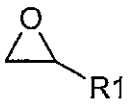
Claims

1. Process for the preparation of polyether carbonate polyols with primary hydroxyl end groups, comprising the steps:
   1. reaction of a starter compound containing active hydrogen atoms with carbon dioxide and with an epoxide of the general formula (II):



(II)

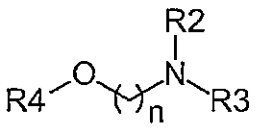
   wherein R1 represents hydrogen, an alkyl radical or an aryl radical and with the proviso that ≥ 0 % by weight to ≤ 30 % by weight, based on the total amount of the epoxide (II) employed, is ethylene oxide,
   wherein the reaction is carried out in the presence of a double metal cyanide catalyst;
   2. reaction of the product obtained in step 1. with a cyclic carboxylic acid anhydride; and
   3. reaction of the product obtained in step 2. with ethylene oxide in the presence of a catalyst which contains at least one nitrogen atom per molecule, excluding non-cyclic tertiary amines with identical substituents.

2. Process according to claim 1, wherein the starter compound employed in step 1. is a poly(oxyalkylene) polyol or a poly(oxyalkylene) carbonate polyol which has a number of hydroxyl groups per molecule of from ≥ 2.0 to ≤ 5.0 and a number-average molecular weight of from ≥ 450 g/mol to ≤ 2,000 g/mol.

3. Process according to claim 1, wherein in the epoxide of the general formula (II) R1 is hydrogen, methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, cyclohexyl and/or phenyl.

4. Process according to claim 1, wherein the cyclic carboxylic acid anhydride employed in step 2. is chosen from the group comprising phthalic anhydride, tetrahydrophthalic anhydride, succinic anhydride and/or maleic anhydride.

5. Process according to claim 1, wherein the catalyst employed in step 3. is chosen from the group comprising:
   (A) amines of the general formula (IX):



(IX)

wherein:

R2 and R3 independently of each other are hydrogen, alkyl or aryl; or

R2 and R3 together with the N atom carrying them form an aliphatic, unsaturated or aromatic heterocycle;

n is an integer from 1 to 10;

R4 is hydrogen, alkyl or aryl; or

R4 represents $-(CH_2)_x-N(R41)(R42)$, wherein:

R41 and R42 independently of each other are hydrogen, alkyl or aryl; or

R41 and R42 together with the N atom carrying them form an aliphatic, unsaturated or aromatic heterocycle;

x is an integer from 1 to 10;

(B) amines of the general formula (X):



(X)

wherein:

R5 is hydrogen, alkyl or aryl;

R6 and R7 independently of each other are hydrogen, alkyl or aryl;

m and o independently of each other are an integer from 1 to 10;

and/or:

(C) diazabicyclo[2.2.2]octane, diazabicyclo[5.4.0]undec-7-ene, dialkylbenzylamine, dimethylpiperazine, 2,2'-dimorpholinyldiethyl ether and/or pyridine.

6. Process according to claim 1, wherein in step 2. the molar ratio of cyclic anhydride to hydroxyl groups in the product obtained in step 1. is ≥ 0.75 : 1 to ≤ 1.3 : 1.

7. Process according to claim 1, wherein in step 3. the catalyst, which contains at least one nitrogen atom per molecule, is present in a content of from ≥ 500 ppm to ≤ 1,500 ppm, based on the total weight of the reaction mixture in steps 2. and 3.

8. Process according to claim 1, wherein in step 3. the molar ratio of ethylene oxide to hydroxyl groups in the product obtained in step 1. is ≥ 0.90 : 1 to ≤ 5.0 : 1.

9. Polyether carbonate polyol with primary hydroxyl end groups, obtainable by a process according to claim 1, comprising a polyether carbonate block, a terminal hydroxyethyl group and a diester unit which joins the polyether carbonate block and the terminal hydroxyethyl group, and wherein the molar content of terminal double bonds, based on all the end groups of the polyether carbonate polyol, is ≥ 0 milliequivalent per kg to ≤ 10 milliequivalents per kg.

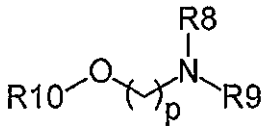
10. Polyether carbonate polyol according to claim 9, wherein the molar content of primary hydroxyl groups is ≥ 50 mol% to ≤ 100 mol%.

