

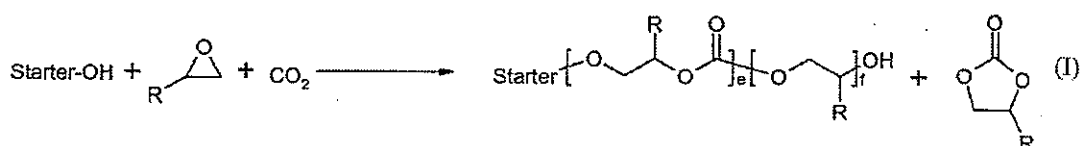
Method for producing polyether carbonate polyols

The present invention relates to a process for preparing polyether carbonate polyols from one or more H-functional starter substances, one or more alkylene oxides and carbon dioxide in the presence of at least one double metal cyanide catalyst, wherein the cyanide-free metal salt or metal cyanide salt used for preparation of the double metal cyanide catalyst, or both of these salts, contain(s) 0.3 to 1.8 mol of base equivalents (based on 1 mol of the metal cyanide salt used for catalyst synthesis) in the form of an alkaline metal hydroxide, metal carbonate and/or metal oxide.

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The preparation of polyether carbonate polyols by catalytic reaction of alkylene oxides (epoxides) and carbon dioxide in the presence or absence of H-functional starter substances (starters) has been studied intensively for more than 40 years (for example Inoue et al, Copolymerization of Carbon Dioxide and Epoxide with Organometallic Compounds; Die Makromolekulare Chemie 130, 210-220, 1969). This reaction, for example using an H-functional starter compound, is shown schematically 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 and f are each an integer, and where the product shown here in scheme (I) for the polyether carbonate polyol should be understood merely such that blocks having the structure shown may occur in principle in the polyether carbonate 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 polyether carbonate polyol shown in scheme (I). This reaction (see scheme (I)) is ecologically very advantageous since this reaction constitutes the conversion of a greenhouse gas such as CO₂ to a polymer. A further product, actually a by-product, formed is the cyclic carbonate shown in formula (I) (for example, where R = CH₃, propylene carbonate).

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Activation in the context of the invention refers to a step in which a portion of alkylene oxide compound, optionally in the presence of CO₂, is added to the DMC

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catalyst and then the addition of the alkylene oxide compound is stopped, with observation of evolution of heat, which can lead to a temperature peak ("hotspot"), due to an exothermic chemical reaction which follows, and of a pressure drop in the reactor due to the conversion of alkylene oxide and possibly CO₂. The process step of activation is the period from the addition of the portion of alkylene oxide compound, optionally in the presence of CO₂, to the DMC catalyst until the occurrence of the evolution of heat. In general, the activation step may be preceded by a step for drying the DMC catalyst and optionally the starter at elevated temperature and/or reduced pressure, though this drying step is not part of the activation step in the context of the present invention.

The formation of copolymers from epoxides (e.g. propylene oxide) and carbon dioxide has long been known. For example, US 4500704 describes the copolymerization of carbon dioxide and propylene oxide using DMC catalysts. Here, for example, 71% of the propylene oxide were converted after 48 hours at 35°C in a reactor proceeding from a starter substance and 12.3 g of propylene oxide (212 mmol) and a carbon dioxide pressure of 48 bar. Of the 150.5 mmol of propylene oxide converted, 27 mmol (18%) reacted to give the generally unwanted propylene carbonate by-product.

WO-A 2006/103213 discloses a process which helps to reduce the formation of cyclic carbonates. This is achieved by adding a CO₂-philic substance (for example perfluorinated compounds) to the DMC catalyst. Even at a high CO₂ pressure of 62 bar, low propylene carbonate contents are found. For example, the propylene carbonate content in example 6 of the publication is only 2.7%, but the polydispersity of 7.98 is undesirably high.

Since propylene carbonate has an exceptionally high boiling point of 240°C at standard pressure, the removal thereof from the reaction mixture is inconvenient and time-consuming. It is therefore desirable to develop a process for copolymerizing epoxides with carbon dioxide, with formation of minimum amounts of cyclic carbonate (for example propylene carbonate). It was therefore an object of the present invention to provide a process with which polyether carbonate polyols can be

prepared with improved selectivity (i.e. minimum ratio of cyclic carbonate to linear polyether carbonate), with a wait time ("time 1" in table 1) before the temperature peak in the copolymerization of less than 120 min. A shorter wait time has an advantageous effect on the economic viability of the process.

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It has now been found that, surprisingly, the abovementioned object is achieved by a process for preparing polyether carbonate polyols from one or more H-functional starter substances, one or more alkylene oxides and carbon dioxide in the presence of at least one DMC catalyst, wherein the cyanide-free metal salt or metal cyanide salt
10 used for preparation of the DMC catalyst, or both of these salts, contain(s) 0.3 to 1.8 mol, preferably 0.6 to 1.6 mol and more preferably 0.8 to 1.4 mol of base equivalents (based on 1 mol of the metal cyanide salt used for catalyst synthesis) in the form of an alkaline metal hydroxide, metal carbonate and/or metal oxide.

15 Base equivalents of an alkaline metal hydroxide, metal carbonate and/or metal oxide are understood in the context of the invention to mean the equivalents of the resulting hydroxide ions in the event of full dissociation of the alkaline metal hydroxides, metal carbonates and/or metal oxides used in water. For example, 0.5 mol of a metal carbonate results in 1.0 mol of base equivalents.

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A preferred embodiment of the present invention is a process for preparing polyether carbonate polyols from one or more H-functional starter substances, one or more alkylene oxides and carbon dioxide in the presence of at least one DMC catalyst, characterized in that the DMC catalyst is prepared by reacting an aqueous solution of
25 a cyanide-free metal salt with the aqueous solution of a metal cyanide salt in the presence of one or more organic complex ligands, for example an ether or alcohol, one or more alkaline metal hydroxides, metal carbonates and/or metal oxides being present either in the aqueous solution of the cyanide-free metal salt or the aqueous solution of the metal cyanide salt, or in both aqueous solutions, and the sum of the
30 alkaline metal hydroxides, metal carbonates and/or metal oxides used being 0.3 to 1.8 mol, preferably 0.6 to 1.6 mol and more preferably 0.8 to 1.4 mol of base equivalents (based on 1 mol of the metal cyanide salt used for catalyst synthesis).

The process for preparing polyether carbonate polyols from at least one H-functional starter substances, at least one alkylene oxide and carbon dioxide in the presence of a DMC catalyst can be performed continuously, semibatchwise or batchwise.

- 5 The polyether carbonate polyols obtained in accordance with the invention generally have a functionality of at least one, preferably of 2 to 8, more preferably of 2 to 6 and most preferably of 2 to 4. The molecular weight is preferably 400 to 10 000 g/mol and more preferably 500 to 6000 g/mol.
- 10 In general, for the process according to the invention, it is possible to use alkylene oxides having 2-24 carbon atoms. 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
- 15 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
- 20 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 alkylloxysilanes, for
- 25 example 3-glycidyloxypropyltrimethoxysilane, 3-glycidyloxypropyltriethoxysilane, 3-glycidyloxypropyltripropoxysilane, 3-glycidyloxypropylmethyldimethoxysilane, 3-glycidyloxypropylethyldiethoxysilane, 3-glycidyloxypropyltriisopropoxysilane. The alkylene oxides used are preferably ethylene oxide and/or propylene oxide, especially propylene oxide.

