

Hydroxy-aminopolymers and method for producing same

The present invention relates to hydroxy-amino polymers, to processes for preparing them, and to the use of such hydroxy-amino polymers for preparing polyurethaneureas.

5 Polymers which both are amine-functional and also carry hydroxyl groups (known as hydroxy-amino polymers) are meeting increasing interest in particular fields of application, especially in the area of the polyurethane industry. The reason for this is that because of the presence of two different types of functional groups, namely the amine functionalities and the hydroxyl groups, it is possible to obtain innovative property profiles and processing profiles. Thus, for example, through the combination of the amino groups, which are significantly more reactive toward
10 isocyanate groups, with the less reactive hydroxyl groups, the possibility exists of exerting influence in a desired way over the time profile of curing processes, which to date has been an impossibility, or only a limited possibility, when only one type of the aforementioned isocyanate-reactive functional groups has been present.

Generally speaking, the amino functionality of hydroxy-amino polymers can be introduced into
15 macromolecules via the addition reaction of primary amines or ammonia onto electron-deficient double bonds, of (meth-)acrylate type, for example. The addition of amines onto (meth-)acrylate group-containing polymers, among others onto (meth-)acrylate group-containing polyethers, is conventional – such processes are referred to, for example, in US 5,739,192 A1, US 5,597,390 A1, US 2005/0171002 A1, DE 196 16 984 A1, DE 195 08 308 A1,
20 WO 2010/090345 A1, JP 2009/22753 A1 and JP 04089860 A1.

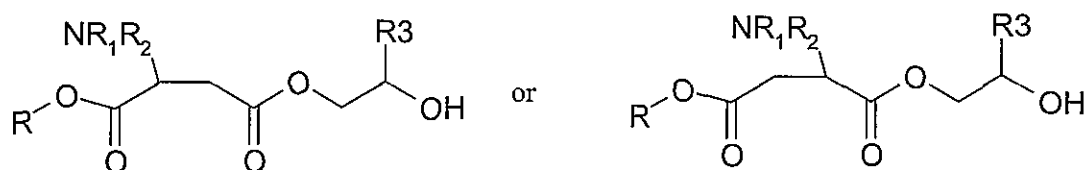
Conversely, the acquisition of the precursor compounds containing the electron-deficient double bonds in the prior art either has not been described or has been accomplished via condensation reactions which proceed in accordance with statistical laws, as for example via the esterification of acrylic acid with difunctional polyethers, or via reaction of acryloyl chloride with difunctional
25 polyethers.

Common to all of the processes described is that the introduction of the double bonds into the precursor compounds of the hydroxy-amino polymers occurs at the expense of the number of hydroxyl functions. Consequently these processes do not make it possible to obtain the original hydroxyl functionality – which in the case of polyether molecules is set in general by the
30 functionality of the starter molecules used in preparing the polyethers – during the introduction of the amino functions.

Processes of the kind described in US 4,874,837 A1, for example, partly solve this problem by reacting mixtures of maleic anhydride and other anhydrides with the hydroxyl groups of low molecular mass polyether polyols, converting the resultant acid groups of the monoesters back
35 into hydroxyl groups by addition reaction of alkylene oxides, and introducing the amine function

by addition reaction of amino alcohols containing primary or secondary amino groups, or of diamines containing primary and/or secondary amino groups, onto the reactive double bonds of the hydroxymaleate.

A structural disadvantage of the hydroxy-amino polyether esters prepared in this way is that the hydroxyl groups and the amino groups have a fixed and small distance of 6 to 7 covalent bond lengths from one another, and only one amino group can be introduced per hydroxyl group. This state of affairs may be represented schematically as follows:



with R = polyether radical, R1, R2 = radicals (hydrogen or alkyl) on the nitrogen atom, and R3 = radical (hydrogen or alkyl on the alkylene oxide used for converting the acid groups into hydroxyl groups)

The two aforesaid products of the Michael addition reaction of the amine onto the double bond are present more or less in equal parts, thus producing a mixture of polymers having 6 and 7 bond lengths between hydroxyl group and amino group.

US 5,554,687 discloses a process in which first of all α,β -unsaturated dicarboxylic acids or their anhydrides are esterified with polyfunctional alcohols or alkylene oxides in order to obtain an unsaturated "polyol polyester prepolymer". In the case of maleic anhydride as the α,β -unsaturated dicarboxylic anhydride, the esterification is to be carried out preferably in the presence of morpholine as isomerization catalyst. The specification does not name further catalysts for the esterification process. In the presence of morpholine (an aminic catalyst), the reaction of maleic anhydride with alkylene oxides installs precisely one alkylene oxide unit between two maleic anhydride units. If ethylene oxide is the alkylene oxide used, therefore, the result is ultimately a polyester as from the reaction of maleic acid with ethylene glycol.

In a second step, the "polyol polyester prepolymer" (a) is then reacted with a polyoxyalkylenamine (b) in an (a)/(b) weight ratio of 0.8 to 50 to give an amine-containing polyester resin. Polyoxyalkylenamines (b) disclosed are polymers comprising polyether blocks with amino end groups, e.g., $\text{H}_2\text{N}-\text{CHXCH}_2-[\text{OCH}_2\text{CHX}]_n-\text{NH}_2$, where X is hydrogen or an alkyl group having 1 to 18 carbon atoms and n is a natural number from 2 to 70. The terminal amino groups undergo addition reaction onto the double bonds of the polyol polyester prepolymer. The ultimate products, therefore, are crosslinked polyester resins in which the polyester chains are linked with one another via polyamino bridges. A process for preparing hydroxy-amino polymers in the sense of poly(ether) ester polyols containing amino groups is neither described nor

suggested in US 5,554,687. In relation to the structure of the chain ends, moreover, the process of US 5,554,687 is subject to the same restrictions as US 4,874,837 A1. Here again, the distance between terminal hydroxyl group and the first amino group may at most be 7 covalent bond lengths.

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The object of the present invention was therefore to provide a process for preparing hydroxy-amino polymers that on the one hand allows the creation of hydroxy-amino polymers having a distance between the amino and the hydroxyl functionality of more than seven covalent bond lengths; on the other hand, the intention is to make it possible to install more than just one amine group per OH group into the polymer; furthermore, this process is to be simple in its application while also very largely avoiding the formation of byproducts, such as transesterification products, for example, meaning that it is generally not necessary to work up the process products.

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The object is achieved by means of a process for preparing a hydroxy-amino polymer, comprising the steps of:

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a) reacting an H-functional starter compound carrying at least one Zerewitinoff-active H atom with an unsaturated cyclic carboxylic anhydride and with at least one alkylene oxide compound, to give a prepolymer carrying hydroxyl groups,

b) addition-reacting a primary amine and/or ammonia onto the double bonds of the hydroxyl-carrying prepolymer obtained by step a), to give the hydroxy-amino polymer,

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where the reaction of the H-functional starter compound with the unsaturated cyclic carboxylic anhydride and/or the addition reaction of the alkylene oxide compound are/is carried out using a double metal cyanide catalyst (DMC catalyst).

