Claims

1. Process for the preparation of polyether carbonate polyols from one or more H-functional starter substances, one or more alkylene oxides and carbon dioxide in the presence of a double metal cyanide catalyst and in the presence of at least one additive A), characterized in that

(α) the H-functional starter substance or a mixture of at least two H-functional starter substances is initially introduced into the reaction vessel, the DMC catalyst being added to the H-functional starter substance or the mixture of at least two H-functional starter substances,

(β) for the activation, a part amount (based on the total amount of the amount of alkylene oxides employed in the activation and copolymerization) of one or more alkylene oxides is added to the mixture resulting from step (α), it being possible for this addition of a part amount of alkylene oxide optionally to be carried out in the presence of CO_2, and the temperature peak which occurs due to the subsequent exothermic chemical reaction and/or a drop in pressure in the reactor then in each case being awaited, and it also being possible for step (β) to be carried out several times for the activation,

(γ) one or more alkylene oxides and carbon dioxide are added to the mixture resulting from step (β) ("copolymerization"), it being possible for the alkylene oxides employed for the copolymerization to be identical to or different from the alkylene oxides employed in the activation,

wherein the additive A) is added in step (α) to the H-functional starter substance or the mixture of at least two H-functional starter substances and/or the additive A) is added in step (β) to the part amount of one or more alkylene oxides to the mixture resulting from step (α), and

wherein the additive A) is at least one compound chosen from the group consisting of sterically non-hindered phenols, catechols, pyrocatechols, thiazines, phenothiazines, thiazoles, benzothiazole, oxazines, phenoxazines, 2,2,6,6-tetramethylpiperidine 1-oxyl and nitrostyrenes.

2. Process according to claim 1, wherein the preparation is carried out in the presence of a DMC catalyst and in the presence of at least one additive A) and in the presence of at least one metal salt B), characterized in that
wherein the additive A) is added in step (α) to the H-functional starter substance or the mixture of at least two H-functional starter substances, and/or the additive A) is added in step (β) to the part amount of one or more alkylene oxides to the mixture resulting from step (α),
wherein the metal salt B) is added in step (α) to the H-functional starter substance or the mixture of at least two H-functional starter substances,
wherein at least one compound chosen from the group consisting of sterically non-hindered phenols, catechols, pyrocatechols, thiazines, phenothiazines, thiazoles, benzothiazoles, 2,2,6,6-tetramethylpiperidine 1-oxyl and nitrostyrenes is employed as the additive A), and
wherein at least one compound chosen from the group consisting of alkaline earth metal halides, alkaline earth metal carboxylates or aluminium carboxylates is employed as the metal salt B).

3. Process according to claim 2, wherein 4-nitrophenol and/or 2,4-dinitrophenol is employed as the additive A) and at least one compound chosen from the group consisting of magnesium acetate, calcium acetate, magnesium stearate, calcium stearate and aluminium stearate is employed as the metal salt B).

4. Process according to one of claims 1 to 3, characterized in that in step (α) the H-functional starter substance or a mixture of at least two H-functional starter substances is initially introduced into the reaction vessel and water is removed by elevated temperature and/or reduced pressure ("drying"), the DMC catalyst, the additive A) and optionally the metal salt B) being added to the H-functional starter substance or the mixture of at least two H-functional starter substances before or after the drying.

5. Process according to one of claims 1 to 4, wherein for the activation according to step (β)
(β1) in a first activation step a first part amount (based on the total amount of the amount of alkylene oxides employed in the activation and copolymerization) of one or more alkylene oxides is added to the mixture resulting from step (α), it being possible for this addition of the part amount of alkylene oxide optionally to be carried out in the presence of CO_2, but preferably in the absence of CO_2, and the temperature peak ("hot spot") which occurs due to the subsequent exothermic chemical reaction and/or a drop in pressure in the reactor then in each case being awaited.

(β2) in a second activation step after the temperature peak reached in the preceding activation step, a second part amount (based on the total amount of the amount of alkylene oxides employed in the activation and copolymerization) of one or more alkylene oxides is added to the mixture resulting from the preceding activation step, it being possible for this addition of the part amount of alkylene oxide optionally to be carried out in the presence of CO_2, but preferably in the absence of CO_2, and the temperature peak ("hot spot") which occurs due to the subsequent exothermic chemical reaction and/or a drop in pressure in the reactor then in each case being awaited.

