weight, based on the total amount of the wash solution in step (iii-2)), is used as a
15 washing solution, and the solids are washed with it one or more times, preferably one to three times.

The isolated and optionally washed solid is subsequently dried, optionally after pulverization, at temperatures of generally 20-100°C and at pressures of generally 0.1 mbar to standard pressure (1013 mbar).

20

A preferred process for isolation of the DMC catalysts from the suspension by filtration, filtercake washing and drying is described in WO-A 01/80994.

After performance of the process of the invention for preparing the polyethercarbonate polyol, the
25 resulting reaction mixture generally comprises the DMC catalyst in the form of finely dispersed solid particles. It may therefore be desirable to remove the DMC catalyst as completely as possible from the resulting reaction mixture. The removal of the DMC catalyst firstly has the advantage that the resulting polyethercarbonate polyol achieves industry- or certification-relevant limits, for example in terms of metal contents or in terms of other emissions resulting from activated catalyst remaining
30 in the product, and secondly facilitates recovery of the DMC catalyst.

The DMC catalyst may be removed very substantially or completely using various methods. The DMC catalyst can be separated from the polyethercarbonate polyol, for example, using membrane filtration (nanofiltration, ultrafiltration or crossflow filtration), using cake filtration, using precoat filtration or by centrifugation.

35 Preferably, removal of the DMC catalyst is accomplished by a multistage process consisting of at least two steps.

For example, in a first step, the reaction mixture to be filtered is divided in a first filtration step into a larger substream (filtrate) in which a majority of the catalyst or all the catalyst has been removed,

and a smaller residual stream (retentate) comprising the removed catalyst. In a second step, the residual stream is then subjected to a dead end filtration. This affords a further filtrate stream in which a majority of the catalyst or all the catalyst has been removed, and a damp to very substantially dry catalyst residue.

- 5 Alternatively, the catalyst present in the polyethercarbonate polyol can be subjected in a first step to an adsorption, agglomeration/coagulation and/or flocculation, followed by, in a second step or a plurality of subsequent steps, the separation of the solid phase from the polyethercarbonate polyol. Suitable adsorbents for mechanical-physical and/or chemical adsorption include activated or nonactivated aluminas and fuller's earths (sepiolite, montmorillonite, talc etc.), synthetic silicates,
- 10 activated carbon, silicas/diatomaceous earths and activated silicas/diatomaceous earths in typical ranges of amount of 0.1% by weight to 2% by weight, preferably 0.8% by weight to 1.2% by weight, based on the polyethercarbonate polyol, at temperatures of from 60°C to 140°C, preferably 90°C to 110°C, and dwell times of 20 min to 100 min, preferably 40 min to 80 min, it being possible to carry out the adsorption step, including blending of the adsorbent, in batchwise or continuous fashion.
- 15 A preferred process for separating this solid phase (consisting, for example, of adsorbent and DMC catalyst) from the polyethercarbonate polyol is precoat filtration. In this method, depending on the filtration characteristics, which are determined by the particle size distribution of the solid phase to be removed, by the average specific resistance of the resulting filtercake and by the total resistance of the precoat layer and filtercake, the filter surface is "precoated" with a permeable filtration aid
- 20 (for example inorganic: Celite, perlite; organic: cellulose) having a layer thickness of 20 mm to 250 mm, preferably 100 mm to 200 mm. The majority of the solid phase (consisting, for example, of adsorbent and DMC catalyst) is removed at the surface of the precoat layer in combination with depth filtration of the smaller particles within the precoat layer. The temperature of the crude product to be filtered is in the range from 50°C to 120°C, preferably 70°C to 100°C.
- 25 In order to ensure a sufficient flow of product through the precoat layer and the cake layer growing thereon, the cake layer and a small part of the precoat layer may be removed (periodically or continuously) using a scraper or blade and removed from the process. This scraper/blade is moved at minimal advance rates of about 20 µm/min-500 µm/min, preferably in the range of 50 µm/min-150 µm/min.
- 30 As soon as the precoat layer has been very substantially or completely removed by this process, the filtration is stopped and a new precoat layer is applied to the filter surface. In this case, the filtration aid may be suspended, for example, in cyclic propylene carbonate.
- This precoat filtration is typically conducted in vacuum drum filters. In order to achieve industrially relevant filtrate throughputs in the range from 0.1 m³/(m²•h) to 5 m³/(m²•h) in the case of a viscous
- 35 feed stream, the drum filter may also be executed as a pressure drum filter with pressure differentials of up to 6 bar and more between the medium to be filtered and the filtrate side.

In principle, the DMC catalyst may be removed from the resulting reaction mixture in the process of the invention either before removal of volatile constituents (for example cyclic propylene carbonate) or after the removal of volatile constituents.

In addition, the separation of the DMC catalyst from the resulting reaction mixture from the process of the invention may be conducted with or without the further addition of a solvent (especially cyclic propylene carbonate) for the purpose of lowering the viscosity before or during the individual steps of catalyst removal described.

As well as the DMC catalysts based on zinc hexacyanocobaltate ($\text{Zn}_3[\text{Co}(\text{CN})_6]_2$) that are used with preference, it is also possible to use other metal complex catalysts based on the metals zinc and/or cobalt that are known to those skilled in the art from the prior art for the copolymerization of epoxides and carbon dioxide for the process of the invention. This especially includes what are called zinc glutarate catalysts (described, for example, in M. H. Chisholm et al., *Macromolecules* 2002, 35, 6494), what are called zinc diiminate catalysts (described, for example, in S. D. Allen, *J. Am. Chem. Soc.* 2002, 124, 14284), what are called cobalt salen catalysts (described, for example, in US 7,304,172 B2, US 2012/0165549 A1), and bimetallic zinc complexes having macrocyclic ligands (described, for example, in M. R. Kember et al., *Angew. Chem., Int. Ed.*, 2009, 48, 931).