The indefinite article "a", "an" means that alternatively there may in each case also be a plurality of these components which can be reacted with one another in the process of the invention.

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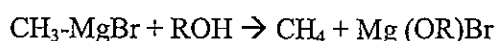
A "*hydroxy-amino polymer*" in the sense of the present invention is a poly(ether)ester polyol containing amino groups, i.e., a polymer which contains amino groups and in which polyether polyol sequences are linked to one another via dicarboxylic ester functionalities.

Surprisingly it has emerged that by addition reaction of amines onto prepolymers which carry hydroxyl groups, obtainable by reaction of at least one Zerewitinoff-active H atom of an H-functional starter compound with an unsaturated cyclic carboxylic anhydride and with at least one alkylene oxide compound, under double metal cyanide (DMC) catalysis, the aforementioned hydroxy-amino polymers are obtainable. This process can be controlled such that, in addition to the hitherto-known hydroxy-amino polymers with at least a distance between the amino function and the hydroxyl group of six or seven covalent bond lengths, it is also possible to prepare structures which have a distance of greater than 7 covalent bond lengths.

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The process may also be embodied, for example, such that after a metered alkylene oxide compound has been consumed by reaction, unsaturated cyclic carboxylic anhydride is supplied –

for example, about 1 mole of carboxylic anhydride per mole of OH groups present. Thereafter a desired amount of alkylene oxide compounds is addition-reacted further, to give the prepolymer carry hydroxyl groups. The above-stated reaction sequence may also be repeated one or more times, to allow a desired number, more particularly more than one double bond, to be installed into the prepolymer per Zerewitinoff-active H atom. Finally, therefore, there may for example be 2 or more, more particularly 3 or more, amine functionalities introduced per Zerewitinoff-active H atom by addition onto the double bonds. The double bonds may of course also be introduced into the prepolymer by parallel metering of one or more alkylene oxide compounds and one or more unsaturated cyclic carboxylic anhydrides to the one or more starter compounds carrying Zerewitinoff-active H atoms. The distribution of the double bonds over the polymer chains of the prepolymer is then in accordance with statistical laws; more particularly, the blocks of the polyether chains based on alkylene oxide units are subject to a relatively broad length distribution. The present invention provides for the H-functional starter compound to carry at least one Zerewitinoff-active H atom. A Zerewitinoff-active H atom for the purposes of the present invention is an acidic H atom or "active" H atom. An atom of this kind may be identified conventionally by reactivity with an appropriate Grignard reagent. The amount of Zerewitinoff-active H atoms is measured typically via the release of methane, which is given off in a reaction of the substance for verification with methylmagnesium bromide (CH₃-MgBr) in accordance with the following equation:



Zerewitinoff-active H atoms originate typically from C-H-acidic organic groups, -OH, -SH, -NH₂ or -NHR with R as organic radical, and also -COOH.

Particularly suitable H-functional starter compounds possess an H functionality of 1 to 35, more particularly 1 to 16, preferably 1 to 8, with the H functionality relating to the aforementioned Zerewitinoff-active H atoms.

The molecular weights of the H-functional starter compounds may vary over wide ranges, with particular preference being given to an average molecular weight of 17 to 1200 g/mol, more particularly of 62 to 1000.

Besides the hydroxy-functional starters for preferred used, amino-functional starters may also be used.

Examples of hydroxy-functional starter compounds are methanol, ethanol, 1-propanol, 2-propanol, and higher aliphatic monools, more particularly fatty alcohols, phenol, alkyl-substituted phenols, propylene glycol, ethylene glycol, diethylene glycol, dipropylene glycol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, hexanediol, pentanediol, 3-methyl-1,5-pentanediol, 1,12-dodecanediol, glycerol, trimethylolpropane, pentaerythritol, sorbitol, sucrose, hydroquinone, pyrocatechol, resorcinol, bisphenol F, bisphenol A, 1,3,5-trihydroxybenzene, and also methylol group-containing condensates of formaldehyde and phenol or urea. High-functionality starter

compounds based on hydrogenated starch hydrolysis products may also be used. Such compounds are described in EP 1525244 A1, for example.

Examples of H-functional starter compounds containing amino groups are ammonia, ethanolamine, diethanolamine, triethanolamine, isopropanolamine, diisopropanolamine, ethylenediamine, hexamethylenediamine, aniline, the isomers of toluidine, the isomers of diaminotoluene, the isomers of diaminodiphenylmethane, and also polycyclic products obtained in the condensation of aniline with formaldehyde to form diaminodiphenylmethane, plus methylol group-containing condensates of formaldehyde and melamine, and also Mannich bases.

As starter compounds it is also possible, moreover, to use ring-opening products formed from cyclic carboxylic anhydrides and polyols. Examples are ring-opening products formed from phthalic anhydride or succinic anhydride on the one hand and from ethylene glycol, diethylene glycol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, hexanediol, pentanediol, 3-methyl-1,5-pentanediol, 1,12-dodecanediol, glycerol, trimethylolpropane, pentaerythritol or sorbitol on the other. In addition it is also possible to use mono- or polyfunctional carboxylic acids directly as starter compounds.

Furthermore, in the process, it is also possible for pre-prepared alkylene oxide adducts of the aforementioned starter compounds, these being polyether polyols preferably having OH numbers of 160 to 1000 mg KOH/g, more preferably 250 to 1000 mg KOH/g, to be used as starter compounds, and/or to be added to the reaction mixture. A further possibility in the process of the invention is to use polyester polyols preferably with OH numbers in the range from 6 to 800 mg KOH/g as co-starters. Polyester polyols suitable for this purpose may be prepared, for example, from organic dicarboxylic acids having 2 to 12 carbon atoms and polyhydric alcohols, preferably diols, having 2 to 12 carbon atoms, preferably 2 to 6 carbon atoms, by known methods.

As H-functional starter substances it is possible, furthermore, to use polycarbonate polyols, polyester carbonate polyols, or polyether carbonate polyols, preferably polycarbonate diols, polyester carbonate diols, or polyether carbonate diols, preferably in each case having OH numbers in the range from 6 to 800 mg KOH/g, as starters or co-starters. They are prepared, for example, by reaction of phosgene, dimethyl carbonate, diethyl carbonate, or diphenyl carbonate with difunctional or higher polyfunctional alcohols or polyester polyols or polyether polyols.

Serving as carriers of the active hydrogens in step a) of the process of the invention are preferably amino group-free, H-functional starter compounds with hydroxyl groups, such as, for example, methanol, ethanol, 1-propanol, 2-propanol, and higher aliphatic monools, more particularly fatty alcohols, phenol, alkyl-substituted phenols, propylene glycol, ethylene glycol, diethylene glycol, dipropylene glycol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, hexanediol, pentanediol, 3-methyl-1,5-pentanediol, 1,12-dodecanediol, glycerol, trimethylolpropane, pentaerythritol, sorbitol, sucrose, hydroquinone, pyrocatechol, resorcinol, bisphenol F, bisphenol A, 1,3,5-trihydroxybenzene, methylol group-containing condensates of formaldehyde and phenol,

and hydrogenated starch hydrolysis products. Mixtures of different H-functional starter compounds may also be used. Where reference is made below to an H-functional starter compound, the reference is therefore in principle also to mixtures of H-functional starter compounds, unless this is expressly excluded.