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Suitable H-functional starter substances used may be compounds having hydrogen atoms active for the alkoxylation. Groups which have active hydrogen atoms and are active for the alkoxylation are, for example, -OH, -NH₂ (primary amines), -NH-

(secondary amines), -SH and -CO₂H, preferably -OH and -NH₂, more preferably -OH. The H-functional starter substance used is, for example, one or more compounds selected from the group consisting of mono- or polyhydric alcohols, mono- or polyfunctional amines, polyhydric thiols, carboxylic acids, amino alcohols, aminocarboxylic acids, thio alcohols, hydroxy esters, polyether polyols, polyester polyols, polyester ether polyols, polyether carbonate polyols, polycarbonate polyols, polycarbonates, polyethyleneimines, polyetheramines (for example those known as Jeffamines[®] from Huntsman, for example D-230, D-400, D-2000, T-403, T-5000, or corresponding products from BASF, for example Polyetheramine D230, D400, D200, T403, T-3000, T5000), polytetrahydrofurans (for example PolyTHF[®] from BASF, for example PolyTHF[®] 250, 650S, 1000, 1000S, 1400, 1800, 2000), polytetrahydrofuranamines (BASF product Polytetrahydrofuranamine 1700), 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 the C₁-C₂₄ alkyl fatty acid esters containing an average of at least 2 OH groups per molecule are commercial products such as Lupranol Balance[®] (from BASF SE), Merginol[®] products (from Hobum Oleochemicals GmbH), Sovermol[®] products (from Cognis Deutschland GmbH & Co. KG) and Soyol[®]TM products (from USSC Co.).

The monofunctional starter substances used may be alcohols, amines, thiols and carboxylic acids. The 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. The 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.

- 5 Polyhydric alcohols suitable as H-functional starter substances are, for example, dihydric alcohols (for example ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, 1,3-propanediol, 1,4-butanediol, 1,4-butenediol, 1,4-butyndiol, neopentyl glycol, 1,5-pentanediol, methylpentanediols (for example 3-methyl-1,5-pentanediol), 1,6-hexanediol; 1,8-octanediol, 1,10-decanediol, 1,12-dodecane-
10 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
15 pentaerythritol); polyalcohols (for example sorbitol, hexitol, sucrose, starch, starch hydrolysates, cellulose, cellulosehydrolysates, hydroxy-functionalized fats and oils, especially castor oil), and all modification products of these aforementioned alcohols with different amounts of ϵ -caprolactone.
- 20 The H-functional starter substances may also be selected from the substance class of the polyether polyols, especially those having a molecular weight M_n in the range from 100 to 4000 g/mol. Preference is given to polyether polyols formed from repeat ethylene oxide and propylene oxide units, preferably having a proportion of 35 to 100% propylene oxide units, more preferably having a proportion of 50 to 100%
25 propylene oxide units. These may be random copolymers, gradient copolymers, alternating copolymers or block copolymers of ethylene oxide and propylene oxide. Suitable polyether polyols formed from repeat propylene oxide and/or ethylene oxide units are, for example, the Desmophen[®], Acclaim[®], Arcol[®], Baycoll[®], Bayfill[®], Bayflex[®], Baygal[®], PET[®], and polyether polyols from Bayer MaterialScience AG
30 (for example Desmophen[®] 3600Z, Desmophen[®] 1900U, Acclaim[®] Polyol 2200, Acclaim[®] Polyol 4000I, Arcol[®] Polyol 1004, Arcol[®] Polyol 1010, Arcol[®] Polyol 1030, Arcol[®] Polyol 1070, Baycoll[®] BD 1110, Bayfill[®] VPPU 0789, Baygal[®] K55, PET[®] 1004, Polyester[®] S180). Further suitable homopolyethylene oxides are, for

example, the Pluriol® E brands from BASF SE, suitable homopolypropylene oxides are, for example, the Pluriol® P brands from BASF SE, and suitable mixed copolymers of ethylene oxide and propylene oxide are, for example, the Pluronic® PE or Pluriol® RPE brands from BASF SE.

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The H-functional starter substances may also be selected from the substance class of the polyester polyols, especially those having a molecular weight M_n in the range from 200 to 4500 g/mol. The polyester polyols used are at least difunctional polyesters. Polyester polyols preferably consist of alternating acid and alcohol units.

10 The 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. The alcohol components used are, for example, ethanediol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, neopentyl glycol, 1,6-hexanediol, 1,4-bis-
15 (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, polyester ether polyols are obtained, which can likewise serve as starter substances for
20 preparation of the polyether carbonate polyols. Preference is given to using polyether polyols with $M_n = 150$ to 2000 g/mol for preparation of the polyester ether polyols.

In addition, the H-functional starter substances used may be polycarbonate diols, especially those having a molecular weight M_n in the range from 150 to 4500 g/mol, preferably 500 to 2500, which are prepared, for example, by conversion of phosgene,
25 dimethyl carbonate, diethyl carbonate or diphenyl carbonate and difunctional alcohols or polyester polyols or polyether polyols. Examples of polycarbonates can be found, for example, in EP-A 1359177. For example, the polycarbonate diols used may be the Desmophen® C products from Bayer MaterialScience AG, for example
30 Desmophen® C 1100 or Desmophen® C 2200.

In a further embodiment of the invention, polyether carbonate polyols can be used as H-functional starter substances. More particularly, polyether carbonate polyols

obtainable by the process according to the invention described here are used. These polyether carbonate polyols used as H-functional starter substances are prepared beforehand in a separate reaction step for this purpose.

- 5 The H-functional starter substances generally have a functionality (i.e. number of hydrogen atoms active for the polymerization per molecule) of 1 to 8, preferably of 2 or 3. The H-functional starter substances are used either individually or as a mixture of at least two H-functional starter substances.
- 10 Preferred H-functional starter substances are alcohols of the general formula (II)



- where x is a number from 1 to 20, preferably an even number from 2 to 20. Examples of alcohols of the formula (II) are ethylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol and 1,12-dodecanediol. Further preferred H-functional starter substances are neopentyl glycol, trimethylol propane, glycerol, pentaerythritol, reaction products of the alcohols of the formula (II) with ϵ -caprolactone, for example reaction products of trimethylolpropane with ϵ -caprolactone, reaction products of glycerol with ϵ -caprolactone, and reaction products of pentaerythritol with ϵ -caprolactone. Further preferred H-functional starter substances used are diethylene glycol, dipropylene glycol, castor oil, sorbitol and polyether polyols formed from repeat polyalkylene oxide units.
- 25 The H-functional starter substances are more preferably one or more compounds selected from the group consisting of ethylene glycol, propylene glycol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 2-methylpropane-1,3-diol, neopentyl glycol, 1,6-hexanediol, 1,8-octanediol, diethylene glycol, dipropylene glycol, glycerol, trimethylolpropane, di- and trifunctional polyether polyols, where
- 30 the polyether polyol is formed from a di- or tri-H-functional starter substance and propylene oxide or a di- or tri-H-functional starter substance, propylene oxide and ethylene oxide. The polyether polyols preferably have a molecular weight M_n in the range from 62 to 4500 g/mol and a functionality of 2 to 3, and especially a molecular

weight Mn in the range from 62 to 3000 g/mol and a functionality of 2 to 3.

The polyether carbonate polyols are prepared by catalytic addition of carbon dioxide and alkylene oxides onto H-functional starter substances. "H-Functional" in the
5 context of the invention is understood to mean the number of hydrogen atoms active for the alkoxylation per molecule of the starter substance.