6. Process according to claim 5, wherein for the activation

(β3) in a third activation step or further activation steps after the temperature peak reached in the preceding activation step, step (β2) is repeated once to five times, this addition of the part amount or these additions of the part amounts of alkylene oxide being carried out in the absence of CO_2.

7. Process according to claim 6, wherein for the activation

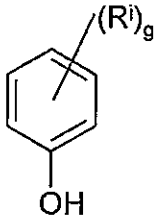
(β4) in a further activation step or further activation steps, after the temperature peak reached in the preceding activation step, step (β3) is repeated once to five times, this addition of the part amount or these additions of the part amounts of alkylene oxide being carried out in the presence of CO_2.

8. Process according to claim 7, wherein the particular part amount of one or more alkylene oxides which is employed in the activation in steps β1 to β4 is 2.0 to 15.0 wt.% (based on the total amount of the amount of alkylene oxides employed in the activation and copolymerization).

9. Process according to one of claims 1 to 8, wherein the amount of the additives A) employed is from 0.2 to 10.0 [mmol of additive A)] / [mmol of Co].

10. Process according to one of claims 2 to 8, wherein the amount of the additive A) employed is from 0.8 to 4.0 [mmol of additive A)] / [mmol of Co] and the amount of the metal salt B) employed is 0.8 to 4.0 [mmol of metal salt B)] / [mmol of Co].

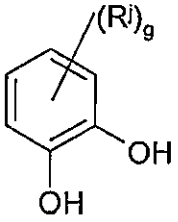
11. Process according to one of claims 1 to 9, wherein as the additive A),
sterically non-hindered phenols according to formula (II)



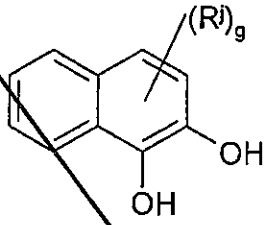
(II)

and/or

catechols according to formula (IIIa) or pyrocatechols according to formula (IIIb)



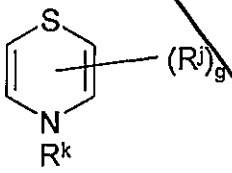
(IIIa)



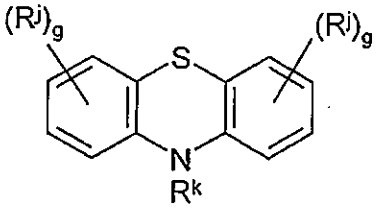
(IIIb)

and/or

thiazine according to formula (IVa) or phenothiazines according to formula (IVb)



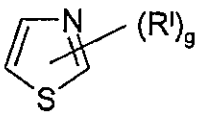
(IVa)



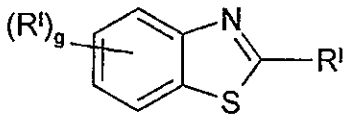
(IVb)

and/or

thiazoles according to formula (Va) or benzothiazoles according to formula (Vb)



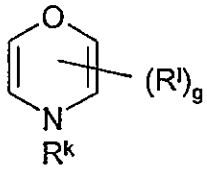
(Va)



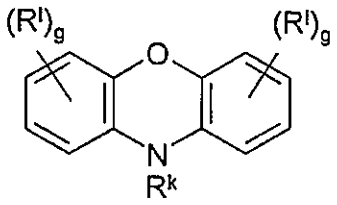
(Vb)

and/or

oxazines according to formula (VIa) or phenoxazines according to formula (VIb)



(VIa)



(VIb)

wherein in the case of the 1,4-oxazines according to the formula (VIa), these can also be the corresponding 1,2-oxazines and/or 1,3-oxazines,

wherein in the above-mentioned formulae

g = 0, 1 or 2 and

R^i represents an amino, bromo, chloro, cyano, fluoro, iodo, methoxy, methyl or nitro group, preferably a nitro group,

R^j represents an acetamido, amino, bromo, n-butyl, iso-butyl, tert-butyl, chloro, cyano, ethoxy, ethyl, fluoro, iodo, methoxy, methyl, nitro, iso-propyl, n-propyl group,

R^k represents an H or a C_1 - C_{20}-alkyl group, preferably H or a methyl, ethyl, iso-propyl, n-propyl, n-butyl, iso-butyl, tert-butyl, hexyl, cyclohexyl group,

R^l represents an H, C_1 - C_{20}-alkyl group (for example methyl, ethyl, iso-propyl, n-propyl, n-butyl, iso-butyl, tert-butyl, hexyl, cyclohexyl group), acetamido, amino, bromo, chloro, cyano, ethoxy, ethyl, fluoro, hydroxyl, iodo, methoxy, nitro group, or wherein the thiazole and/or the benzothiazole fragments are linked to one another via disulfide bridges,

and/or

α-nitrostyrene or β-nitrostyrene, are employed.