5 Compounds contemplated for the unsaturated cyclic carboxylic anhydride used in the context of the process of the invention include all compounds known as such to the skilled person. These compounds are, for example, unsaturated cyclic dicarboxylic anhydrides such as maleic anhydride, tetrahydrophthalic anhydride, more particularly 3,4,5,6-tetrahydrophthalic anhydride, and also combinations thereof.

10 Where two or more unsaturated cyclic carboxylic anhydrides are used, they may likewise be metered individually, in a mixture, or blockwise. A further possibility is to supply the cyclic carboxylic anhydride or the cyclic carboxylic anhydrides to the reaction mixture in parallel with the alkylene oxide (or oxides) or as a separate block, without simultaneous metering of alkylene oxide. Where reference is made below to an unsaturated cyclic carboxylic anhydride, the
15 reference is therefore in principle also to mixtures of unsaturated cyclic carboxylic anhydrides, unless this is expressly excluded.

As an alkylene oxide compound which can be used in accordance with the invention, selection may be made of those representatives which have 2 to 24 carbon atoms, more particularly 2 to 12 carbon atoms, more preferably 2 to 6 carbon atoms, and also the combination of different alkylene
20 oxide compounds of the aforementioned kind. The alkylene oxides having 2 to 24 carbon atoms are, for example, one or more compounds selected from the group consisting of ethylene oxide, propylene oxide, 1-butene oxide, 2,3-butene oxide, 2-methyl-1,2-propene oxide (isobutene oxide), 1-pentene oxide, 2,3-pentene oxide, 2-methyl-1,2-butene oxide, 3-methyl-1,2-butene oxide, 1-hexene oxide, 2,3-hexene oxide, 3,4-hexene oxide, 2-methyl-1,2-pentene oxide, 4-methyl-1,2-
25 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, singly or multiply epoxidized fats in the form of mono-, di-, and triglycerides, epoxidized fatty acids, C₁-C₂₄ esters
30 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 also epoxide-functional alkyloxysilanes such as, for example, 3-glycidyloxypropyltrimethoxysilane, 3-glycidyloxypropyltriethoxysilane, 3-glycidyloxypropyltripropoxysilane, 3-glycidyloxypropylmethyldimethoxysilane, 3-glycidyloxypropylethyldiethoxy-
35 silane, and 3-glycidyloxypropyltriisopropoxysilane.

Alkylene oxides used for preparing the polyether ester polyols in step a) are preferably ethylene oxide and/or propylene oxide. The alkylene oxides may be metered individually, in a mixture, or

blockwise. Where reference is made below to an alkylene oxide or an alkylene oxide compound, the reference is therefore in principle also to mixtures of alkylene oxides or alkylene oxide compounds, or to the blockwise metering of different alkylene oxides and/or alkylene oxide compounds, unless expressly specified.

5 Preference is given to using ethylene oxide and/or propylene oxide. Particular preference is given to using ethylene oxide in fractions of greater than 50 wt%, very preferably in fractions of greater than 60 wt%, based on the overall mass of the alkylene oxides to be metered. With the process of the invention, provision may further be made for the amount-of-substance ratio between carboxylic anhydride and the number of Zerewitinoff-active H atoms in the starter compound to
10 be selected such that as far as possible all of these Zerewitinoff-active H atoms are reacted. For this stoichiometric conversion, the amount-of-substance ratio between the carboxylic anhydride and the number of Zerewitinoff-active H atoms in the H-functional starter compound may be about 1:1 to 1.5:1, more particularly 1:1 to 1.2:1.

According to one particularly preferred embodiment of the process of the invention, the amount-
15 of-substance ratio between the alkylene oxide compound and the carboxylic anhydride is set to at least 1.1:1, preferably to at least 2:1, more preferably at least to 2.5:1. With this embodiment of the process of the invention it is possible to synthesize hydroxy-amino polymers having an average distance of more than seven covalent bond lengths between the amine functionality and the hydroxyl group.

20 The process of the invention is not confined, moreover, to the use of the aforesaid monomers and comonomers. Thus, for example, it is possible to react in step a) at least one further comonomer, which in particular is selected from lactones, lactides, saturated or aromatic cyclic carboxylic anhydrides, cyclic carbonates and/or carbon dioxide. In this way the profile of properties of the resulting hydroxy-amino polymer may be modified further, in relation, for example, to its
25 reactivity toward isocyanate groups, its polarity, and in relation to other chemical or physical properties of the hydroxy-amino polymer and/or the reaction product thereof with a polyisocyanate.

One of the provisions in the context of the process of the invention is the addition reaction of a primary amine or ammonia onto the double bond of the hydroxyl group-carrying prepolymer.

30 Examples of suitable amines are ammonia, aliphatic, cycloaliphatic and/or araliphatic monoamines having a primary amino group such as, for example, methylamine, ethylamine, 1-aminopropane, 2-aminopropane, 1-aminobutane, 2-aminobutane, isobutylamine, 1-aminohexane, 2-ethyl-1-aminohexane, dodecylamine, octadecylamine, cyclohexylamine, and benzylamine; aliphatic, cycloaliphatic and/or araliphatic monoamines having a primary amino
35 group and a secondary amino group, it also being possible for the secondary amino group to be part of a ring system, such as, for example, N-methylethylenediamine, N-methylpropylenediamine, N-(2-aminoethyl)piperazine, and 3-amino-1,2,4-triazole; aliphatic, cycloaliphatic and/or

heterocyclic diamines having a primary and a tertiary amino group and optionally a secondary amino group, such as, for example, N,N-dimethylethylenediamine, N,N-dimethyl-1,3-diaminopropane, N,N-dimethyl-1,8-diaminooctane, N,N-dimethyl-1,4-diaminocyclohexane; aliphatic diamines having two primary and at least one secondary amino group, such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and bis(3-aminopropyl)amine, for example. Additionally suitable for the process of the invention are amines which as well as the primary amino group also include hydroxyl groups, such as ethanolamine or isopropanolamine, for example. Preference in this context is given to primary amines selected from the group consisting of ethylamine, 1-aminobutane, dodecylamine, cyclohexylamine, benzylamine, N,N-dimethyl-1,3-diaminopropane, ethanolamine, and isopropanolamine.