DMC catalysts 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
10 catalysts 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 in the homopolymerization of epoxides and enable the preparation of polyether polyols with very low catalyst concentrations (25 ppm or less), such that removal of the catalyst from the finished product is generally no longer required. A
15 typical example is that of the high-activity DMC catalysts which are described in EP-A 700 949 and which comprise, as well as a double metal cyanide compound (e.g. zinc hexacyanocobaltate(III)) and an organic complex ligand (e.g. tert-butanol), also a polyether having a number-average molecular weight greater than 500 g/mol.

20 The preparation of alkaline DMC catalysts was disclosed in US 5 783 513. The invention described provided DMC catalysts having an alkalinity in the range from 0.2 to about 2.0% by weight in the form of metal oxide based on the mass of metal salt which was used for preparation of the catalyst. These substantially noncrystalline catalysts led to an improvement in viscosity and a lower degree of unsaturation in the
25 preparation of polyether polyols from alkylene oxides. The catalysts were thus used only in the homopolymerization of propylene oxide. There are no pointers to copolymerization using carbon dioxide in the document.

US 6 716 788 B2 discloses the preparation of alkaline DMC catalysts in the presence
30 of 0.03 to 0.4 mol of an alkaline metal compound (addition of oxides and/or hydroxides) based on the amount of metal salt used which is reacted with metal cyanide salt. The DMC catalysts thus prepared are used in the homopolymerization of epoxides in the absence of carbon dioxide. There are no pointers to

copolymerization using carbon dioxide.

The inventive DMC catalysts are preferably obtained by

- 5 (i) in the first step, reacting an aqueous solution of a cyanide-free metal salt with the aqueous solution of a metal cyanide salt in the presence of one or more organic complex ligands, for example an ether or alcohol, one or more alkaline metal hydroxides, metal carbonates and/or metal oxides being present either in the aqueous solution of the cyanide-free metal salt or the aqueous solution of the metal cyanide salt, or in both aqueous solutions, and
10 the sum of the alkaline metal hydroxides, metal carbonates and/or metal oxides used being 0.3 to 1.8 mol, preferably 0.6 to 1.6 mol and more preferably 0.8 to 1.4 mol of base equivalents (based on 1 mol of the metal cyanide salt used for catalyst synthesis),
- (ii) in the second step, removing the solids from the suspension obtained from (i)
15 by known techniques (such as centrifugation or filtration),
- (iii) in a third step, optionally washing the isolated solids with an aqueous solution of an organic complex ligand (for example by resuspension and subsequent reisolation by filtration or centrifugation),
- (iv) then drying the resulting solids, optionally after pulverization, at temperatures
20 of generally 20-100°C and at pressures of generally 0.1 mbar to standard pressure (1013 mbar),

and, in the first step or immediately after the precipitation of the double metal cyanide compound (second step), one or more organic complex ligands are added, preferably in excess (based on the double metal cyanide compound), and optionally
25 further complex-forming components.

The double metal cyanide compounds present in the inventive DMC catalysts are the reaction products of water-soluble cyanide-free metal salts and water-soluble metal cyanide salts, the cyanide-free metal salt or metal cyanide salt used for preparation of
30 the DMC catalyst, or both of these salts, containing 0.3 to 1.8 mol, preferably 0.6 to 1.6 mol and more preferably 0.1 to 1.4 mol of base equivalents (based on 1 mol of the metal cyanide salt used for catalyst synthesis) in the form of an alkaline metal hydroxide, metal carbonate and/or metal oxide,

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
 5 formed, the potassium hexacyanocobaltate used having been mixed beforehand with 0.3 to 1.8 mol, preferably 0.6 to 1.6 mol and more preferably 0.8 to 1.4 mol of base equivalents (based on 1 mol of the metal cyanide salt used for catalyst synthesis) of alkaline metal hydroxide, metal carbonate and/or metal oxide.

10

Cyanide-free metal salts suitable for preparation of the double metal cyanide compounds preferably have the general formula (III)



15

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 preferably being Zn^{2+} , Fe^{2+} , Co^{2+} , or Ni^{2+} ,

X is one or more (i.e. different) anions, preferably one anion selected from the group
 20 of the 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, cyanate, thiocyanate, isocyanate, isothiocyanate or nitrate,

25

or suitable cyanide-free metal salts have the general formula (IV)



30 where

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

X is one or more (i.e. different) anions, preferably one anion selected from the group of the 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, cyanate, thiocyanate, isocyanate, isothiocyanate, carboxylate or nitrate,

5

or suitable cyanide-free metal salts have the general formula (V)



10 where

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

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

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

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

or suitable cyanide-free metal salts have the general formula (VI)

20



where

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

25 X is one or more (i.e. different) anions, preferably one anion selected from the group of the 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

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

Examples of suitable cyanide-free 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, cobalt(II) chloride, cobalt(II) thiocyanate, nickel(II) chloride and nickel(II) nitrate. It is also possible to use mixtures of different metal salts.

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



- 10 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' preferably being 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),

- 15 Y is selected from one or more metal cations from the group consisting of alkali metal (i.e. La^+ , Na^+ , K^+ , Rb^+ , Cs^+) and alkaline earth metal (i.e. Be^{2+} , Ca^{2+} , Mg^{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, carboxylate, oxalate or nitrate and

- 20 a, b and c are each integers, where the values of a, b and c are selected so as to give electrical 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 of 0.

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

- 30 Preferred double-cyanide compounds present in the inventive DMC catalysts are compounds of the general formula (VIII)



in which M is as defined in formulae (III) to (VI) and

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

x, x', y and z are each integers and are selected so as to give the electrical neutrality of the double metal cyanide compound.

5

Preferably

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

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

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

10

Examples of suitable double metal halide 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 15 29-66). Particular preference is given to using zinc hexacyanocobaltate(III).

The alkaline metal hydroxides, carbonates and oxides used for preparation of the inventive DMC catalysts are preferably the oxides or hydroxides of metals of groups 1a and 2a of the Periodic Table of the Elements (see, for example, "Handbook of 20 Chemistry and Physics, 63rd edition"). Examples of suitable alkaline metal hydroxides, metal oxides and metal carbonates are sodium carbonate, sodium hydroxide, potassium carbonate, potassium hydroxide, calcium oxide, calcium hydroxide, barium hydroxide or barium oxide.

25 The organic complex ligands added in the course of 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). For example, the organic complex ligands used are water-soluble organic compounds having 30 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-buten-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). Highly preferred organic complex ligands are selected from one or more compounds from the group consisting of dimethoxyethane, tert-butanol, 2-methyl-3-buten-2-ol, 2-methyl-3-buten-2-ol, ethylene glycol mono-tert-butyl ether and 3-methyl-3-oxetanemethanol.

10

Optionally, in the course of preparation of the inventive DMC catalysts, 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, polyalkyl acrylates, polyalkyl methacrylates, polyvinyl methyl ether, polyvinyl ethyl ether, polyvinyl acetate, polyvinyl alcohol, poly-N-vinylpyrrolidone, poly(N-vinylpyrrolidone-co-acrylic acid), 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 the glycidyl ether, glycosides, carboxylic esters of polyhydric alcohols, gallic acids or the salts, esters or amides thereof, cyclodextrins, phosphorus compounds, α,β -unsaturated carboxylic esters or ionic surface- or interface-active compounds are used.