11. Polyether carbonate polyol according to claim 9, with an OH number of from ≥ 10 mg of KOH/g to ≤ 100 mg of KOH/g.

12. Polyether carbonate polyol according to claim 9, with an acid number of from ≥ 0.01 mg of KOH/g to ≤ 5 mg of KOH/g.

13. Polyether carbonate polyol composition, comprising a polyether carbonate polyol according to claim 10 and furthermore:

(A) amines of the general formula (XI):



(XI)

wherein:

R8 and R9 independently of each other are hydrogen, alkyl or aryl; or

R8 and R9 together with the N atom carrying them form an aliphatic, unsaturated or aromatic heterocycle;

p is an integer from 1 to 10, that is to say 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10;

R10 is hydrogen, alkyl or aryl; or

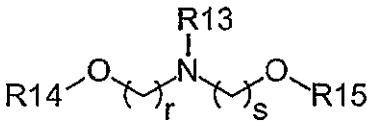
R10 represents $-(CH_2)_y-N(R11)(R12)$, wherein:

R11 and R12 independently of each other are hydrogen, alkyl or aryl; or

R11 and R12 together with the N atom carrying them form an aliphatic, unsaturated or aromatic heterocycle;

y is an integer from 1 to 10, that is to say 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10;

(B) amines of the general formula (XII):



(XII)

wherein:

R13 is hydrogen, alkyl or aryl;

R14 and R15 independently of each other are hydrogen, alkyl or aryl;

r and s independently of each other are an integer from 1 to 10, that is to say 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10;

and/or:

(C) diazabicyclo[2.2.2]octane, diazabicyclo[5.4.0]undec-7-ene, dialkylbenzylamine, dimethylpiperazine, 2,2'-dimorpholinyldiethyl ether and/or pyridine.

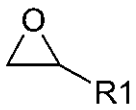
14. Polyurethane polymer obtainable from the reaction of a polyisocyanate with a polyether carbonate polyol according to claim 9 or a polyether carbonate polyol composition according to claim 13.

15. Polyurethane polymer according to claim 14, which is a polyurethane flexible block foam or a polyurethane flexible moulded foam.

Claims

1. Process for the preparation of polyether carbonate polyols with primary hydroxyl end groups, comprising the steps:

1. reaction of a starter compound containing active hydrogen atoms with carbon dioxide and with at least one epoxide (alkylene oxide) of the general formula (II):



(II)

chosen from the group consisting of ethylene oxide, propylene oxide, 1-butene oxide, 2,3-butene oxide, 2-methyl-1,2-propene oxide (isobutene oxide), 1-pentene oxide, 2,3-pentene oxide, 2-methyl-1,2-butene oxide, 3-methyl-1,2-butene oxide, 1-hexene oxide, 2,3-hexene oxide, 3,4-hexene oxide, 2-methyl-1,2-pentene oxide, 4-methyl-1,2-pentene oxide, 2-ethyl-1,2-butene oxide, 1-heptene oxide, 1-octene oxide, 1-nonene oxide, 1-decene oxide, 1-undecene oxide, 1-dodecene oxide, 4-methyl-1,2-pentene oxide, butadiene monoxide, isoprene monoxide, cyclopentene oxide, cyclohexene oxide, cycloheptene oxide, cyclooctene oxide, styrene oxide, methylstyrene oxide, pinene oxide, mono- or polyepoxidized fats as mono-, di- and triglycerides, epoxidized fatty acids, C_1-C_{24} esters of epoxidized fatty acids, epichlorohydrin, glycidol, and derivatives of glycidol, such as, for example, methyl glycidyl ether, ethyl glycidyl ether, 2-ethylhexyl glycidyl ether, allyl glycidyl ether, glycidyl methacrylate and epoxide-functional alkyloxysilanes, such as, for example, 3-glycidyloxypropyltrimethoxysilane, 3-glycidyloxypropyltriethoxysilane, 3-glycidyloxypropyltripropoxysilane, 3-glycidyloxypropylmethyldimethoxysilane, 3-glycidyloxypropylethyldiethoxysilane and 3-glycidyloxypropyltriisopropoxysilane, in each case with the proviso that $\geq$0 % by weight to $\leq$30 % by weight, based on the total amount of the epoxide (II) employed, is ethylene oxide,

wherein the reaction is carried out in the presence of a double metal cyanide catalyst;

2. reaction of the product obtained in step 1. with a cyclic carboxylic acid anhydride; and

3. reaction of the product obtained in step 2. with ethylene oxide in the presence of a catalyst which contains at least one nitrogen atom per molecule, excluding non-cyclic tertiary amines with identical substituents.