Alkylene oxide

In general, it is possible to use alkylene oxides (epoxides) having 2-24 carbon atoms for the process of the invention. The alkylene oxides having 2-24 carbon atoms are, for example, one or more compounds selected from the group consisting of ethylene oxide, propylene oxide, 1-butene oxide, 2,3-butene oxide, 2-methyl-1,2-propene oxide (isobutene oxide), 1-pentene oxide, 2,3-pentene oxide, 2-methyl-1,2-butene oxide, 3-methyl-1,2-butene oxide, 1-hexene oxide, 2,3-hexene oxide, 3,4-hexene oxide, 2-methyl-1,2-pentene oxide, 4-methyl-1,2-pentene oxide, 2-ethyl-1,2-butene oxide, 1-heptene oxide, 1-octene oxide, 1-nonene oxide, 1-decene oxide, 1-undecene oxide, 1-dodecene oxide, 4-methyl-1,2-pentene oxide, butadiene monoxide, isoprene monoxide, cyclopentene oxide, cyclohexene oxide, cycloheptene oxide, cyclooctene oxide, styrene oxide, methylstyrene oxide, pinene oxide, mono- or polyepoxidized fats as mono-, di- and triglycerides, epoxidized fatty acids, C1-C24 esters of epoxidized fatty acids, epichlorohydrin, glycidol, and derivatives of glycidol, for example methyl glycidyl ether, ethyl glycidyl ether, 2-ethylhexyl glycidyl ether, allyl glycidyl ether, glycidyl methacrylate and epoxy-functional alkoxysilanes, for example 3-glycidyloxypropyltrimethoxysilane, 3-glycidyloxypropyltriethoxysilane, 3-glycidyloxypropyltripropoxysilane, 3-glycidyloxypropylmethyldimethoxysilane, 3-glycidyloxypropylethyldiethoxysilane, 3-glycidyloxypropyltriisopropoxysilane. Preferably, the alkylene oxides used are ethylene oxide and/or propylene oxide or a mixture of ethylene oxide and propylene oxide, especially propylene oxide.

H-functional starter compound

According to the invention, in step (γ), a mixture comprising nonactivated DMC catalyst and an H-functional starter compound, where the H-functional starter compound is a polyol having a number-average molar mass of 550 to 2000 g/mol, is metered in continuously. The polyol used in the mixture
5 in accordance with the invention has a functionality of at least 2, preferably 2 to 8, more preferably 2 to 4 and especially preferably 2 to 3. The number-average molar mass of the polyol is 550 to 2000 g/mol, preferably 600 to 1500 g/mol, especially preferably 650 to 1250 g/mol and most preferably 700 to 1200 g/mol. The polyol is preferably selected from the group consisting of polyether polyol, polyester polyol, polyetherester polyol, polycarbonate polyol, polyethercarbonate
10 polyol and polyacrylate polyol, more preferably from the group consisting of polyether polyol and polyethercarbonate polyol. The polyol used in accordance with the invention is preferably prepared with a DMC catalyst.

In a particularly preferred embodiment, the polyol is at least one compound from the group consisting of polyether polyols having a molecular weight M_n in the range from 550 to 2000 g/mol with a
15 functionality of 2 to 3 and polyethercarbonate polyols having a molecular weight M_n in the range from 550 to 2000 g/mol with a functionality of 2 to 3, with the polyether polyols and polyethercarbonate polyols most preferably having been prepared with a DMC catalyst.

In a most preferred embodiment, the polyol is a polyether polyol having a molecular weight M_n in the range from 550 to 2000 g/mol with a functionality of 2 to 3.

20 The polyol having a number-average molar mass of 550 to 2000 g/mol may contain one or more of the compounds mentioned.

It is possible that the polyol includes a proportion of activated DMC catalyst. The amount of activated DMC catalyst in the polyol used is preferably 500 ppm or less, more preferably 250 ppm or less, especially preferably 125 ppm or less, based in each case on the amount of polyol used in the mixture
25 containing nonactivated double metal cyanide catalyst and an H-functional started compound, where the H-functional starter compound is a polyol having a number-average molar mass of 550 to 2000 g/mol.

In a preferred embodiment, the proportion of nonactivated DMC catalyst in the mixture comprising nonactivated DMC catalyst and polyol having a number-average molar mass of 550 to 2000 g/mol
30 is 50% to 97% by weight, more preferably 60% to 90% by weight, most preferably 70% to 80% by weight, based in each case on the sum total of the mass of nonactivated and activated DMC catalyst.

In addition to the polyol having a number-average molar mass of 550 to 2000 g/mol, further H-functional starter substances may be used in the process of the invention.

35 Suitable further H-functional starter substances ("starters") that may be used are compounds having alkoxylation-active H atoms which have a molar mass of 18 to 4500 g/mol, preferably of 62 to 500 g/mol and more preferably of 62 to 182 g/mol.