Preferably, in the course of preparation of the inventive DMC catalysts, 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 cyanide-free metal salt to metal cyanide salt of 2.25:1.00, and the metal cyanide salt (e.g. potassium hexacyanocobaltate) are converted in the presence of the organic complex ligand (e.g. tert-butanol), with presence of one or more alkaline metal hydroxides, metal carbonates and/or metal oxides either in the aqueous solution of the cyanide-free metal salt or in the aqueous solution of the metal cyanide salt, or in both aqueous solutions, so as to form a suspension comprising the double metal cyanide compound

30

(e.g. zinc hexacyanocobaltate), water, excess cyanide-free metal salt and the organic complex ligand.

The organic complex ligand may be present in the aqueous solution of the cyanide-free metal salt and/or of the metal cyanide salt, or it is added to the suspension obtained directly after precipitation of the double metal cyanide compound. It has been found to be advantageous to mix the aqueous solutions of the cyanide-free metal salt and of the metal cyanide salt, with presence of one or more alkaline metal hydroxides, metal carbonates and/or metal oxides either in the aqueous solution of the cyanide-free metal salt or the aqueous solution of the metal cyanide salt, or in both aqueous solutions, and the organic complex ligands with vigorous stirring. Optionally, the suspension formed in the first step is subsequently treated with a further complex-forming component. The 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 suspension) is effected using a mixing nozzle, more preferably using a jet disperser as described in WO-A 01/39883.

In the second step, the solids (i.e. the precursor of the inventive catalyst) are isolated from the suspension by known techniques, such as centrifugation or filtration.

In a preferred embodiment, the isolated solids are 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 inventive catalyst. The amount of the organic complex ligand in the aqueous wash solution is preferably between 40 and 80% by weight based on the overall solution.

Optionally, in the third step, further complex-forming component is added to the aqueous wash solution, 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. Preference is given to washing in a first wash step (iii-1) with an aqueous solution of the unsaturated alcohol (for example by resuspension and subsequent reisolation by filtration or centrifugation), in order in this way to remove, for example, water-soluble by-products such as potassium chloride from the inventive catalyst. More preferably, the amount of the unsaturated alcohol in the aqueous wash solution is between 40 and 80% by weight, based on the overall solution of the first wash step. In the further wash steps (iii-2), either the first wash step is repeated once or more than once, preferably once to three times, or, preferably, a nonaqueous solution, for example a mixture or solution of organic complex ligand 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 of step (iii-2)), is used as the wash solution and the solids are washed once or more than once therewith, preferably once to three times.

15

The isolated and optionally washed solids are subsequently, optionally after pulverization, dried 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 isolating the inventive DMC catalysts from the suspension by filtration, filtercake washing and drying is described in WO-A 01/80994.

The invention also provides a process for preparing polyether carbonate polyols from one or more H-functional starter substances, one or more alkylene oxides and carbon dioxide in the presence of at least one DMC catalyst, wherein the cyanide-free metal salt or metal cyanide salt used for preparation of the DMC catalyst, or both of these salts, contain(s) 0.3 to 1.8 mol, preferably 0.6 to 1.6 mol and more preferably 0.8 to 1.4 mol of base equivalents (based on 1 mol of the metal cyanide salt used for catalyst synthesis) in the form of an alkaline metal hydroxide, metal carbonate and/or metal oxide, and wherein

30

(α) the H-functional starter substance or a mixture of at least two H-functional starter substances is initially charged and water and/or other volatile

compounds are optionally removed by means of elevated temperature and/or reduced pressure ("drying"), the DMC catalyst being added to the H-functional starter substance or to the mixture of at least two H-functional starter substances before or after the drying,

5

(β) activation is accomplished by

(β 1) in a first activation step, adding a first portion (based on the total amount of the amount of alkylene oxides used in the activation and copolymerization) of one or more alkylene oxides to the mixture resulting from step (α), where
10 this addition of the portion of alkylene oxide can optionally be effected in the presence of CO₂, but preferably in the absence of CO₂, and in each case awaiting the temperature peak ("hotspot") which occurs due to the exothermic chemical reaction which follows and/or a pressure drop in the reactor,

15

(β 2) in a second activation step, after the temperature peak attained in the preceding activation step, adding a second portion (based on the total amount of the amount of alkylene oxides used in the activation and copolymerization) of one or more alkylene oxides to the mixture resulting from the preceding activation step, where this addition of the portion of alkylene oxide can
20 optionally be effected in the presence of CO₂, but preferably in the absence of CO₂, and in each case awaiting the temperature peak ("hotspot") which occurs due to the exothermic chemical reaction which follows and/or a pressure drop in the reactor,

25

(β 3) optionally, in a third activation step or further activation steps, after the temperature peak attained in the preceding activation step, repeating step (β 2) zero to five times, preferably once to four times, more preferably exactly once, where this addition of the portion or these additions of the portions of alkylene oxide are effected in the absence of CO₂, and then in each case
30 awaiting the temperature peak ("hotspot") which occurs due to the exothermic chemical reaction which follows and/or a pressure drop in the reactor,

- 5 (β4) optionally, in a further activation step or further activation steps, after the temperature peak attained in the preceding activation step, repeating step (β3) once to five times, preferably once to four times, more preferably exactly once, where this addition of the portion or these additions of the portions of alkylene oxide are effected in the presence of CO₂, and then in each case awaiting the temperature peak ("hotspot") which occurs due to the exothermic chemical reaction which follows and/or a pressure drop in the reactor,
- 10 (γ) one or more alkylene oxides and carbon dioxide are added continuously to the mixture resulting from step (β) ("copolymerization"). The alkylene oxides used for the copolymerization may be the same as or different than the alkylene oxides used in the activation.
- 15 In a preferred embodiment, the portion of one or more alkylene oxides used in the activation in each of steps β1 to β4 is 2.0 to 15.0% by weight, preferably 2.5 to 14.0% by weight, more preferably 3.0 to 13.0% by weight (based on the total amount of the amount of alkylene oxides used in the activation and copolymerization).
- 20 Step (α):
For preparation of polyether carbonate polyols by catalytic addition of alkylene oxides (epoxides) and carbon dioxide onto H-functional starter substances (starters) in the presence of the inventive DMC catalysts, the H-functional starter substance or a mixture of at least two H-functional starter substances is initially charged.
- 25 Optionally, in step (α):
- (α1) the H-functional starter substance or a mixture of at least two H-functional starter substances is initially charged and
- (α2) the temperature of the starter substance or of the mixture 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. At the same time, it is also possible to pass a nitrogen stream
- 30 through the reactor.

The DMC catalyst may already be initially charged in the H-functional starter substance or the mixture of at least two H-functional starter substances, but it is also possible to add the DMC catalyst which has then been dried only after the drying of
5 the H-functional starter substance or the mixture of H-functional starter substances. The DMC catalyst can be added in solid form or as a suspension in an H-functional starter substance. If the catalyst is added as a suspension, this is preferably added prior to the drying of the H-functional starter substance(s).