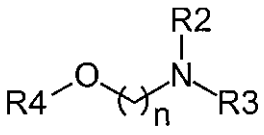
2. Process according to claim 1, wherein the starter compound employed in step 1. is a poly(oxyalkylene) polyol or a poly(oxyalkylene) carbonate polyol which has a number of hydroxyl groups per molecule of from ≥2.0 to ≤5.0 and a number-average molecular weight of from ≥450 g/mol to ≤2,000 g/mol.

3. Process according to claim 1, wherein in the epoxide of the general formula (II) R1 is hydrogen, methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, cyclohexyl and/or phenyl.

4. Process according to claim 1, wherein the cyclic carboxylic acid anhydride employed in step 2. is chosen from the group comprising phthalic anhydride, tetrahydrophthalic anhydride, succinic anhydride and/or maleic anhydride.

5. Process according to claim 1, wherein the catalyst employed in step 3. is chosen from the group comprising:

(A) amines of the general formula (IX):



(IX)

wherein:

R2 and R3 independently of each other are hydrogen, methyl, ethyl, propyl or phenyl; or

R2 and R3 together with the N atom carrying them form an aliphatic, unsaturated or aromatic heterocycle;

n is an integer from 1 to 10;

R4 is hydrogen, methyl, ethyl, propyl or phenyl; or

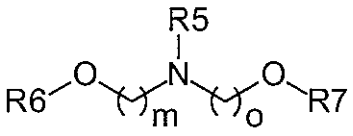
R4 represents $-(CH_2)_x-N(R41)(R42)$, wherein:

R41 and R42 independently of each other are hydrogen, methyl, ethyl, propyl or phenyl; or

R41 and R42 together with the N atom carrying them form an aliphatic, unsaturated or aromatic heterocycle;

x is an integer from 1 to 10;

(B) amines of the general formula (X):



(X)

wherein:

R5 is hydrogen, methyl, ethyl, propyl or phenyl;

R6 and R7 independently of each other are hydrogen, methyl, ethyl, propyl or phenyl;

m and o independently of each other are an integer from 1 to 10;

and/or:

(C) diazabicyclo[2.2.2]octane, diazabicyclo[5.4.0]undec-7-ene, dialkylbenzylamine, dimethylpiperazine, 2,2'-dimorpholinyldiethyl ether and/or pyridine.

6. Process according to claim 1, wherein in step 2. the molar ratio of cyclic anhydride to hydroxyl groups in the product obtained in step 1. is ≥0.75 : 1 to ≤1.3 : 1.

7. Process according to claim 1, wherein in step 3. the catalyst, which contains at least one nitrogen atom per molecule, is present in a content of from ≥500 ppm to ≤1,500 ppm, based on the total weight of the reaction mixture in steps 2. and 3.

8. Process according to claim 1, wherein in step 3. the molar ratio of ethylene oxide to hydroxyl groups in the product obtained in step 1. is ≥0.90 : 1 to ≤5.0 : 1.

9. Polyether carbonate polyol with primary hydroxyl end groups, obtainable by a process according to claim 1, comprising a polyether carbonate block, a terminal hydroxyethyl group and a diester unit which joins the polyether carbonate block and the terminal hydroxyethyl group, and wherein the molar content of terminal double bonds, based on all the end groups of the polyether carbonate polyol, is ≥0 milliequivalent per kg to ≤10 milliequivalents per kg.

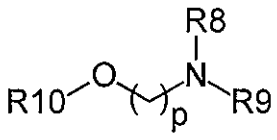
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11. Polyether carbonate polyol according to claim 9, with an OH number of from ≥10 mg of KOH/g to ≤100 mg of KOH/g.

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13. Polyether carbonate polyol composition, comprising a polyether carbonate polyol according to claim 10 and furthermore:

(A) amines of the general formula (XI):



(XI)

wherein:

R8 and R9 independently of each other are hydrogen, methyl, ethyl, propyl or phenyl; or

R8 and R9 together with the N atom carrying them form an aliphatic, unsaturated or aromatic heterocycle;

p is an integer from 1 to 10, that is to say 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10;

R10 is hydrogen, methyl, ethyl, propyl or phenyl; or

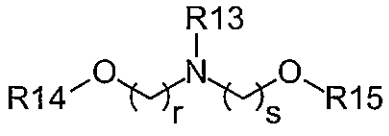
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(B) amines of the general formula (XII):



(XII)

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