Alkoxylation-active groups having active H atoms are, for example, -OH, -NH₂ (primary amines), -NH- (secondary amines), -SH, and -CO₂H, preferably -OH and -NH₂, more preferably -OH. H-Functional starter substances used are, for example, one or more compounds selected from the group consisting of mono- and polyhydric alcohols, polyfunctional amines, polyfunctional thiols, amino alcohols, thio alcohols, hydroxy esters, polyether polyols, polyester polyols, polyester ether polyols, polyethercarbonate polyols, polycarbonate polyols, polycarbonates, polyethyleneimines, polyetheramines, polytetrahydrofurans (e.g. PolyTHF® from BASF), polytetrahydrofuran amines, polyether thiols, polyacrylate polyols, castor oil, the mono- or diglyceride of ricinoleic acid, monoglycerides of fatty acids, chemically modified mono-, di- and/or triglycerides of fatty acids, and C1-C24 alkyl fatty acid esters containing an average of at least 2 OH groups per molecule. Examples of C1-C24 alkyl fatty acid esters containing on average at least 2 OH groups per molecule are commercial products such as Lupranol Balance® (from BASF AG), Merginol® products (from Hobum Oleochemicals GmbH), Sovermol® products (from Cognis Deutschland GmbH & Co. KG), and Soyol® products (from USSC Co.).

Mono-H-functional starter compounds used may be alcohols, amines, thiols and carboxylic acids. Monofunctional alcohols used may be: methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, tert-butanol, 3-buten-1-ol, 3-butyne-1-ol, 2-methyl-3-buten-2-ol, 2-methyl-3-butyne-2-ol, propargyl alcohol, 2-methyl-2-propanol, 1-tert-butoxy-2-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 1-hexanol, 2-hexanol, 3-hexanol, 1-heptanol, 2-heptanol, 3-heptanol, 1-octanol, 2-octanol, 3-octanol, 4-octanol, phenol, 2-hydroxybiphenyl, 3-hydroxybiphenyl, 4-hydroxybiphenyl, 2-hydroxypyridine, 3-hydroxypyridine, 4-hydroxypyridine. Useful monofunctional amines include: butylamine, tert-butylamine, pentylamine, hexylamine, aniline, aziridine, pyrrolidine, piperidine, morpholine. Monofunctional thiols used may be: ethanethiol, 1-propanethiol, 2-propanethiol, 1-butanethiol, 3-methyl-1-butanethiol, 2-butene-1-thiol, thiophenol. Monofunctional carboxylic acids include: formic acid, acetic acid, propionic acid, butyric acid, fatty acids such as stearic acid, palmitic acid, oleic acid, linoleic acid, linolenic acid, benzoic acid, acrylic acid.

Examples of polyhydric alcohols suitable as H-functional starter compounds include dihydric alcohols (for example ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, propane-1,3-diol, butane-1,4-diol, butene-1,4-diol, butyne-1,4-diol, neopentyl glycol, pentane-1,5-diol, methylpentanediols (for example 3-methylpentane-1,5-diol), hexane-1,6-diol, octane-1,8-diol, decane-1,10-diol, dodecane-1,12-diol, bis(hydroxymethyl)cyclohexanes (for example 1,4-bis(hydroxymethyl)cyclohexane), triethylene glycol, tetraethylene glycol, polyethylene glycols, dipropylene glycol, tripropylene glycol, polypropylene glycols, dibutylene glycol, and polybutylene glycols); trihydric alcohols (for example trimethylolpropane, glycerol, trishydroxyethyl isocyanurate, castor oil); tetrahydric alcohols (for example pentaerythritol); polyalcohols (for

example sorbitol, hexitol, sucrose, starch, starch hydrolyzates, cellulose, cellulose hydrolyzates, hydroxy-functionalized fats and oils, especially castor oil), and also all products of modification of these aforementioned alcohols having different amounts of ϵ -caprolactone.

- 5 The H-functional starter compounds may also be selected from the substance class of polyether polyols having a molecular weight M_n in the range from 18 to 4500 g/mol and a functionality of 1-8, preferably 2 to 3. Preference is given to polyether polyols formed from repeating ethylene oxide and propylene oxide units, preferably having a proportion of propylene oxide units of 35% to 100%, more preferably having a proportion of propylene oxide units of 50% to 100%. These may be random
10 copolymers, gradient copolymers, alternating copolymers or block copolymers of ethylene oxide and propylene oxide.

- The H-functional starter substances may also be selected from the substance class of the polyester polyols. Polyester polyols used are at least difunctional polyesters. Polyester polyols preferably
15 consist of alternating acid and alcohol units. Acid components used are, for example, succinic acid, maleic acid, maleic anhydride, adipic acid, phthalic anhydride, phthalic acid, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, tetrahydrophthalic anhydride, hexahydrophthalic anhydride or mixtures of the acids and/or anhydrides mentioned. Alcohol components used are, for example, ethanediol, propane-1,2-diol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol,
20 neopentyl glycol, hexane-1,6-diol, 1,4-bis(hydroxymethyl)cyclohexane, diethylene glycol, dipropylene glycol, trimethylolpropane, glycerol, pentaerythritol or mixtures of the alcohols mentioned. When the alcohol components used are dihydric or polyhydric polyether polyols, this affords polyester ether polyols that can likewise serve as starter compounds for preparing the polyether carbonate polyols.

- 25 In addition, H-functional starter compounds used may be polycarbonate diols which are prepared, for example, by reaction of phosgene, dimethyl carbonate, diethyl carbonate or diphenyl carbonate and difunctional alcohols or polyester polyols or polyether polyols. Examples of polycarbonates may be found, for example, in EP-A 1359177.

- 30 In a further embodiment of the invention, it is possible to use polyethercarbonate polyols as H-functional starter compounds. For this purpose, these polyethercarbonate polyols used as H-functional starter compounds are prepared in a separate reaction step beforehand.