10 Step (β):

The metered addition of one or more alkylene oxides and optionally of the carbon dioxide follows the drying of a starter substance or of the mixture of a plurality of starter substances and the addition of the DMC catalyst, which is added before or after the drying of the starter substance in solid form or in the form of a suspension.
15 If the DMC catalyst is added after the drying of the starter substance, this DMC catalyst should preferably be dried, for example in an analogous process to the drying of the starter substance. One or more alkylene oxides and the carbon dioxide can in principle be metered in in different ways. The metered addition can be commenced from reduced pressure or at a supply pressure selected beforehand. The
20 supply pressure is preferably established by introducing an inert gas, for example nitrogen, the (absolute) pressure set being between 10 mbar to 10 bar, preferably 100 mbar to 8 bar and preferably 500 mbar to 6 bar. In a particularly preferred embodiment, the mixture of one or more starter substances and the DMC catalyst resulting from step (α) is contacted at a temperature of 100°C to 130°C at least once,
25 preferably three times, with 1.5 bar to 10 bar (absolute), more preferably 3 bar to 6 bar (absolute), of an inert gas (nitrogen or a noble gas, for example argon) and, in each case immediately thereafter, the elevated pressure is reduced to 1 bar (absolute) within 15 min. Alternatively, in a likewise particularly preferred embodiment, inert gas (nitrogen or a noble gas, for example argon) is introduced into the mixture of one
30 or more starter compounds and the DMC catalyst resulting from step (α) at a temperature of 40°C to 150°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.

Step (γ):

One or more alkylene oxides and the carbon dioxide can be metered in simultaneously or sequentially, and it is possible to add the entire amount of carbon dioxide all at once or to meter it in over the reaction time. Preference is given to metered addition of the carbon dioxide. One or more alkylene oxides are metered in simultaneously or sequentially with respect to the carbon dioxide metering. If a plurality of alkylene oxides are used for synthesis of the polyether carbonate polyols, they can be metered in simultaneously or sequentially each via separate metering points or via one or more metering points, in which case at least two alkylene oxides are metered in as a mixture. The method of metered addition of the alkylene oxides and of the carbon dioxide makes it possible to synthesize random, alternating, block or gradient polyether carbonate polyols. The concentration of free alkylene oxides during the reaction in the reaction mixture is preferably > 0 to 40% by weight, more preferably > 0 -25% by weight, most preferably > 0 -15% by weight (based in each case on the weight of the reaction mixture).

Preference is given to using an excess of carbon dioxide based on the calculated amount of carbon dioxide incorporated in the polyether carbonate polyol, since an excess of carbon dioxide is advantageous due to the slowness of carbon dioxide to react. The amount of carbon dioxide can be fixed via the total pressure under the respective reaction conditions. An advantageous total pressure (absolute) has been found to be the range from 0.01 to 120 bar, preferably 0.1 to 110 bar, more preferably from 1 to 100 bar, for the copolymerization for preparation of the polyether carbonate polyols. For the process according to the invention, it has also been found that the copolymerization for preparation of the polyether carbonate polyols is performed advantageously at 50 to 150°C, preferably at 60 to 145°C, more preferably at 70 to 140°C and most preferably at 110 to 120°C. If temperatures below 50°C are established, the reaction stops. At temperatures above 150°C, the amount of unwanted by-products rises significantly. It should additionally be noted that the CO₂, given the selection of pressure and temperature, is converted from the gaseous state very substantially to the liquid and/or supercritical liquid state. CO₂ can, however, also be added to the reactor in solid form, and then be converted to the liquid and/or supercritical liquid state under the selected reaction conditions.

Particularly preferred reactors are: tubular reactors, stirred tanks, loop reactors. Polyether polycarbonate polyols can be prepared in a stirred tank, in which case the stirred tank, according to the embodiment and mode of operation, is cooled by means of the reactor jacket, internal cooling surfaces and/or cooling surfaces present in a pumped circulation system. For safety reasons, the content of free epoxide should not exceed 15% by weight in the reaction mixture of the stirred tank (see, for example, WO-A 2004/081082; page 3 line 14). Both in the semibatchwise application, where the product is withdrawn only after the end of the reaction, and in the continuous application, where the product is withdrawn continuously, particular attention should therefore be paid to the metering rate of the epoxide. It should be adjusted such that, in spite of the inhibiting effect of the carbon dioxide, the epoxide is depleted rapidly enough. It is possible to supply the carbon dioxide continuously or batchwise. This depends on whether the epoxide is consumed quickly enough and whether the product is to contain any CO₂-free polyether blocks. The amount of carbon dioxide (reported as the pressure) may likewise vary in the course of addition of the epoxide. It is possible to gradually increase or lower the CO₂ pressure during the addition of the epoxide, or to leave it at the same level.

A further possible embodiment in the stirred tank for the copolymerization (step γ) is characterized in that one or more H-functional starter compounds are metered continuously into the reactor during the reaction. The amount of the H-functional starter compounds which are metered continuously into the reactor during the reaction is preferably at least 20 mol% equivalents, more preferably 70 to 95 mol% equivalents (based in each case on the total amount of H-functional starter compounds).

The activated catalyst-starter mixture can be copolymerized (further) with epoxide and carbon dioxide in a stirred tank, or else in another reaction vessel (tubular reactor or loop reactor).

In the tubular reactor, activated catalyst and starter, and epoxide and carbon dioxide, are pumped continuously through a tube. The molar ratio of the reactants vary

according to the desired polymer. In a preferred embodiment, carbon dioxide is metered in here in the supercritical form thereof, i.e. effectively in liquid form, in order to enable better miscibility of the components. Advantageously, mixing elements are incorporated for better mixing of the reactants, as sold, for example, by
5 Ehrfeld Mikrotechnik BTS GmbH, or mixer-heat exchanger elements which simultaneously improve mixing and heat removal.

Even loop reactors can be used for preparation of polyether polycarbonate polyols. These generally include reactors with recycling, for example a jet loop reactor which
10 can also be operated continuously, or a loop of tubular reactors. The use of a loop reactor is especially advantageous because backmixing can be implemented here, and so the epoxide concentration should be low. In order to achieve full conversion, a tube ("dwell tube") is frequently connected downstream.

15 The polyether carbonate polyols obtainable by the process according to the invention have a low content of by-products and can be processed without any problem, especially by reaction with di- and/or polyisocyanates to give polyurethanes, especially flexible polyurethane foams. For polyurethane applications, preference is given to using polyether carbonate polyols based on an H-functional starter
20 compound having a functionality of at least 2. In addition, the polyether carbonate polyols obtainable by the process according to the invention can be used in applications such as washing and cleaning composition formulations, drilling fluids, fuel additives, ionic and nonionic surfactants, lubricants, process chemicals for papermaking or textile production or cosmetic formulations. The person skilled in
25 the art is aware that, depending on the particular field of use, the polyether carbonate polyols to be used must fulfill certain properties, for example molecular weight, viscosity, polydispersity, functionality and/or hydroxyl number.

Examples

The weight- and number-average molecular weight of the polymers formed were determined by means of gel permeation chromatography (GPC). The procedure of
5 DIN 55672-1 was followed: "Gel permeation chromatography, part 1 - tetrahydrofuran as elution solvent". This was done using polystyrene samples of known molar mass for calibration.

The OH number (hydroxyl number) was determined based on DIN 53240-2, except
10 using pyridine rather than THF/dichloromethane as the solvent. Titration was effected with 0.5 molar ethanolic KOH (end point recognition by means of potentiometry). The test substance used was castor oil with certified OH number. The statement of the unit in "mg/g" relates to mg[KOH]/g[polyether carbonate polyol].

15 The proportion of incorporated CO₂ in the resulting polyether carbonate polyol and the ratio of propylene carbonate to polyether carbonate polyol were determined by means of ¹H NMR (from Bruker, DPX 400, 400 MHz; zg30 pulse program, wait time d1: 10 s, 64 scans). The sample was dissolved in each case in deuterated chloroform.
20 The relevant resonances in the ¹H NMR (based on TMS = 0 ppm) are as follows:
cyclic carbonate (which was formed as a by-product) resonance at 4.5 ppm, carbonate resulting from carbon dioxide incorporated in the polyether carbonate polyol (resonances at 5.1 to 4.8 ppm), unreacted PO with resonances at 2.4 ppm, polyether polyol (i.e. without incorporated carbon dioxide) with resonances at 1.2 to
25 1.0 ppm, the 1,8-octanediol incorporated as a starter molecule with a resonance at 1.6 to 1.52 ppm.