Likewise suitable are (cyclo)aliphatic diamines. These are compounds having two primary amino groups, with the general formula $\text{NH}_2\text{-R-NH}_2$, in which R is an aliphatic or cycloaliphatic radical having 2 to 21, preferably 2 to 15, and more preferably 2 to 10 carbon atoms. Examples include ethylenediamine, 1,2- and 1,3-propylenediamine, 1,4-diaminobutane, 1,6-diaminohexane, 2,2,4- and 2,4,4-trimethyl-1,6-diaminohexane, 1,4-diaminocyclohexane, 1,5-diamino-2-methylpentane, 5-amino-1-aminomethyl-1,3,3-trimethylcyclohexane (isophoronediamine), bis(4-aminocyclohexyl)methane, bis(4-amino-3-methylcyclohexyl)methane, 1-amino-1-methyl-3(4)-aminomethylcyclohexane, bis(4-amino-3,5-diethylcyclohexyl)methane, bisaminomethylhexahydro-4,7-methanoindane, 2,3-, 2,4- and 2,6-diamino-1-methylcyclohexane, and mixtures of these diamines. Preference here is given to (cyclo)aliphatic diamines selected from the group consisting of ethylenediamine, 1,4-diaminobutane, 1,6-diaminohexane, 1,5-diamino-2-methylpentane, bis(4-aminocyclohexyl)methane, and bis(4-amino-3-methylcyclohexyl)methane.

The stated monoamines and oligoamines may of course also be used as a mixture. Where reference is made below to an amine for addition reaction, the reference is therefore in principle to all mixtures of amines for addition, unless expressly specified.

The molar ratio of primary amino groups to double bonds that are amenable to addition is preferably 0.01:1 to 1.1:1, more preferably 0.1:1 to 1.1:1, very preferably 0.5:1 to 1.1:1, and especially preferably 1:1 to 1.1:1. The reaction may be carried out with or without catalysis. Examples of suitable catalysts are copper acetate, tin chloride, or acetic acid. The addition reaction of the amines takes place preferably without addition of catalyst. A reaction temperature range suitable for this step is, for example, that from 0°C to 150°C, preferably from 10°C to 100°C, and more preferably from 20°C to 80°C.

For the process of the invention it is provided that in step a), in other words for the reaction of the H-functional starter compound with the unsaturated cyclic carboxylic anhydride and/or the addition of the alkylene oxide compound, a DMC catalyst is employed. It is also possible here to use mixtures of different DMC catalysts.

Suitable DMC catalysts are known in principle from the prior art and are disclosed in

US 3,404,109 A1, US 3,829,505 A1, US 3,941,849 A1, and US 5,158,922 A1, for example.

DMC catalysts, which are described in, for example, US 5,470,813 A1, EP 700949 A1, EP 743 093 A1, EP 761 708 A1, WO 97/40086 A1, WO 98/16310 A1, and WO 00/47649 A1, possess a very high activity in the polymerization of alkylene oxides and optionally in the copolymerization of alkylene oxides and unsaturated cyclic carboxylic anhydrides, and allow the preparation of polyether polyols at very low catalyst concentrations (25 ppm or less), meaning that it is no longer necessary to separate off the catalyst from the finished product, generally speaking. A typical example are the high-activity DMC catalysts described in EP 700 949 A1, which in addition to a double metal cyanide compound such as zinc hexacyanocobaltate(III) and an organic complexing ligand such as tert-butanol, further include a polyether having a number-average molecular weight of greater than 500 g/mol. It is also possible to employ the alkaline DMC catalysts disclosed in EP Application Number 10163170.3.

Cyanide-free metal salts suitable for preparing the double metal cyanide compounds preferably possess the general formula (I),



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 selected from the group of the halides, (i.e., fluoride, chloride, bromide, iodide), hydroxide, sulfate, carbonate, cyanate, thiocyanate, isocyanate, isothiocyanate, carboxylate, oxalate, and nitrate;

n is 1 if X is sulfate, carbonate, or oxalate and

n is 2 if X is halide, hydroxide, cyanate, thiocyanate, isocyanate, isothiocyanate, or nitrate.

Further-suitable cyanide-free metal salts possess the general formula (II),



where

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

X stands for one type or different types of anions, the anion being preferably 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 if X is sulfate, carbonate, or oxalate, and

r is 1 if X is halide, hydroxide, cyanate, thiocyanate, isocyanate, isothiocyanate, carboxylate, or nitrate.

Other cyanide-free metal salts possess the general formula (III),



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 selected from the group of the halides, (i.e., fluoride, chloride, bromide, iodide), hydroxide, sulfate, carbonate, cyanate, thiocyanate, isocyanate, isothiocyanate, carboxylate, oxalate, and nitrate;

s is 2 if X is sulfate, carbonate, or oxalate, and

5 s is 4 if X is halide, hydroxide, cyanate, thiocyanate, isocyanate, isothiocyanate, carboxylate, or nitrate.

Likewise cyanide-free metal salts possess the general formula (IV),



where

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

X is one or more (i.e., different) anions, preferably 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 if X is sulfate, carbonate, or oxalate, and

15 t is 6 if X is halide, hydroxide, cyanate, thiocyanate, isocyanate, isothiocyanate, 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.

20 Mixtures of different metal salts can also be used.

Metal cyanide salts suitable for preparing the double metal cyanide compounds preferably possess the general formula (V)



where

25 M' is selected from one or more metal cations of 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), with M' preferably being one or metal cations of the group consisting of Co(II), Co(III), Fe(II), Fe(III), Cr(III), Ir(III), and Ni(II),

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

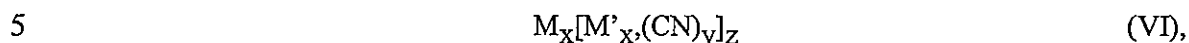
A is selected from one or more anions of the group consisting of halides (i.e., fluoride, chloride, bromide, iodide), hydroxide, sulfate, carbonate, cyanate, thiocyanate, isocyanate, isothiocyanate, carboxylate, oxalate, or nitrate, and

35 a, b, and c are integral numbers, with the values for a, b, and c being selected such as to ensure the electroneutrality of the metal cyanide salt; a is preferably 1, 2, 3, or 4; b is preferably 4, 5, or 6; c preferably possesses the value 0.

Examples of suitable metal cyanide salts are potassium hexacyanocobaltate(III), potassium

hexacyanoferrate(II), potassium hexacyanoferrate(III), calcium hexacyanocobaltate(III), and lithium hexacyanocobaltate(III).

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



in which M is defined as in formula (I) to (IV) and

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

x, x', y, and z are integral and are selected such as to ensure the electronic neutrality of the double metal cyanide compound.

10 Preference is given to

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

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

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

15 Examples of double metal cyanide compounds used with preference are zinc hexacyanocobaltate(III), zinc hexacyanoiridate(III), zinc hexacyanoferrate(III), and cobalt(II) hexacyanocobaltate(III). Other examples of suitable double metal cyanide compounds can be found in US 5,158,922 A1, for example. Used with particular preference is zinc hexacyanocobaltate(III).

The organic complex ligands added when preparing the DMC catalysts are disclosed in, for example, US-A 5,158,922 A1, US 3,404,109 A1, US 3,829,505 A1, US 3,941,849 A1, EP 700949 A1, EP 761708 A1, JP 4145123 A1, US 5,470,813 A1, EP 743 093 A1, and WO 97/40086 A1.