- 35 The H-functional starter compounds generally have a functionality (i.e. the number of polymerization-active H atoms per molecule) of 1 to 8, preferably of 2 or 3. The H-functional starter compounds are used either individually or as a mixture of at least two H-functional starter compounds.

It is particularly preferable when the H-functional starter compounds are one or more compounds selected from the group consisting of ethylene glycol, propylene glycol, propane-1,3-diol, butane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, 2-methylpropane-1,3-diol, neopentyl glycol, 1,6-
 5 hexanediol, 1,8-octanediol, diethylene glycol, dipropylene glycol, glycerol, trimethylolpropane, pentaerythritol, sorbitol and polyether polyols having a molecular weight M_n in the range from 150 to 4500 g/mol and a functionality of 2 to 3.

The polyether carbonate polyols are prepared by catalytic addition reaction of carbon dioxide and
 10 alkylene oxides onto H-functional starter compounds. "H-functional" in the context of the present invention is understood to mean the number of hydrogen atoms that are active in respect of the alkoxylation per molecule of the starter compound.

Component K

15 Compounds suitable as component K are characterized in that they contain at least one phosphorus-oxygen-hydrogen group. Preferably, component K is selected from at least one compound from the group consisting of
 phosphoric acid,
 mono- and dialkyl esters of phosphoric acid,
 20 mono- and diaryl esters of phosphoric acid,
 mono- and dialkaryl esters of phosphoric acid,
 $(\text{NH}_4)_2\text{HPO}_4$,
 phosphonic acid,
 monoalkyl esters of phosphonic acid,
 25 monoaryl esters of phosphonic acid,
 monoalkaryl esters of phosphonic acid,
 phosphorous acid,
 mono- and dialkyl esters of phosphorous acid,
 mono- and diaryl esters of phosphorous acid,
 30 mono- and dialkaryl esters of phosphorous acid and
 phosphinic acid.

The mono- or dialkyl esters of phosphoric acid are preferably the mono- or dialkyl esters of orthophosphoric acid, mono-, di- or trialkyl esters of pyrophosphoric acid and mono-, di-, tri-, tetra- or polyalkyl esters of polyphosphoric acid, more preferably the respective esters with alcohols having
 35 1 to 30 carbon atoms. The mono- or diaryl esters of phosphoric acid are preferably the mono- or diaryl esters of orthophosphoric acid, mono-, di- or triaryl esters of pyrophosphoric acid and mono-, di-, tri-, tetra- or polyaryl esters of polyphosphoric acid, more preferably the respective esters with alcohols having 6 to 10 carbon atoms. The mono- or dialkaryl esters of phosphoric acid are preferably

the mono- or dialkaryl esters of orthophosphoric acid, mono-, di- or trialkaryl esters of pyrophosphoric acid and mono-, di-, tri-, tetra- or polyalkaryl esters of polyphosphoric acid, more preferably the respective esters with alcohols having 7 to 30 carbon atoms. Examples of compounds suitable as component K include: diethyl phosphate, monoethyl phosphate, dipropyl phosphate, 5 monopropyl phosphate, dibutyl phosphate, monobutyl phosphate, diphenyl phosphate, dicresyl phosphate, fructose 1,6-biphosphate, glucose 1-phosphate, bis(4-nitrophenyl) phosphate, dibenzyl phosphate, diethyl 3-butenyl phosphate, dihexadecyl phosphate, diphenyl phosphate, diphenyl chlorophosphate, 2-hydroxyethyl methacrylate phosphate.

10 Monoalkyl esters of phosphonic acid used with preference are the respective esters with alcohols having 1 to 30 carbon atoms. Monoaryl esters of phosphonic acid used with preference are the respective esters with alcohols having 6 to 10 carbon atoms. Monoalkaryl esters of phosphonic acid used with preference are the respective esters with alcohols having 7 to 30 carbon atoms.

Mono- and dialkyl esters of phosphorous acid used with preference are esters with alcohols having 15 1 to 30 carbon atoms. This includes, for example, phenylphosphonic acid, butylphosphonic acid, dodecylphosphonic acid, ethylhexylphosphonic acid, octylphosphonic acid, ethylphosphonic acid, methylphosphonic acid and octadecylphosphonic acid. Mono- and diaryl esters of phosphorous acid used with preference are the respective esters with alcohols having 6 to 10 carbon atoms. Mono- and dialkaryl esters of phosphorous acid used with preference are the respective esters with alcohols 20 having 7 to 30 carbon atoms.

Component K is more preferably selected from at least one compound from the group consisting of phosphoric acid, phosphonic acid and phosphinic acid. Component K is most preferably phosphoric acid.

The alcohols having 1 to 30 carbon atoms mentioned in the description of component K are, for 25 example, methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, octadecanol, nonadecanol, methoxymethanol, ethoxymethanol, propoxymethanol, butoxymethanol, 2-ethoxyethanol, 2-propoxyethanol, 2-butoxyethanol, phenol, ethyl hydroxyacetate, propyl hydroxyacetate, ethyl hydroxypropionate, propyl hydroxypropionate, ethane-1,2-diol, propane-1,2- 30 diol, 1,2,3-trihydroxypropane, 1,1,1-trimethylolpropane or pentaerythritol.

Also suitable as component K are compounds of phosphorus that can form one or more phosphorus-oxygen-hydrogen groups by reaction with OH-functional compounds (such as water for example). Examples of such compounds of phosphorus that are useful include phosphorus(V) sulfide, phosphorus tribromide, phosphorus trichloride and phosphorus triiodide.

35 It is also possible to use any desired mixtures of the abovementioned compounds as component K. Component K may also be used in admixture with suspension medium or in admixture with trialkyl phosphate (especially triethyl phosphate).