The molar proportion of the carbonate incorporated in the polymer in the reaction mixture is calculated by formula (IX) as follows, using the following abbreviations:
30 F(4.5) = area of the resonance at 4.5 ppm for cyclic carbonate (corresponds to one hydrogen atom)
F(5.1-4.8) = area of the resonance at 5.1-4.8 ppm for polyether carbonate polyol and a hydrogen atom for cyclic carbonate

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

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

F(1.6-1.52) = area of the resonance at 1.6 to 1.52 ppm for 1,8-octanediol (starter)

- 5 Taking account of the relative intensities, conversion to mol% was effected by the following formula (IX) for the polymer-bound carbonate ("linear carbonate" LC) in the reaction mixture:

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

- 10 The proportion by weight (in % by weight) of polymer-bound carbonate (LC') in the reaction mixture was calculated by formula (X)

$$LC' = \frac{[F(5.1-4.8) - F(4.5)] * 102}{N} * 100\% \quad (X)$$

where the value for N ("denominator" N) is calculated by formula (XI):

15

$$N = [F(5.1-4.8) - F(4.5)] * 102 + F(4.5) * 102 + F(2.4) * 58 + 0.33 * F(1.2-1.0) * 58 + 0.25 * F(1.6-1.52) * 146 \quad (XI)$$

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 1,8-octanediol starter used.

20

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

$$CC' = \frac{F(4.5) * 102}{N} * 100\% \quad (XII)$$

25

where the value for N is calculated by formula (XI).

In order to use the values for the composition of the reaction mixture to calculate the

composition based on the polymer content (consisting of polyether polyol which has been formed from starter and propylene oxide during the activation steps which take place under CO₂-free conditions, and polyether carbonate polyol formed from starter, propylene oxide and carbon dioxide during the activation steps which take place in the presence of CO₂ and during the copolymerization), the non-polymer constituents of the reaction mixture (i.e. cyclic propylene carbonate and any unconverted propylene oxide present) were eliminated by calculation. The proportion by weight of the carbonate repeat units in the polyether carbonate polyol was converted to a proportion by weight of carbon dioxide by means of the factor $F = 44/(44 + 58)$. The statement of the CO₂ content in the polyether carbonate polyol ("incorporated CO₂"; see examples which follow and table 1) is normalized to the proportion of the polyether carbonate polyol molecule which has been formed in the copolymerization and optionally the activation steps in the presence of CO₂ (i.e. the proportion of the polyether carbonate polyol molecule which results from the starter (1,8-octanediol) and from the reaction of the starter with epoxide which was added under CO₂-free conditions was not taken into account here).

H-functional starter compound used:

1,8-octanediol from Sigma Aldrich

Examples 1 to 7: The catalysts were prepared as follows:

Example 1 (comparative): Preparation of a DMC catalyst without addition of NaOH
The catalyst was prepared with an apparatus according to fig. 4 from WO-A 01/39883.

In a loop reactor comprising a jet disperser according to fig. 2 from WO-A 01/39883 with one hole (diameter 0.7 mm), a solution of 258 g of zinc chloride in 937 g of distilled water and 135 g of tert-butanol was circulated at 50°C. For this purpose, a solution of 26 g of potassium hexacyanocobaltate (0.078 mol) in 332 g of distilled water was metered in. The pressure drop in the jet disperser was 2.5 bar. Subsequently, the dispersion formed was circulated at 50°C and a pressure drop in the jet disperser of 2.5 bar for 60 min. Thereafter, a mixture of 5.7 g of tert-butanol, 159 g of distilled water and 27.6 g of polypropylene glycol 1000 was metered in and

then the dispersion was circulated at 50°C and a pressure drop in the jet disperser of 2.5 bar for 80 min.

230 g of the dispersion obtained were filtered in a pressurized suction filter with filter area 20 cm³ and then washed with a mixture of 82 g of tert-butanol, 42.3 g of distilled water and 1.7 g of polypropylene glycol 1000. The washed filtercake was squeezed mechanically between 2 strips of filter paper and finally dried at 60°C under high vacuum at approx. 0.05 bar (absolute) for 2 h.

Example 2 (comparative): Preparation of a DMC catalyst with 0.25 mol of base equivalents per mole of potassium hexacyanocobaltate

The catalyst was prepared with an apparatus according to fig. 4 from WO-A 01/39883.

In a loop reactor comprising a jet disperser according to fig. 2 from WO-A 01/39883 with one hole (diameter 0.7 mm), a solution of 258 g of zinc chloride in 937 g of distilled water, 135 g of tert-butanol and 7.8 g of a 10% aqueous NaOH (0.0195 mol of base equivalents) was circulated at 50°C. For this purpose, a solution of 26 g of potassium hexacyanocobaltate (0.078 mol) in 332 g of distilled water was metered in. The pressure drop in the jet disperser was 2.5 bar. Subsequently, the dispersion formed was circulated at 50°C and a pressure drop in the jet disperser of 2.5 bar for 60 min. Thereafter, a mixture of 5.7 g of tert-butanol, 159 g of distilled water and 27.6 g of polypropylene glycol 1000 was metered in and then the dispersion was circulated at 50°C and a pressure drop in the jet disperser of 2.5 bar for 80 min.

230 g of the dispersion obtained were filtered in a pressurized suction filter with filter area 20 cm³ and then washed with a mixture of 82 g of tert-butanol, 42.3 g of distilled water and 1.7 g of polypropylene glycol 1000. The washed filtercake was squeezed mechanically between 2 strips of filter paper and finally dried at 60°C under high vacuum at approx. 0.05 bar (absolute) for 2 h.

Example 3: Preparation of a DMC catalyst with 0.55 mol of base equivalents per mole of potassium hexacyanocobaltate

A 1 l round-bottom flask was initially charged with a solution of 7.4 g (0.022 mol) of potassium hexacyanocobaltate, 39 g of tert-butanol and 302 g of dist. water, and heated to 30°C while stirring vigorously by means of a laboratory stirrer (1000 rpm).

152 g of a 50% aqueous solution of zinc chloride (alkalinity 0.64% by weight of ZnO, corresponding to 0.012 mol of base equivalents) were added dropwise to the stirred solution within 3 min. Subsequently, the mixture was stirred at 30°C for a further 30 min (1000 rpm). The suspension formed was filtered by means of a suction filter. Subsequently, 8.0 g of the moist filtercake were dispersed while stirring vigorously (1000 rpm) in a mixture of 110 g of tert-butanol and 60 g of dist. water. Once all of the solids had been dispersed homogeneously in the wash solution, the mixture was stirred for a further 30 min. The suspension was filtered again by means of a suction filter and the moist filtercake was finally dispersed once again in 144 g of tert-butanol. After filtering the dispersion, the filtercake was dried at 45°C under reduced pressure (300 mbar) overnight.