12. Process according to one of claims 1 to 11, wherein the H-functional starter substances employed are chosen from at least one of the group consisting of alcohols, amines, thiols, amino alcohols, thioalcohols, hydroxy esters, polyether polyols, polyester polyols, polyester ether polyols, polycarbonate polyols, polyether carbonate polyols, polyethyleneimines,

polyether-amines, polytetrahydrofurans, polyether thiols, polyacrylate polyols, castor oil, the mono- or diglyceride of ricinoleic acid, monoglycerides of fatty acids, and chemically modified mono-, di- and/or triglycerides of fatty acids and C_1-C_{24}-alkyl fatty acid esters which contain on average at least 2 OH groups per molecule.

13. Process according to one of claims 1 to 12, wherein the double metal cyanide catalyst employed contains at least one double metal cyanide compound chosen from the group consisting of zinc hexacyanocobaltate(III), zinc hexacyanoiridate(III), zinc hexacyanoferrate(III) and cobalt(II) hexacyanocobaltate(III).

14. Process according to claim 13, wherein the double metal cyanide catalyst employed additionally contains at least one organic complexing ligand chosen from the group consisting of aliphatic ethers, ethanol, isopropanol, n-butanol, iso-butanol, sec-butanol, tert-butanol, 2-methyl-3-buten-2-ol, 2-methyl-3-butyn-2-ol, ethylene glycol mono-tert-butyl ether, diethylene glycol mono-tert-butyl ether, tripropylene glycol monomethyl ether and 3-methyl-3-oxetane-methanol.

15. Process according to one of claims 1 to 13, which is carried out in a tube reactor, stirred tank or loop reactor.

Claims

1. Process for the preparation of polyether carbonate polyols from one or more H-functional starter substances, one or more alkylene oxides and carbon dioxide in the presence of a double metal cyanide catalyst and in the presence of at least one additive A), characterized in that

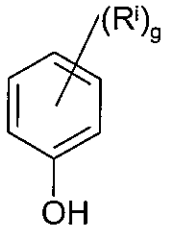
   (α) the H-functional starter substance or a mixture of at least two H-functional starter substances is initially introduced into the reaction vessel, the DMC catalyst being added to the H-functional starter substance or the mixture of at least two H-functional starter substances,

   (β) for the activation, a part amount (based on the total amount of the amount of alkylene oxides employed in the activation and copolymerization) of one or more alkylene oxides is added to the mixture resulting from step (α), it being possible for this addition of a part amount of alkylene oxide optionally to be carried out in the presence of CO_2, and the temperature peak which occurs due to the subsequent exothermic chemical reaction and/or a drop in pressure in the reactor then in each case being awaited, and it also being possible for step (β) to be carried out several times for the activation,

   (γ) one or more alkylene oxides and carbon dioxide are added to the mixture resulting from step (β) ("copolymerization"), it being possible for the alkylene oxides employed for the copolymerization to be identical to or different from the alkylene oxides employed in the activation,

   wherein the additive A) is added in step (α) to the H-functional starter substance or the mixture of at least two H-functional starter substances and/or the additive A) is added in step (β) to the part amount of one or more alkylene oxides to the mixture resulting from step (α), and

wherein the additive A) is at least one compound chosen from the group consisting of sterically non-hindered phenols according to formula (II)

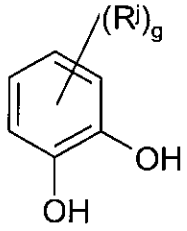


(II)

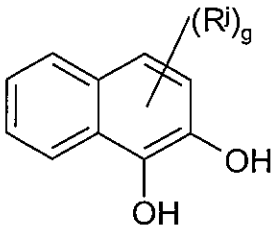
wherein

g = 0, 1, 2, preferably 1 or 2, and

R^i represents an amino, bromo, chloro, cyano, fluoro, iodo, methoxy, methyl or nitro group, preferably a nitro group, catechols according to formula (IIIa) and pyrocatechols according to formula (IIIb)



(IIIa)



(IIIb)

wherein

g has the above-mentioned meaning and

R^j represents an acetamido, amino, bromo, n-butyl, iso-butyl, tert-butyl, chloro, cyano, ethoxy, ethyl, fluoro, iodo, methoxy, methyl, nitro, iso-propyl, n-propyl group, phenothiazines, benzothiazole, phenoxazines, 2,2,6,6-tetramethylpiperidine 1-oxyl and nitrostyrenes.