In a preferred embodiment of the invention, component K is selected from at least one compound from the group consisting of phosphoric acid, phosphonic acid, phosphorous acid, phosphinic acid, phosphonous acid, phosphinous acid, phosphine oxides, and salts, esters, halides and amides of phosphoric acid, phosphonic acid, phosphorous acid, phosphinic acid, phosphonous acid and phosphinous acid, phosphorus(V) sulfide, phosphorus tribromide, phosphorus trichloride and phosphorus triiodide.

Component K may be metered in in any step of the process, with component K preferably being metered in in such a way that the reaction product resulting from step (γ) contains an amount of 5 to 2000 ppm, more preferably 10 to 1000 ppm, especially preferably 30 to 500 ppm. It is advantageous to meter in component K in step (γ); especially preferably, component K is metered in mixed with H-functional starter compound. It is also advantageous to add component K to the reaction mixture in the postreactor in step (δ). It is additionally advantageous to add component K to the reaction mixture obtained only after the postreaction (step (δ)).

In a preferred embodiment, the polyol in the mixture in step (γ) contains a component K in a proportion of 5 to 2000 ppm, where component K is selected from at least one compound from the group consisting of phosphoric acid, phosphonic acid, phosphorous acid, phosphinic acid, phosphonous acid, phosphinous acid, phosphine oxides, and salts, esters, halides and amides of phosphoric acid, phosphonic acid, phosphorous acid, phosphinic acid, phosphonous acid and phosphinous acid, phosphorus(V) sulfide, phosphorus tribromide, phosphorus trichloride and phosphorus triiodide.

In one possible embodiment of the invention, during the postreaction (step (δ)), component K is added in an amount of 5 ppm to 1000 ppm, more preferably 10 ppm to 500 ppm, most preferably 20 ppm to 200 ppm, based in each case on the reaction mixture obtained in step (γ). Component K is added during the postreaction more preferably at a free alkylene oxide content of 0.1% by weight to 10% by weight, most preferably of 1% by weight to 10% by weight, of alkylene oxide and most especially preferably of 5% by weight to 10% by weight. When conducting the process of the invention using a tubular reactor for the postreaction in step (δ), component K is more preferably metered in in the second half of the distance that the reaction mixture traverses in the tubular reactor.

The polyether carbonate polyols obtained in accordance with the invention have a functionality, for example, of at least 2, preferably of 2 to 8, more preferably of 2 to 6 and most preferably of 2 to 4. The molecular weight is preferably 800 to 10 000 g/mol and more preferably 1200 to 6000 g/mol.

The polyether carbonate polyols obtainable by the process of the invention have a low content of by-products and can be processed without difficulty, especially by reaction with di- and/or polyisocyanates to give polyurethanes, in particular flexible polyurethane foams. For polyurethane

applications, it is preferable to use polyethercarbonate polyols based on an H-functional starter compound having a functionality of at least 2.

In addition, the polyethercarbonate polyols obtainable by the process of the invention can be used in applications such as washing and cleaning composition formulations, drilling fluids, fuel additives,
5 ionic and nonionic surfactants, lubricants, process chemicals for papermaking or textile manufacture, or cosmetic formulations.

The person skilled in the art is aware that, depending on the respective field of use, the polyethercarbonate polyols to be used have to fulfill certain physical properties, for example molecular weight, viscosity, functionality and/or hydroxyl number.

Examples

The invention is illustrated in detail by the examples which follow, but is not restricted thereto.

The DMC catalyst used in the examples was prepared according to example 6 of WO-A 01/80994.

The values for pressure refer to the absolute pressure.

5 GPC:

The number-average M_n and the weight-average M_w molecular weight and the polydispersity (M_w/M_n) of the products were determined by gel permeation chromatography (GPC). The procedure of DIN 55672-1 was followed (March 2016): "Gel permeation chromatography, Part 1 - Tetrahydrofuran as eluent" (SECurity GPC System from PSS Polymer Service, flow rate 1.0 ml/min; 10 columns: 2×PSS SDV linear M, 8×300 mm, 5 μ m; RID detector). Polystyrene samples of known molar mass were used for calibration.

CO₂ content in the polyethercarbonate polyol:

The proportion of incorporated CO₂ in the resulting polyethercarbonate polyol and the ratio of 15 propylene carbonate to polyethercarbonate polyol were determined by ¹H-NMR (Bruker DPX 400, 400 MHz; pulse programme zg30, d1 relaxation delay: 10s, 64 scans). Each sample was dissolved in deuterated chloroform. The relevant resonances in the ¹H NMR (based on TMS = 0 ppm) are as follows:

Cyclic carbonate (which was formed as a by-product) having a resonance at 4.5 ppm, carbonate 20 resulting from carbon dioxide incorporated in the polyethercarbonate polyol having resonances at 5.1 to 4.8 ppm, unreacted PO having a resonance at 2.4 ppm, polyether polyol (i.e. without incorporated carbon dioxide) having resonances at 1.2 to 1.0 ppm, the 1,8-octanediol incorporated as starter molecule (if present) having a resonance at 1.6 to 1.52 ppm.

25 The mole fraction of the carbonate incorporated in the polymer in the reaction mixture is calculated by formula (VIII) as follows using the following abbreviations:

A(4.5) = area of the resonance at 4.5 ppm for cyclic carbonate (corresponds to one hydrogen atom)

A(5.1-4.8) = area of the resonance at 5.1-4.8 ppm for polyethercarbonate polyol and one hydrogen 30 atom for cyclic carbonate

A(2.4) = area of the resonance at 2.4 ppm for free, unreacted PO

A(1.2-1.0) = area of the resonance at 1.2-1.0 ppm for polyether polyol

A(1.6-1.52) = area of the resonance at 1.6 to 1.52 ppm for octane-1,8-diol (starter), if present.