Example 4: Preparation of a DMC catalyst with 0.372 mol of base equivalents per mole of potassium hexacyanocobaltate

15 The catalyst was prepared with an apparatus according to fig. 4 from WO-A 01/39883.

In a loop reactor comprising a jet disperser according to fig. 2 from WO-A 01/39883 with one hole (diameter 0.7 mm), a solution of 258 g of zinc chloride in 937 g of distilled water, 135 g of tert-butanol and 15.3 g of a 10% aqueous sodium carbonate solution (0.0145 mol) was circulated at 50°C. For this purpose, a solution of 26 g of potassium hexacyanocobaltate (0.078 mol) in 332 g of distilled water was metered in. The pressure drop in the jet disperser was 2.5 bar. Subsequently, the dispersion formed was circulated at 50°C and a pressure drop in the jet disperser of 2.5 bar for 60 min. Thereafter, a mixture of 5.7 g of tert-butanol, 159 g of distilled water and 27.6 g of polypropylene glycol 1000 was metered in and then the dispersion was circulated at 50°C and a pressure drop in the jet disperser of 2.5 bar for 80 min.

230 g of the dispersion obtained were filtered in a pressurized suction filter with filter area 20 cm³ and then washed with a mixture of 82 g of tert-butanol, 42.3 g of distilled water and 1.7 g of polypropylene glycol 1000. The washed filtercake was squeezed mechanically between 2 strips of filter paper and finally dried at 60°C under high vacuum at approx. 0.05 bar (absolute) for 2 h.

Example 5 (comparative): Preparation of a DMC catalyst with 0.20 mol of base

equivalents per mole of potassium hexacyanocobaltate

The catalyst was prepared with an apparatus according to fig. 4 from WO-A 01/39883.

- 5 In a loop reactor comprising a jet disperser according to fig. 2 from WO-A 01/39883 with one hole (diameter 0.7 mm), a solution of 258 g of zinc chloride in 937 g of distilled water, 135 g of tert-butanol and 15.3 g of a 10% aqueous sodium monomethyl carbonate solution (0.0156 mol) was circulated at 50°C. For this purpose, a solution of 26 g of potassium hexacyanocobaltate (0.078 mol) in 332 g of distilled water was metered in. The pressure drop in the jet disperser was 2.5 bar.
- 10 Subsequently, the dispersion formed was circulated at 50°C and a pressure drop in the jet disperser of 2.5 bar for 60 min. Thereafter, a mixture of 5.7 g of tert-butanol, 159 g of distilled water and 27.6 g of polypropylene glycol 1000 was metered in and then the dispersion was circulated at 50°C and a pressure drop in the jet disperser of 2.5 bar for 80 min.
- 15 230 g of the dispersion obtained were filtered in a pressurized suction filter with filter area 20 cm³ and then washed with a mixture of 82 g of tert-butanol, 42.3 g of distilled water and 1.7 g of polypropylene glycol 1000. The washed filtercake was squeezed mechanically between 2 strips of filter paper and finally dried at 60°C under high vacuum at approx. 0.05 bar (absolute) for 2 h.

20

Example 6: Preparation of a DMC catalyst with 1.25 mol of base equivalents per mole of potassium hexacyanocobaltate

The catalyst was prepared with an apparatus according to fig. 4 from WO-A 01/39883.

- 25 In a loop reactor comprising a jet disperser according to fig. 2 from WO-A 01/39883 with one hole (diameter 0.7 mm), a solution of 427 g of zinc bromide in 937 g of distilled water, 135 g of tert-butanol and 39.0 g of a 10% aqueous NaOH (0.0975 mol) was circulated at 50°C. For this purpose, a solution of 26 g of potassium hexacyanocobaltate (0.078 mol) in 332 g of distilled water was metered
- 30 in. The pressure drop in the jet disperser was 2.5 bar. Subsequently, the dispersion formed was circulated at 50°C and a pressure drop in the jet disperser of 2.5 bar for 60 min. Thereafter, a mixture of 5.7 g of tert-butanol, 159 g of distilled water and 27.6 g of polypropylene glycol 1000 was metered in and then the dispersion was

circulated at 50°C and a pressure drop in the jet disperser of 2.5 bar for 80 min.

230 g of the dispersion obtained were filtered in a pressurized suction filter with filter area 20 cm³ and then washed with a mixture of 82 g of tert-butanol, 42.3 g of distilled water and 1.7 g of polypropylene glycol 1000. The washed filtercake was
5 squeezed mechanically between 2 strips of filter paper and finally dried at 60°C under high vacuum at approx. 0.05 bar (absolute) for 2 h.

Example 7 (comparative): Preparation of a DMC catalyst with 2.0 mol of base equivalents per mole of potassium hexacyanocobaltate

10 The catalyst was prepared with an apparatus according to fig. 4 from WO-A 01/39883.

In a loop reactor comprising a jet disperser according to fig. 2 from WO-A 01/39883 with one hole (diameter 0.7 mm), a solution of 427 g of zinc bromide in 937 g of distilled water, 135 g of tert-butanol and 62.4 g of a 10% aqueous NaOH (0.156 mol)
15 was circulated at 50°C. For this purpose, a solution of 26 g of potassium hexacyanocobaltate (0.078 mol) in 332 g of distilled water was metered in. The pressure drop in the jet disperser was 2.5 bar. Subsequently, the dispersion formed was circulated at 50°C and a pressure drop in the jet disperser of 2.5 bar for 60 min. Thereafter, a mixture of 5.7 g of tert-butanol, 159 g of distilled water and 27.6 g of
20 polypropylene glycol 1000 was metered in and then the dispersion was circulated at 50°C and a pressure drop in the jet disperser of 2.5 bar for 80 min.

230 g of the dispersion obtained were filtered in a pressurized suction filter with filter area 20 cm³ and then washed with a mixture of 82 g of tert-butanol, 42.3 g of distilled water and 1.7 g of polypropylene glycol 1000. The washed filtercake was
25 squeezed mechanically between 2 strips of filter paper and finally dried at 60°C under high vacuum at approx. 0.05 bar (absolute) for 2 h.

Examples 8 to 14: The catalysts were tested in the preparation of polyether carbonate polyols as follows:

30 A 1 liter pressure reactor with a gas metering device was initially charged with 141 mg of dried DMC catalyst according to examples 1 to 7 (see table 1 below) and dried 51 g of 1,8-octanediol (starter). The reactor was heated to 130°C and inertized by repeated injection of nitrogen to approx. 5 bar and subsequent decompression to

approx. 1 bar. This operation was performed 3 times. At 130°C and in the absence of CO₂, 25 g of propylene oxide (PO) were metered rapidly into the reactor. The activation of the catalyst was perceptible by a temperature peak ("hotspot") and by a pressure drop to the starting pressure (approx. 1 bar). After the first pressure drop,

5 20 g of PO and then 19 g of PO were metered in rapidly, as a result of which there was again a temperature peak and a pressure drop in each case. Once the reactor had been charged with 50 bar of CO₂, 50 g of PO were metered in rapidly, as a result of which there was a temperature peak after a wait time [time 1]. At the same time, the pressure of carbon dioxide CO₂ began to fall. The pressure was regulated such that,

10 when it fell below the target value, new CO₂ was added. Only thereafter was the residual propylene oxide (435 g) pumped continuously into the reactor at approx. 1.8 g/min, while the temperature was lowered to 105°C after 10 minutes in steps of 5°C per five minutes. After PO addition had ended, stirring was continued (1500 rpm) at 105°C and the pressure stated above until no further consumption of