20 Organic complex ligands employed are, for example, water-soluble organic compounds having heteroatoms, such as oxygen, nitrogen, phosphorus, or sulfur, which are able to 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.

25 Particularly preferred organic complex ligands are aliphatic ethers (such as dimethoxyethane), water-soluble aliphatic alcohols (such as ethanol, isopropanol, n-butanol, isobutanol, sec-butanol, tert-butanol, 2-methyl-3-buten-2-ol, and 2-methyl-3-butyne-2-ol), compounds which contain not only aliphatic or cycloaliphatic ether groups but also aliphatic hydroxyl groups (such as ethylene glycol mono-tert-butyl ether, diethylene glycol mono-tert-butyl ether, tripropylene glycol monomethyl ether, and 3-methyl-3-oxetane-methanol), for example. Very preferred organic complex ligands are selected from one or more compounds of the group consisting of dimethoxyethane, tert-butanol, 2-methyl-3-buten-2-ol, 2-methyl-3-butyne-2-ol, ethylene glycol mono-tert-butyl ether, and 3-methyl-3-oxetane-methanol.

30 Used optionally when preparing the inventively preferred DMC catalysts are one or more complex-forming components 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 ethers, polyvinyl ethyl ethers, 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 copolymers and maleic anhydride copolymers, hydroxyethylcellulose, and polyacetals, or of the glycidyl ethers, glycosides, carboxylic esters of polyhydric alcohols, gallic acids or their salts, esters, or amides, cyclodextrins, phosphorus compounds, α,β -unsaturated carboxylic esters, or ionic surface-active or interface-active compounds.

Preferably, in the preparation of the inventively preferred DMC catalysts, in the first step, the aqueous solutions of the metal salt (e.g., zinc chloride), used in 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 of the metal cyanide salt (e.g., potassium hexacyanocobaltate), are reacted in the presence of the organic complex ligand (e.g., tert-butanol), to form a suspension which comprises the double metal cyanide compound (e.g., zinc hexacyanocobaltate), water, excess, cyanide-free metal salt, and the organic complex ligand. This organic complex ligand may be present in the aqueous solution of the cyanide-free metal salt and/or of the metal cyanide salt, or is added directly to the suspension obtained following precipitation of the double metal cyanide compound. It has proven advantageous to mix the aqueous solutions of the cyanide-free metal salt and of the metal cyanide salt and the organic complex ligand with vigorous stirring. Subsequently the suspension formed in the first step is optionally treated with a further complex-forming component. This complex-forming component is used preferably in a mixture with water and organic complex ligand. One preferred process for implementing the first step (i.e., preparing the suspension) is accomplished using a mixing nozzle, more preferably using a jet disperser as described in WO 01/39883 A1.

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 one preferred variant embodiment for the preparation of the catalyst, the isolated solids are subsequently washed in a third process step with an aqueous solution of the organic complex ligand (e.g., by resuspension and subsequent reisolation by filtration or centrifugation). In this way it is possible, for example, for water-soluble byproducts, such as potassium chloride, to be removed from the inventive catalyst. The amount of the organic complex ligand in the aqueous wash solution is preferably between 40 and 80 wt%, based on the overall solution.

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

It is also advantageous to wash the isolated solids more than once. For this purpose, for example, the first wash operation can be repeated. For further wash operations, however, preference is given to using nonaqueous solutions, such as a mixture of organic complexing ligand and other

complex-forming component.

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

5 A preferred process for isolating the inventive DMC catalysts from the suspension by filtration, filtercake washing, and drying is described in WO 01/80994 A1.

The concentration of DMC catalyst used in step a) is 5 to 1000 ppm, preferably 10 to 900 ppm, and more preferably 20 to 800 ppm, based on the amount of the hydroxyl-carrying prepolymer to be prepared. Depending on the profile of requirements of the application following the amine
10 addition reaction, the DMC catalyst may be left in the product or (partly) removed. (Partial) removal of the DMC catalyst may be accomplished, for example, by treatment with adsorbents. Methods for removing DMC catalysts are described for example in US 4,987,271 A1, DE 313 22 58 A1, EP 406 440 A1, US 5,391,722 A1, US 5,099,075 A1, US 4,721,818 A1, US 4,877,906 A1, and EP 385 619 A1.

15 Before being contacted with the DMC catalyst, the H-functional compound may optionally be admixed with small amounts of an inorganic mineral acid, preferably phosphoric acid, in order to neutralize any traces of base in the H-functional starter compound.

Where the process of the invention is carried out using double metal cyanide catalysts, a further advantage is to introduce initially the H-functional starter compound and the catalyst, to meter in
20 a portion of the alkylene oxide compound and also, optionally, of further comonomers, and only then to add the unsaturated cyclic carboxylic anhydride. Starting from the H-functional starter compound, it is possible in this way first to construct a polymer framework which is free from double bonds. For this purpose, all of the aforementioned alkylene oxide compounds and/or, optionally, additional comonomers may be used. The unsaturated cyclic carboxylic anhydride is
25 typically then supplied to the reaction mixture when the aforementioned addition reaction of the alkylene oxide compound onto the H-functional starter compound has concluded.

After the unsaturated cyclic carboxylic anhydride has been added, the alkylene oxide compound, and also any further comonomer, are subsequently added again. In this case, by choosing the amounts of substance of the alkylene oxide compound(s) in relation to the amount-of-substance
30 content of the added unsaturated cyclic carboxylic anhydride, it is possible to adjust the distance between the amine functionality and the hydroxyl group in the manner described above, with addition in particular of more than 1 mol of the alkylene oxide compound per mole of Zerewitinoff-active hydrogen. By adding further comonomers as well it is possible to influence the distance of these two functionalities from one another. As already mentioned above, further
35 carboxylic anhydride may be subsequently added, and further alkylene oxide compound may be added after the anhydride has been consumed by reaction, in order to provide the possibility for incorporation of more than one amine function per Zerewitinoff-active H atom.

Step a) of the process of the invention is described in detail below, although the present invention is not confined to the following presentation:

In one embodiment of the process of the invention, the H-functional compound is first charged with the DMC catalyst to a reactor/reactor system. Before being contacted with the DMC catalyst, the H-functional compound may optionally be admixed with small amounts of an inorganic mineral acid, preferably phosphoric acid, in order to neutralize any traces of base in the H-functional starter compound, and/or in order to make the production process generally more stable.

After having been heated to temperatures of 50 to 160°C, more particularly 60 to 140°C, very preferably 70 to 140°C, the reactor contents are in one preferred process variant stripped with inert gas over a period of preferably 10 to 60 minutes, with stirring. In the course of the stripping with inert gas, volatile constituents are removed with introduction of inert gases into the liquid phase with an accompanying applied vacuum, at an absolute pressure of 5 to 500 mbar. Following the metered introduction of typically 5 to 20 wt% of one or more alkylene oxides, optionally already containing a small amount of the unsaturated cyclic carboxylic anhydride and/or of further comonomer, based on the amount of H-functional compound introduced, the DMC catalyst is activated.