35 Taking account of the relative intensities, the values for the polymer-bound carbonate ("linear carbonate" LC) in the reaction mixture were converted to mol% as per the following formula (VIII):

$$LC = \frac{A(5.1 - 4.8) - A(4.5)}{A(5.1 - 4.8) + A(2.4) + 0.33 * A(1.2 - 1.0) + 0.25 * A(1.6 - 1.52)} * 100 \quad (\text{VIII})$$

The weight fraction (in % by weight) of polymer-bonded carbonate (LC') in the reaction mixture was calculated by formula (IX),

5

$$LC' = \frac{[A(5.1 - 4.8) - A(4.5)] * 102}{D} * 100\% \quad (\text{IX})$$

where the value of D ("denominator" D) is calculated by formula (X):

10

$$D = [A(5.1 - 4.8) - A(4.5)] * 102 + A(4.5) * 102 + A(2.4) * 58 + 0.33 * A(1.2 - 1.0) * 58 + 0.25 * A(1.6 - 1.52) * 146 \quad (\text{X})$$

15

The factor of 102 results from the sum of the molar masses of CO₂ (molar mass 44 g/mol) and of propylene oxide (molar mass 58 g/mol), the factor of 58 results from the molar mass of propylene oxide, and the factor of 146 results from the molar mass of the octane-1,8-diol starter used (if present).

20

The proportion by weight (in % by weight) of cyclic carbonate (CC') in the reaction mixture was calculated by formula (XI),

$$CC' = \frac{A(4.5) * 102}{D} * 100\% \quad (\text{XI})$$

where the value of D is calculated by formula (X).

25

30

In order to calculate the composition based on the polymer component (consisting of polyether polyol formed from starter and propylene oxide during the activation steps that take place in the absence of CO₂ and polyethercarbonate polyol formed from starter, propylene oxide, and carbon dioxide during the activation steps that take place in the presence of CO₂ and during the copolymerization) from the values for the composition of the reaction mixture, the nonpolymeric constituents of the reaction mixture (i.e. cyclic propylene carbonate and any unreacted propylene oxide present) were mathematically eliminated. The proportion by weight of the repeat carbonate units in the polyethercarbonate polyol was converted to a proportion by weight of carbon dioxide using the factor $A = 44/(44+58)$. The value for the CO₂ content in the polyethercarbonate polyol is normalized to the proportion of the polyethercarbonate polyol molecule which was formed in the copolymerization and in any activation steps in the presence of CO₂ (i.e. the proportion of the polyethercarbonate polyol

molecule resulting from the starter (octane-1,8-diol, if present) and from the reaction of the starter with epoxide which was added under CO₂-free conditions was not taken into account here).

Example 1: Copolymerization of propylene oxide and CO₂ using a nonactivated DMC catalyst

5 *Preparation of catalyst-polyol mixture 1*

In a first vessel, 6.108 g of DMC catalyst (unactivated) and 170 ppm of H₃PO₄ (85%) were mixed into 10 kg of poly(oxypropylene) polyol having a number-average molar mass of 683 g/mol and a functionality of 2.8. The poly(oxypropylene) polyol already contained 65 ppm of activated DMC catalyst.

10 *Step (α)*

A nitrogen-purged pressure reactor with gas metering device (gas inlet tube) and product discharge tube was initially charged with a suspension of 0.83 g of DMC catalyst (unactivated) and 5 kg of polyethercarbonate polyol having a number-average molar mass of 2914 g/mol, a functionality of 2.8 and a CO₂ content of 14.6%.

15 *Step (β)*

The reactor was adjusted by an addition of CO₂ to a pressure of 30 bar and correspondingly heated to 120°C. 0.25 kg of propylene oxide (PO) was metered into the reactor at 120°C while stirring within 2 min. The onset of the reaction was signaled by a temperature spike ("hotspot"). There was a second addition of 0.25 kg of propylene oxide within 2 min. The onset of the reaction was again signaled by
20 a temperature spike.

Step (γ)

On completion of activation, the reactor contents were adjusted to a temperature of 120°C. Thereafter, propylene oxide at 7.7 kg/h, the catalyst-polyol mixture 1 at 2.7 kg/h and carbon dioxide were metered simultaneously into the reactor, so as to result in a dwell time of 2.5 h and a total
25 pressure of 30 bar in steady-state continuous operation of the stirred reactor. The concentration of free propylene oxide (measured in the reactor by means of MIR probe) in the steady continuous state was 1.1% by weight, and the reaction temperature was 107°C. The catalyst concentration in the reactor was 100 ppm.

Step (δ)

30 Thereafter, the reaction mixture was conveyed out of the pressure reactor through a tubular postreactor (reaction volume 2 liters) heated to 120°C. Before the cyclic propylene carbonate was separated off, the buffer tank was operated at 120°C and with an average dwell time of 4 h.

Finally, the product, for separation of the cyclic propylene carbonate, was subjected to a two-stage thermal workup, namely in a first stage by means of a falling-film evaporator, followed, in a second stage, by a stripping column operated in a nitrogen countercurrent.

The falling-film evaporator was operated here at a temperature of 169°C and a pressure of 17 mbar (absolute).

The nitrogen stripping column was operated at a temperature of 160°C, a pressure of 80 mbar (absolute) and a nitrogen flow rate of 0.6 kg N₂/kg product.