15 CO₂ was observed.

Table 1: Preparation of polyether carbonate polyols

Example	Catalyst used from example	Alkalinity [mol of base equiv. per mole of K ₃ [Co(CN) ₆]]	Time 1 [min]	CO ₂ incorporated [% by wt.]	Selectivity cyclic/linear	OH number [mg/g]	Poly-dispersity
8 (comp.)	1 (comp.)	--	30	21.0	0.20	65.5	1.70
9 (comp.)	2 (comp.)	0.25	38	21.0	0.21	64.6	1.52
10	3	0.55	74	19.3	0.16	66.6	1.68
11	4	0.372	58	18.7	0.17	65.3	1.52
12 (comp.)	5 (comp.)	0.20	114	22.4	0.22	75.2	1.91
13	6	1.25	50	18.8	0.14	48.7 *	1.44
14 (comp.)	7 (comp.)	2.0	188	18.5	0.14	57.3 *	1.59

comp. = comparative example

*) OH number of the reaction mixture without prior removal of propylene carbonate

20 formed

It becomes clear from the results in table 1 that a minimum amount of base is needed

to achieve an improvement in the selectivity relative to a DMC catalyst without addition of base. Thus, the selectivity without addition of base (ex. 8 (comp.)) is not improved by addition of 0.2 (ex. 12 (comp.)) or 0.25 (ex. 9 (comp.)) base equivalent per mole of $K_3[Co(CN)_6]$ in the preparation of the DMC catalyst. Only from an alkalinity of more than 0.25 base equivalent per mole of $K_3[Co(CN)_6]$, e.g. 0.37 base equivalent per mole of $K_3[Co(CN)_6]$ according to ex. 11, is the selectivity improved in favor of the desired linear polyether carbonate polyol. An excessive proportion of base equivalents per mole of $K_3[Co(CN)_6]$, in contrast, worsens the economic viability of the process; even a proportion of 2.0 mol of base equivalents per mole of $K_3[Co(CN)_6]$ prolongs time 1 to more than 120 min (ex. 14 (comp.)).

Claims

1. A process for preparing polyether carbonate polyols from one or more H-functional starter substances, one or more alkylene oxides and carbon dioxide in the presence of at least one double metal cyanide catalyst, wherein the cyanide-free metal salt or metal cyanide salt used for preparation of the double metal cyanide catalyst, or both of these salts, contain(s) 0.3 to 1.8 mol of base equivalents (based on 1 mol of the metal cyanide salt used for catalyst synthesis) of alkaline metal hydroxide, metal carbonate and/or metal oxide.
2. The process as claimed in claim 1, characterized in that the DMC catalyst is prepared by reacting an aqueous solution of a cyanide-free metal salt with the aqueous solution of a metal cyanide salt in the presence of one or more organic complex ligands, one or more alkaline metal hydroxides, metal carbonates and/or metal oxides being present either in the aqueous solution of the cyanide-free metal salt or the aqueous solution of the metal cyanide salt, or in both aqueous solutions, and the sum of the alkaline metal hydroxides, metal carbonates and/or metal oxides used being 0.3 to 1.8 mol of base equivalents (based on 1 mol of the metal cyanide salt used for catalyst synthesis).
3. The process as claimed in claim 1, wherein the DMC catalyst is prepared by
 - (i) in the first step, reacting an aqueous solution of a cyanide-free metal salt with the aqueous solution of a metal cyanide salt in the presence of one or more organic complex ligands, one or more alkaline metal hydroxides and/or metal carbonates and/or metal oxides being present either in the aqueous solution of the cyanide-free metal salt or the aqueous solution of the metal cyanide salt, or in both aqueous solutions, and the sum of the alkaline metal hydroxides and/or metal carbonates and/or metal oxides used being 0.3 to 1.8 mol of base equivalents (based on 1 mol of the metal cyanide salt used for catalyst synthesis),
 - (ii) in the second step, removing the solids from the suspension obtained from (i),

- (iii) in a third step, washing the isolated solids with an aqueous solution of an organic complex ligand,
(iv) then drying the resulting solids,
and, in the first step or immediately after the precipitation of the double metal cyanide compound (second step), one or more organic complex ligands are added.
- 5
4. The process as claimed in any of claims 1 to 3, wherein the cyanide-free metal salt or metal cyanide salt used for preparation of the double metal cyanide catalyst contains, or both of these salts contain, 0.6 to 1.6 mol of base equivalents (based on 1 mol of the metal cyanide salt used for catalyst synthesis) in the form of an alkaline metal hydroxide, metal carbonate and/or metal oxide.
- 10
5. The process as claimed in any of claims 1 to 4, wherein the alkaline metal hydroxide, metal carbonate and/or metal oxide used is selected from at least one of the group consisting of the oxides or hydroxides of metals of groups 1a and 2a of the Periodic Table of the Elements.
- 15
6. The process as claimed in claim 5, wherein the alkaline metal hydroxide, metal oxide and/or metal carbonate used is selected from at least one of the group consisting of sodium carbonate, sodium hydroxide, potassium hydroxide, potassium carbonate, calcium oxide, calcium hydroxide, barium hydroxide and barium oxide.
- 20
7. The process as claimed in claim 2 or 3, wherein the cyanide-free metal salt used for formation of the DMC compound is selected from at least one of the group consisting of zinc chloride, zinc bromide, zinc iodide, zinc acetate, zinc acetylacetonate, zinc benzoate, zinc nitrate, iron(II) sulfate, iron(II) bromide, iron(II) chloride, cobalt(II) chloride, cobalt(II) thiocyanate, nickel(II) chloride and nickel(II) nitrate.
- 25
8. The process as claimed in claim 2 or 3, wherein the metal cyanide salt used is
- 30

selected from at least one of the group consisting of potassium hexacyanocobaltate(III), potassium hexacyanoferrate(II), potassium hexacyanoferrate(III), calcium hexacyanocobaltate(III) and lithium hexacyanocobaltate(III).

5

9. The process as claimed in any of claims 1 to 8, characterized in that

(α) the H-functional starter substance or a mixture of at least two H-functional starter substances is initially charged and water and/or other volatile compounds are optionally removed by means of elevated temperature and/or reduced pressure ("drying"), the DMC catalyst being added to the H-functional starter substance or to the mixture of at least two H-functional starter substances before or after the drying,

10

(β) activation is accomplished by

(β 1) in a first activation step, adding a first portion (based on the total amount of the amount of alkylene oxides used in the activation and copolymerization) of one or more alkylene oxides to the mixture resulting from step (α), and in each case awaiting the temperature peak ("hotspot") which occurs due to the exothermic chemical reaction which follows and/or a pressure drop in the reactor,

15

(β 2) in a second activation step, after the temperature peak attained in the preceding activation step, adding a second portion (based on the total amount of the amount of alkylene oxides used in the activation and copolymerization) of one or more alkylene oxides to the mixture resulting from the preceding activation step, and in each case awaiting the temperature peak ("hotspot") which occurs due to the exothermic chemical reaction which follows and/or a pressure drop in the reactor,

20

25

(γ) one or more alkylene oxides and carbon dioxide are added to the mixture resulting from step (β) ("copolymerization").

30

10. The process as claimed in any of claims 1 to 9, characterized in that the copolymerization of alkylene oxides and carbon dioxide is effected under a pressure of 1 to 200 bar.

11. The process as claimed in any of claims 1 to 10, characterized in that the copolymerization of alkylene oxides and carbon dioxide (step γ) is effected within the temperature range from 60 to 150°C.
- 5
12. The process as claimed in any of claims 1 to 11, which is performed in a tubular reactor, stirred tank or loop reactor.
- 10
13. The process as claimed in any of claims 1 to 11 performed in a stirred tank, characterized in that, in step γ), one or more H-functional starter compounds are metered continuously into the reactor during the reaction.