The addition of one or more alkylene oxides and optionally of a small amount of the unsaturated cyclic carboxylic anhydride and/or further comonomer may occur before, during, or after the heating of the reactor contents to temperatures of 50 to 160°C, preferably 60 to 140°C, very preferably 70 to 140°C; it takes place preferably after the stripping. The activation of the catalyst is manifested by an accelerated drop in the reactor pressure, thereby indicating the onset of alkylene oxide conversion/conversion of the unsaturated cyclic carboxylic anhydride.

The reaction mixture can then be supplied continuously with the desired amount of alkylene oxide or alkylene oxide mixture, optionally together with the target metering amount of unsaturated cyclic carboxylic anhydride and/or further comonomer, with a reaction temperature selected of 20 to 200°C, but preferably of 50 to 160°C. The reaction temperature is in many cases identical to the activation temperature. Prior to the metered addition of the unsaturated cyclic carboxylic anhydride, the reaction mixture or the H-functional compound may optionally be admixed with an inhibitor such as a phenol derivative, vitamin E, or phenothiazine, for example.

Catalyst activation is often already so quick that there is no need to meter a separate amount of alkylene oxide/unsaturated cyclic carboxylic anhydride for catalyst activation, and it is possible to commence the continuous metering of the alkylene oxide and of the unsaturated cyclic carboxylic anhydride, optionally at first with a reduced metering rate. The reaction temperature as well may be varied within the described limits during the alkylene oxide metering phase/the metering of the unsaturated cyclic carboxylic anhydride. Likewise, the alkylene oxides and the cyclic carboxylic anhydride may be supplied to the reactor in various ways: metering into the gas phase or directly

into the liquid phase is possible, as for example via an immersed tube or a distributor ring close to the reactor base in a zone with good mixing.

In the case of DMC-catalyzed processes, metering into the liquid phase is the preferred variant. The alkylene oxide and the unsaturated cyclic carboxylic anhydride ought to be supplied to the reactor continuously in such a way that the safety-related pressure limits of the reactor system used are not exceeded. Especially when co-metering ethylene oxide-containing alkylene oxide mixtures or pure ethylene oxide, it should be ensured that a sufficient partial pressure of inert gas is maintained in the reactor during the start-up and metering phases. This partial pressure may be established, for example, using noble gases or nitrogen.

In the case of metering into the liquid phase, the metering assemblies ought to be of self-emptying design by the provision, for example, of metering holes on the underside of the distributor ring. Generally speaking, apparatus-related measures, such as the installation of nonreturn valves, should be taken to prevent backflow of reaction medium into the metering assemblies and reactant reservoirs. If an alkylene oxide/carboxylic anhydride mixture is being metered, the respective alkylene oxides and the respective unsaturated cyclic carboxylic anhydrides may be supplied to the reactor separately or as a mixture. Premixing of the alkylene oxides with one another and with the unsaturated cyclic carboxylic anhydride may be achieved, for example, by a mixing assembly located in the joint metering section (inline blending). It has also been found useful to meter the alkylene oxides and optionally the unsaturated cyclic carboxylic anhydride, on the pump pressure side, individually or in premixed form into a pumped circulation system which is conducted, for example, through heat exchangers. For effective mixing with the reaction medium, it is advantageous in that case to integrate a high-shear mixing assembly into the alkylene oxide/carboxylic anhydride/reaction medium stream. The temperature of the exothermic ring-opening addition reaction is maintained at the desired level by cooling. In accordance with the prior art on the design of polymerization reactors for exothermic reactions (e.g., Ullmann's Encyclopedia of Industrial Chemistry, Vol. B4, pp 167ff, 5th Ed., 1992), such cooling takes place generally via the reactor walls (e.g., jacket, half-coil pipe) and also by means of further heat exchange surfaces disposed internally in the reactor and/or externally in the pumped circulation system – for example, in cooling coils, cooling cartridges, or plate, shell-and-tube, or mixer heat exchangers. These should be designed so that cooling can be carried out effectively even at the beginning of the metering phase, i.e., at a low fill level.

Generally speaking, effective mixing of the reactor contents ought to be ensured in all reaction phases, through design and use of standard commercial stirring elements, with suitability here being possessed in particular by stirrers arranged over one or more levels, or stirrer types which act extensively over the fill height (see, for example, Handbuch Apparate [Apparatus Handbook]; Vulkan-Verlag Essen, 1st edn. (1990), pp. 188-208). Of particular technical relevance here is a mixing energy which is introduced on average over the entire reactor contents and which is

situated in general in the range from 0.2 to 5 W/l, with correspondingly higher local power inputs in the region of the stirring elements themselves and optionally in the case of low fill levels. In order to achieve an optimum stirring action, combinations of flow baffles (for example, flat or tubular baffles) and cooling coils (or cooling cartridges) may be arranged within the reactor in accordance with the general prior art, and may also extend over the vessel base. The stirring power of the mixing assembly may also be varied as a function of fill level during the metering phase, in order to ensure a particularly high energy input in critical phases of reaction. It may be advantageous, for example, to bring about particularly vigorous mixing of solids-containing dispersions, which may be present at the start of reaction, such as when using sucrose, for example.

Moreover, when solid H-functional starter compounds are employed, in particular, the stirring assembly should be selected so as to ensure that there is sufficient dispersing of the solids in the reaction mixture. Preference here is given to using stirrer levels passing close to the bottom, and stirring elements that are particularly suitable for suspension. Moreover, the stirrer geometry ought to contribute to reducing the foaming of reaction products. The foaming of reaction mixtures may be observed, for example, after the end of the metering phase and after-reaction phase, if residual epoxides are removed additionally under reduced pressure, at absolute pressures in the range from 1 to 500 mbar. For such cases, those stirring elements which have proven suitable are those which bring about continuous mixing of the liquid surface. According to the requirement, the stirring shaft has a base bearing and optionally further support bearings in the vessel. The stirrer shaft may be driven from the top or the bottom (with central or eccentric arrangement of the shaft).

Alternatively it is also possible to achieve the necessary mixing exclusively by means of a pumped circulation system guided via a heat exchanger, or to operate said system additionally to the stirring assembly as a further mixing component, the reactor contents being pumped in circulation as required (typically 1 to 50 times an hour).

A very wide variety of different types of reactor are suitable for implementing the process of the invention. Preference is given to using cylindrical vessels possessing a height/diameter ratio of 1:1 to 10:1. Reactor bases contemplated include, for example, hemispherical, dished, flat, or conical bases.