Example 2: Copolymerization of propylene oxide and CO₂ using a nonactivated DMC catalyst

The process in example 2 was conducted analogously to example 1, except so as to give a dwell time of 1.7 h in steady-state continuous operation of the stirred reactor in step (γ).

Example 3: Copolymerization of propylene oxide and CO₂ using a nonactivated DMC catalyst

The process in example 2 was conducted analogously to example 1, except so as to give a dwell time of 1.4 h in steady-state continuous operation of the stirred reactor in step (γ).

Example 4 (comparative): Copolymerization of propylene oxide and CO₂ using an activated DMC catalyst

Preparation of catalyst-polyol mixture 2

In a first reactor, 4.476 g of DMC catalyst (unactivated) was mixed into 10 kg of poly(oxypropylene) polyol having a number-average molar mass of 716 g/mol and a functionality of 2.8. The poly(oxypropylene) polyol was heated to 100°C and stripped at 10 mbara with addition of N₂ for 60 min. Thereafter, the vessel contents were heated to 130°C, and a pressure of 30 bar was established by means of addition of CO₂. With addition of 2.9 kg of propylene oxide, the catalyst was activated, which was signaled by a temperature spike. This activation step was repeated twice more, with the onset of the reaction being signaled each time by a temperature spike. 170 ppm of H₃PO₄ (85%) was added to the catalyst-polyol mixture 2.

Step (α)

A nitrogen-inertized pressure reactor with gas metering device (gas inlet tube) and product discharge tube was initially charged with a suspension of 0.5 g of DMC catalyst (unactivated) and 5 kg of polyethercarbonate polyol having a number-average molar mass of 2914 g/mol, a functionality of 2.8 and a CO₂ content of 14.6%.

Step (β)

The reactor was adjusted by an addition of CO₂ to a pressure of 30 bar and correspondingly heated to 120°C. 0.225 kg of propylene oxide (PO) was metered into the reactor at 120°C while stirring within 2 min. The onset of the reaction was signaled by a temperature spike ("hotspot"). There was

a second addition of 0.225 kg of propylene oxide (PO) within 2 min. The onset of the reaction was again signaled by a temperature spike ("hotspot").

Step (γ)

On completion of activation, the reactor contents were adjusted to a temperature of 120°C. Thereafter, propylene oxide at 6.6 kg/h, the catalyst-polyol mixture 2 at 3.45 kg/h and carbon dioxide were metered simultaneously into the reactor, so as to result in a dwell time of 2.9 h and a pressure of 30 bar in steady-state continuous operation of the stirred reactor. The catalyst concentration in the reactor was 100 ppm. The temperature was to be lowered stepwise to a target value of 112°C, but a free propylene oxide content of more than 5% (measured in the reactor by MIR probe) had built up after 6 h when it was lowered to 114°C, and so it was no longer possible to run a stable process on account of significant temperature and pressure fluctuations. Thereafter, after slow reduction of the free propylene oxide concentration, the experiment was restarted at 120°C, the temperature was lowered gradually to 117°C, and steady-state operation was continued at that temperature. The concentration of free propylene oxide (measured in the reactor by means of MIR probe) in the steady continuous state was 3.8% by weight. For reasons of process stability, it was not possible to increase the throughputs for shortening of the dwell times in the main reactor. The reaction mixture was withdrawn from the reactor continuously in each case via the product discharge tube.

Step (δ)

For completion of the reaction, the reaction mixture was conveyed through a tubular reactor heated to 120°C. Before the separation, the buffer tank was operated at 120°C and with an average dwell time of 4 h. The cyclic propylene carbonate was separated from the polyethercarbonate polyol analogously to the method in examples 1 to 3.

Example 5 (comparative): Copolymerization of propylene oxide and CO₂ using a short-chain starter

Preparation of catalyst-polyol mixture 3

In a first reactor, 26.5 g of DMC catalyst (nonactivated) was mixed into 5 kg of a mixture of glycerol (4.25 kg) and propylene glycol (0.75% by weight), corresponding to a mixture functionality of 2.8. 170 ppm of H₃PO₄ (85%) was added to the catalyst-polyol mixture 3.

Step (α)

A nitrogen-inertized pressure reactor with a gas metering device (gas inlet tube) and product discharge tube was initially charged with a suspension of 1 g of DMC catalyst (nonactivated) and 4.7 kg of propylene carbonate.

Step (β)

The reactor was adjusted by an addition of CO₂ to a pressure of 30 bar and correspondingly heated to 120°C. 0.225 kg of propylene oxide (PO) was metered into the reactor at 120°C while stirring within 2 min. The onset of the reaction was signaled by a temperature spike ("hotspot"). There was a second addition of 0.225 kg of propylene oxide (PO) within 2 min. The onset of the reaction was again signaled by a temperature spike ("hotspot").

Step (γ)

On completion of activation, the reactor contents were adjusted to a temperature of 120°C. Thereafter, propylene oxide at 7.4 kg/h, the catalyst-polyol mixture 3 at 0.26 kg/h and carbon dioxide were metered simultaneously into the reactor, so as to result in a dwell time of 3.8 h and a pressure of 30 bar in steady-state continuous operation of the stirred reactor. The catalyst concentration in the reactor was 150 ppm. The temperature was lowered stepwise to a target value of 107°C. The concentration of free propylene oxide (measured in the reactor by means of MIR probe) in the steady continuous state was 2.4% by weight. The reaction mixture was withdrawn from the reactor continuously in each case via the product discharge tube.