2. Process according to claim 1, wherein the preparation is carried out in the presence of a DMC catalyst and in the presence of at least one additive A) and in the presence of at least one metal salt B), characterized in that

wherein the additive A) is added in step (α) to the H-functional starter substance or the mixture of at least two H-functional starter substances, and/or the additive A) is added in step (β) to the part amount of one or more alkylene oxides to the mixture resulting from step (α),

wherein the metal salt B) is added in step (α) to the H-functional starter substance or the mixture of at least two H-functional starter substances,

wherein at least one compound chosen from the group consisting of alkaline earth metal halides, alkaline earth metal carboxylates or aluminium carboxylates is employed as the metal salt B).

3. Process according to claim 2, wherein 4-nitrophenol and/or 2,4-dinitrophenol is employed as the additive A) and at least one compound chosen from the group consisting of magnesium acetate, calcium acetate, magnesium stearate, calcium stearate and aluminium stearate is employed as the metal salt B).

4. Process according to one of claims 1 to 3, characterized in that in step (α) the H-functional starter substance or a mixture of at least two H-functional starter substances is initially introduced into the reaction vessel and water is removed by elevated temperature and/or reduced pressure ("drying"), the DMC catalyst, the additive A) and optionally the metal salt B) being added to the H-functional starter substance or the mixture of at least two H-functional starter substances before or after the drying.

5. Process according to one of claims 1 to 4, wherein for the activation according to step (β)

(β1) in a first activation step a first part amount (based on the total amount of the amount of alkylene oxides employed in the activation and copolymerization) of one or more alkylene oxides is added to the mixture resulting from step (α), it being possible for this addition of the part amount of alkylene oxide optionally to be carried out in the presence of CO_2, but preferably in the absence of CO_2, and the temperature peak ("hot spot") which occurs due to the subsequent exothermic chemical reaction and/or a drop in pressure in the reactor then in each case being awaited.

(β2) in a second activation step after the temperature peak reached in the preceding activation step, a second part amount (based on the total amount of the amount of alkylene oxides employed in the activation and copolymerization) of one or more alkylene oxides is added to the mixture resulting from the preceding activation step, it being possible for this addition of the part amount of alkylene oxide optionally to be carried out in the presence of CO_2, but preferably in the absence of CO_2, and the temperature peak ("hot spot") which occurs due to the subsequent exothermic chemical reaction and/or a drop in pressure in the reactor then in each case being awaited.

6. Process according to claim 5, wherein for the activation

(β3) in a third activation step or further activation steps after the temperature peak reached in the preceding activation step, step (β2) is repeated once to five times, this addition of the part amount or these additions of the part amounts of alkylene oxide being carried out in the absence of CO_2.

7. Process according to claim 6, wherein for the activation

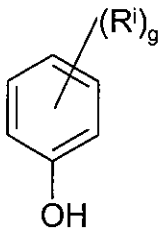
(β4) in a further activation step or further activation steps, after the temperature peak reached in the preceding activation step, step (β3) is repeated once to five times, this addition of the part amount or these additions of the part amounts of alkylene oxide being carried out in the presence of CO_2.

8. Process according to claim 7, wherein the particular part amount of one or more alkylene oxides which is employed in the activation in steps β1 to β4 is 2.0 to 15.0 wt.% (based on the total amount of the amount of alkylene oxides employed in the activation and copolymerization).

9. Process according to one of claims 1 to 8, wherein the amount of the additives A) employed is from 0.2 to 10.0 [mmol of additive A)] / [mmol of Co].

10. Process according to one of claims 2 to 8, wherein the amount of the additive A) employed is from 0.8 to 4.0 [mmol of additive A)] / [mmol of Co] and the amount of the metal salt B) employed is 0.8 to 4.0 [mmol of metal salt B)] / [mmol of Co].