After the metering of the alkylene oxide and the unsaturated cyclic carboxylic anhydride, and also, optionally, further comonomers, in step a) has ended, an after-reaction phase may follow, in which residual alkylene oxide/unsaturated cyclic carboxylic anhydride/further comonomer are consumed by reaction. The end of this after-reaction phase is achieved when it is no longer possible to detect any pressure drop in the reaction vessel. Traces of unreacted alkylene oxides/unsaturated cyclic carboxylic anhydrides may be removed quantitatively after the reaction phase, optionally under reduced pressure, at an absolute pressure of 1 to 500 mbar, or by

stripping. Stripping removes volatile constituents, such as (residual) alkylene oxides, for example, with introduction of inert gases or steam into the liquid phase, in conjunction with an applied vacuum (for example, by passing inert gas through the system at an absolute pressure of 5 to 500 mbar). The removal of volatile constituents, such as unreacted epoxides, for example, either
5 under reduced pressure or by stripping, takes place at temperatures of 20 to 200°C, preferably at 50 to 160°C, and preferably with stirring. Such stripping operations may also be carried out in columns known as stripping columns, in which a stream of inert gas or of steam is conveyed countercurrently to the product stream. Stripping is carried out preferably with inert gases in the absence of steam. When constant pressure has been reached or when volatile constituents have
10 been removed by reduced pressure and/or by stripping, the product may be discharged from the reactor.

In the case of process variant A), the metering of the cyclic carboxylic anhydride in step a) may also be accomplished by interrupting the alkylene oxide metering/metering of further comonomers and, optionally after an after-reaction phase, supplying the unsaturated cyclic
15 carboxylic anhydride to the reactor and resuming the alkylene oxide metering/metering of further comonomers after the desired amount of unsaturated cyclic carboxylic anhydride has been supplied. This procedure may of course also be repeated a number of times during one reaction batch. Particularly preferable in the case of this procedure is the fact that the concluding alkylene oxide block comprises an amount of greater than 1 mol of alkylene oxide per mole of active H
20 atoms from the H-functional compounds used as starter compounds. Here as well, the reaction mixture or the H-functional compound may optionally be admixed with an inhibitor, such as a phenol derivative, vitamin E, or phenothiazine, for example, prior to the metering of the unsaturated cyclic carboxylic anhydride.

It is also possible to vary the ratio of the metering rates of alkylene oxide metering and the
25 metering of the unsaturated cyclic carboxylic anhydride during the metered-introduction phase, in other words to vary the joint metering of these two components relative to one another, continuously or in stages, by means, for example, of adopting values of 0:1 to 1:0 for the ratio of the metering rate of the unsaturated cyclic carboxylic anhydride to that of the alkylene oxide/alkylene oxides.

A characteristic of DMC catalysts is their pronounced sensitivity to high concentrations of hydroxyl groups, brought about, for example, by large quantities of starters such as ethylene glycol, propylene glycol, glycerol, trimethylolpropane, sorbitol, or sucrose, and to polar impurities in the reaction mixture and/or in the starter or starters. In that case the DMC catalysts cannot be converted into the polymerization-active form during the phase of reaction initiation. Impurities
35 may be, for example, water or compounds having a large number of closely adjacent hydroxyl groups, such as carbohydrates and carbohydrate derivatives. Substances with carbonyl groups in close vicinity or with carbonyl groups adjacent to hydroxyl groups are also deleterious to the

catalyst activity.

In order nevertheless to be able to subject starters with high concentrations of OH groups, or starters with impurities that may be regarded as being catalyst poisons, to DMC-catalyzed alkylene oxide addition reactions, the hydroxyl group concentration ought to be lowered and/or the catalyst poisons ought to be rendered harmless. For this purpose, these starter compounds may first be converted by means of basic catalysis into prepolymers, which subsequently, after having been worked up, may be converted by means of DMC catalysis into the desired, high-molar-mass alkylene oxide adducts. These prepolymers include, for example, the "pre-prepared alkylene oxide adducts" referred to above and suitable as starters. A disadvantage with this procedure is that such prepolymers, often obtained by means of basic catalysis, must be worked up very carefully in order to rule out the deactivation of the DMC catalyst by basic catalyst traces entrained via the prepolymers.

This disadvantage can be overcome by the method known as that of continuous starter metering. In this case, critical starter compounds are not charged to the reactor at the start, but instead are supplied continuously to the reactor, in addition to the alkylene oxides, during the reaction. As a starting medium for the reaction it is possible in this process to introduce prepolymers initially; the use of small amounts of the product to be prepared as a starting medium itself is also possible. Consequently there is no need first to separately prepare prepolymers suitable for further alkylene oxide additions.

In variant B) of step a) of the process of the invention, therefore, a starter polyol and the DMC catalyst are charged initially to the reactor system, and the H-functional compound is supplied continuously together with the alkylene oxide and the unsaturated cyclic carboxylic anhydride. Suitability as starter polyol in step a) is possessed by alkylene oxide adducts such as, for example, polyether polyols, polyester polyols, polyetherester polyols, polycarbonate polyols, polyester carbonate polyols, and polyether carbonate polyols, in each case, for example, having OH numbers in the range from 3 to 1000 mg KOH/g, preferably of 3 to 300 mg KOH/g, and/or intermediate prepared separately in accordance with step a). Intermediate prepared separately in accordance with step a) is employed preferably as starter polyol in step a).

In a less-preferred variant of this embodiment B), it is likewise possible for the ratio of the metering rates of the alkylene oxide metering and the metering of the unsaturated cyclic carboxylic anhydride during the metered-addition phase of the three components to be varied continuously or in stages relative to one another, by, for example, adopting values of 0:1 to 1:0 for the ratio of the metering rate of the unsaturated cyclic carboxylic anhydride to that of the alkylene oxide/epoxides. This embodiment is less preferred since it produces the intermediate in a less unitary form after step A).

In embodiment B) of step a), the metering of the H-functional compound and that of the alkylene oxide and also of the unsaturated cyclic carboxylic anhydride are preferably ended

simultaneously, or first of all the H-functional compound and a first portion of alkylene oxide and a first portion of the unsaturated cyclic carboxylic anhydride are metered in together, and subsequently the second portion of alkylene oxide and of unsaturated cyclic carboxylic anhydride is metered in, with the sum totals of the first and second portions of alkylene oxide and of the first and second portions of unsaturated cyclic carboxylic anhydride corresponding to the total amount of amount of one or more alkylene oxides and/or of one or more unsaturated cyclic carboxylic anhydrides employed in step a). The first portion is preferably 60 to 98 wt% and the second portion is 40 to 2 wt% of the total amount of alkylene oxide to be metered in step a). The first portion is preferably 0 to 100 wt% and the second portion is 100 to 0 wt% of the total amount of one or more unsaturated cyclic carboxylic anhydrides to be metered in step a).

If the composition of the alkylene oxides and/or the composition/metering rate of the one or more unsaturated cyclic carboxylic anhydrides is changed after the end of the metering of the H-functional compound, it is also possible to produce products having multiblock structures by process variant B). With process variant B) as well it is preferred to end the metering of the unsaturated cyclic carboxylic anhydride before the alkylene oxide metering, with particular preference such that this concluding alkylene oxide block comprises an amount of more than 1 mol of alkylene oxide per mole of active H atoms from the H-functional compounds used as starter compounds. Following metered introduction of the reagents, there may be an after-reaction phase, in which the consumption of alkylene oxide/unsaturated cyclic carboxylic anhydride can be quantified by monitoring of the pressure. When constant pressure has been reached, the product may be discharged, optionally after application of vacuum or by stripping for the removal of unreacted alkylene oxides, as described above.