Step (δ)

For completion of the reaction, the reaction mixture was conveyed through a tubular reactor heated to 120°C. Before the separation, the buffer tank was operated at 120°C and with an average dwell time of 4 h. The cyclic propylene carbonate was separated from the polyethercarbonate polyol analogously to the method in examples 1 to 3.

20

Table 1:

	Residence time [h]	CO ₂ incorporation [% by wt.]	PDI [Mw/Mn]	Selectivity c/l ** [-]	Concentration of free PO [% by wt.]
Example 1	2.5	13.2	1.11	0.08	1.1
Example 2	1.7	12.6	1.11	0.08	2.0
Example 3	1.4	12.3	1.12	0.08	2.2
Example 4*	2.9	12.6	1.69	0.107	3.8
Example 5*	3.8	14.7	1.12	0.165	2.4

*Comparative examples

** Ratio of cyclic carbonate/linear carbonate

Claims

1. A process for preparing polyethercarbonate polyols, comprising the step of reaction of alkylene oxide with carbon dioxide in the presence of an H-functional starter compound and double metal cyanide catalyst, **characterized in that**
 - 5 (α) a portion of H-functional starter substance and/or suspension medium containing no H-functional groups is initially charged in a reactor, in each case together with DMC catalyst,
 - (β) a portion of alkylene oxide is added to the mixture from step (α) at temperatures of 90 to 150°C, and then the addition of the alkylene oxide is stopped,
 - 10 (γ) alkylene oxide, carbon dioxide and a mixture comprising nonactivated double metal cyanide catalyst and an H-functional starter compound, where the H-functional starter compound is a polyol having a number-average molar mass to DIN 55672-1 of 550 to 2000 g/mol, is metered continuously into the mixture resulting from (β).
2. The process as claimed in claim 1, characterized in that the reaction product resulting from step
15 (γ) is removed continuously from the reactor.
3. The process as claimed in claim 2, characterized in that the average dwell time of the reaction mixture in step (γ) is 0.5 to 5.0 hours.
4. The process as claimed in claim 2, characterized in that the average dwell time of the reaction mixture in step (γ) is 1.5 to 5.0 hours.
- 20 5. The process as claimed in any of claims 1 to 4, characterized in that the mixture comprising nonactivated double metal cyanide catalyst and an H-functional starter compound contains 500 ppm or less of an activated double metal cyanide catalyst, based on the H-functional starter compound.
6. The process as claimed in any of claims 1 to 5, characterized in that the proportion of
25 nonactivated DMC catalyst in the mixture comprising nonactivated DMC catalyst and an H-functional starter compound is 50% to 97% by weight, based on the sum total of the mass of the nonactivated and activated DMC catalyst in the mixture.
7. The process as claimed in any of claims 1 to 6, characterized in that a component K is added such that a component K is present in a proportion of 5 to 2000 ppm in the reaction product
30 resulting from step (γ).
8. The process as claimed in claim 7, characterized in that component K is selected from at least one compound from the group consisting of phosphoric acid, phosphonic acid, phosphorous acid, phosphinic acid, phosphonous acid, phosphinous acid, phosphine oxides, and salts, esters, halides and amides of phosphoric acid, phosphonic acid, phosphorous acid, phosphinic acid,

phosphonous acid and phosphinous acid, phosphorus(V) sulfide, phosphorus tribromide, phosphorus trichloride and phosphorus triiodide.

9. The process as claimed in any of claims 1 to 7, characterized in that the polyol in the mixture in step (γ) contains a component K in a proportion of 5 to 2000 ppm, where component K is selected from at least one compound from the group consisting of phosphoric acid, phosphonic acid, phosphorous acid, phosphinic acid, phosphonous acid, phosphinous acid, phosphine oxides, and salts, esters, halides and amides of phosphoric acid, phosphonic acid, phosphorous acid, phosphinic acid, phosphonous acid and phosphinous acid, phosphorus(V) sulfide, phosphorus tribromide, phosphorus trichloride and phosphorus triiodide.
10. The process as claimed in any of claims 1 to 9, characterized in that the polyol in the mixture in step (γ) has a number-average molar mass to DIN 55672-1 of 600 to 1500 g/mol.
11. The process as claimed in any of claims 1 to 10, characterized in that the polyol in the mixture in step (γ) is selected from at least one compound from the group consisting of polyether polyol, polyester polyol, polyesterether polyol, polycarbonate polyol, polyethercarbonate polyol and polyacrylate polyol.
12. The process as claimed in any of claims 1 to 9, characterized in that the H-functional starter compound in the mixture comprising nonactivated double metal cyanide catalyst and an H-functional starter compound in step (γ) is selected from at least one compound from the group consisting of polyether polyols having a molecular weight M_n to DIN 55672-1 in the range from 550 to 2000 g/mol with a functionality of 2 to 3, and polyethercarbonate polyols having a molecular weight M_n in the range from 550 to 2000 g/mol with a functionality of 2 to 3.
13. The process as claimed in any of claims 1 to 12, characterized in that the double metal cyanide catalyst is present in step (γ) in a proportion of 10 to 10 000 ppm, based on the overall reaction mixture.
14. The process as claimed in any of claims 1 to 13, characterized in that the alkylene oxide used is ethylene oxide, propylene oxide or a mixture of propylene oxide and ethylene oxide.
15. The process as claimed in any of claims 1 to 14, characterized in that the double metal cyanide catalyst used comprises at least one compound selected from the group consisting of zinc hexacyanocobaltate(III), zinc hexacyanoiridate(III), zinc hexacyanoferrate(III) and cobalt(II) hexacyanocobaltate(III).