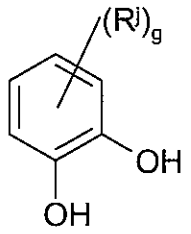
11. Process according to one of claims 1 to 9, wherein as the additive A),
sterically non-hindered phenols according to formula (II)



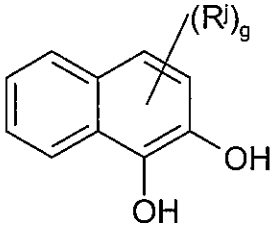
(II)

and/or

catechols according to formula (IIIa) or pyrocatechols according to formula (IIIb)



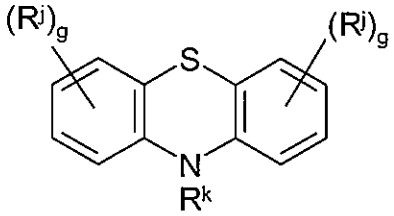
(IIIa)



(IIIb)

and/or

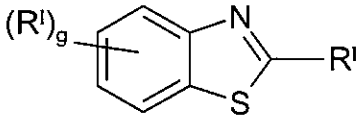
phenothiazines according to formula (IVb)



(IVb)

and/or

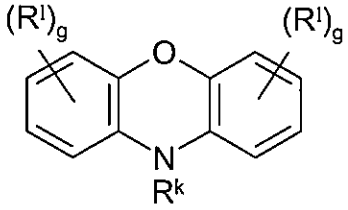
benzothiazoles according to formula (Vb)



(Vb)

and/or

phenoxazines according to formula (VIb)



(VIb)

wherein in the case of the 1,4-oxazines according to the formula (VIa), these can also be the corresponding 1,2-oxazines and/or 1,3-oxazines,

wherein in the above-mentioned formulae

g = 0, 1 or 2 and

R^i represents an amino, bromo, chloro, cyano, fluoro, iodo, methoxy, methyl or nitro group, preferably a nitro group,

R^j represents an acetamido, amino, bromo, n-butyl, iso-butyl, tert-butyl, chloro, cyano, ethoxy, ethyl, fluoro, iodo, methoxy, methyl, nitro, iso-propyl, n-propyl group,

R^k represents an H or a C_1 - C_{20}-alkyl group, preferably H or a methyl, ethyl, iso-propyl, n-propyl, n-butyl, iso-butyl, tert-butyl, hexyl, cyclohexyl group,

R^l represents an H, C_1 - C_{20}-alkyl group (for example methyl, ethyl, iso-propyl, n-propyl, n-butyl, iso-butyl, tert-butyl, hexyl, cyclohexyl group), acetamido, amino, bromo, chloro, cyano, ethoxy, ethyl, fluoro, hydroxyl, iodo, methoxy, nitro group, or wherein the thiazole and/or the benzothiazole fragments are linked to one another via disulfide bridges,

and/or

α-nitrostyrene or β-nitrostyrene, are employed.

12. Process according to one of claims 1 to 11, wherein the H-functional starter substances employed are chosen from at least one of the group consisting of alcohols, amines, thiols, amino alcohols, thioalcohols, hydroxy esters, polyether polyols, polyester polyols, polyester ether polyols, polycarbonate polyols, polyether carbonate polyols, polyethyleneimines, polyether-amines, polytetrahydrofurans, polyether thiols, polyacrylate polyols, castor oil, the mono- or diglyceride of ricinoleic acid, monoglycerides of fatty acids, and chemically modified mono-, di- and/or triglycerides of fatty acids and C_1-C_{24}-alkyl fatty acid esters which contain on average at least 2 OH groups per molecule.

13. Process according to one of claims 1 to 12, wherein the double metal cyanide catalyst employed contains at least one double metal cyanide compound chosen from the group consisting of zinc hexacyanocobaltate(III), zinc hexacyanoiridate(III), zinc hexacyanoferrate(III) and cobalt(II) hexacyanocobaltate(III).

14. Process according to claim 13, wherein the double metal cyanide catalyst employed additionally contains at least one organic complexing ligand chosen from the group consisting of aliphatic ethers, ethanol, isopropanol, n-butanol, iso-butanol, sec-butanol, tert-butanol, 2-methyl-3-buten-2-ol, 2-methyl-3-butyn-2-ol, ethylene glycol mono-tert-butyl ether, diethylene glycol mono-tert-butyl ether, tripropylene glycol monomethyl ether and 3-methyl-3-oxetane-methanol.

15. Process according to one of claims 1 to 13, which is carried out in a tube reactor, stirred tank or loop reactor.