In variant C) of step a) of the process of the invention, the intermediates may be prepared fully continuously. For this purpose, as well as alkylene oxide and the H-functional compound and also the unsaturated cyclic carboxylic anhydride, the DMC catalyst as well is added continuously to the reactor or to a reactor system, under alkoxylation conditions, and the product is withdrawn continuously from the reactor or the reactor system after a preselectable average residence time. With process variant C) it is preferred to use a reactor cascade as the reactor system, in which there is a third, continuously operated reactor located between the after-reactor and the actual reactor, the one or more alkylene oxides being continuously metered exclusively into this third reactor. In one particularly preferred embodiment of process variant C), this concluding alkylene oxide block comprises an amount of more than 1 mol of alkylene oxide per mole of active H atoms from the H-functional compounds used as starter compounds.

Continuous after-reaction steps may follow, in a reactor cascade or in a tube reactor, for example. Volatile constituents may be removed under reduced pressure and/or by stripping, as described above.

The OH numbers of the unsaturated polyetherester polyols obtained after the DMC-catalyzed

addition reaction step a) preferably have values of 3 mg KOH/g to 200 mg KOH/g, more preferably of 10 to 60 mg KOH/g, very preferably of 20 to 50 mg KOH/g.

The OH number may be determined, for example, by titrimetry in accordance with DIN 53240, or spectroscopically by NIR.

- 5 Equivalent molar mass means the total mass of the material comprising active hydrogen atoms, divided by the number of active hydrogen atoms. In the case of materials containing hydroxyl groups, its relation to the OH number is as follows:

$$\text{Equivalent molar mass} = 56\,100 / \text{OH number [mg KOH/g]}$$

10

The intermediates obtainable according to step a) of the process of the invention may optionally be admixed with aging inhibitors such as antioxidants, for example.

Step b) of the process of the invention is described in detail hereinafter. This representation as well is given only by way of example, and should not be understood as restricting the present invention:

15

For step b), a suitable amine is reacted with the products from step a) at temperatures of 0°C to 150°C, preferably 10°C to 100°C, and more preferably 20°C to 80°C. The molar ratio of primary amino groups to double bonds amenable to addition reaction is, for example, about 1:1 to 1.1:1. While the reaction can be catalyzed using copper acetate, tin chloride, or acetic acid, it is preferably carried out without addition of catalyst.

20

Generally speaking, the amines are supplied under inert gas to the initially introduced intermediate from step a), and the batch is stirred at the stated temperatures for a period of 1 h to about 48 h. Preliminary mixing of the amines with the intermediate from step a) is likewise possible, by means, for example, of a mixing assembly located in the joint metering section ("inline blending").

25

The progress of reaction can be quantified using commonplace methods, such as, for example, online- or offline-conducted gas-chromatographic analyses or spectroscopic methods, such as NMR or IR spectroscopy, for example. Traces of unreacted amines or any amine excess can be removed quantitatively after the reaction phase, optionally under reduced pressure, at an absolute pressure of 1 to 500 mbar, or by stripping.

30

The reaction of the component from step a) with the amine or amines in step b) may in principle take place in the same reactor as for the preparation of the component according to step a). It is preferred, however, to carry out the reaction according to step b) in a different reactor, since traces of amine remaining in the reactor may hinder the implementation of the subsequent DMC-catalyzed step a).

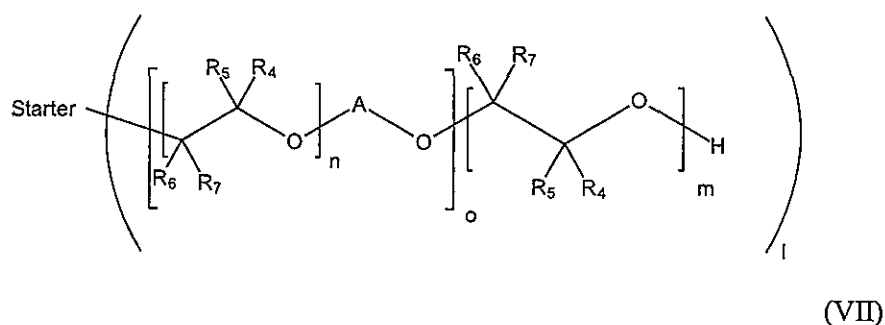
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It has proven advantageous, very generally, to handle polyols for polyurethane(urea) applications

always under an inert gas atmosphere. This is true especially of conventional alkaline polyether polyols, of the kind obtained, for example, under alkali metal hydroxide catalysis, before the catalyst is separated off, or of products obtained under amine catalysis. For salt-free, worked-up and stabilized intermediates and finished products as well, or for those prepared under DMC catalysis, handling and storage in the absence of oxygen are advisable. The same applies to the hydroxy-amino polymers obtainable by the process of the invention, and to their precursors obtainable according to step a). Examples of suitable inert gases include noble gases, nitrogen, or carbon dioxide, with noble gases or nitrogen being particularly suitable. Barring access to oxygen allows instances of product discoloration to be very largely avoided, especially so at elevated temperatures, which are generally utilized in order to facilitate the handling of the intermediates/products through a lowering in the viscosity. Moreover, under an inert gas atmosphere, there are also far fewer peroxide groups formed, which present opportunities, with breaking of the ether bonds, for the formation of further low molecular mass oxidative degradation products such as, for example, acetaldehyde, methanol, formic acid, formic esters, acetone, and formaldehyde. Accordingly, the amount of volatile organic compounds in the intermediates/products can be lowered, and instances of odor nuisance, health adversity, and quality detracting can be avoided.

The present invention relates further to a hydroxy-amino polymer which is obtainable by the process of the invention, where the amount-of-substance ratio between the alkylene oxide compound and the carboxylic anhydride is at least 1.1:1, preferably at least 2:1, more preferably at least 2.5:1, and where, with further preference, the hydroxy-amino polymer is not subjected to any purification.

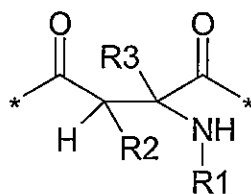
With particular preference the hydroxy-amino polymer of the invention possesses a structure in accordance with the general formula (VII),



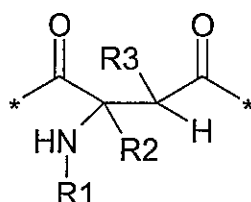
where

"Starter" stands for the radical of the H-functional starter compound,

A is an aspartate group of the following structure, of the formula (VIIIa) or (VIIIb)



(VIIIa)



(VIIIb),

in which

R2 and, R3 independently of one another are hydrogen or an aliphatic or aromatic radical, and R2 and R3 may also be part of a cycloaliphatic ring system,

R1 is hydrogen or an aliphatic, cycloaliphatic, or aromatic radical, which may also contain heteroatoms, more particularly nitrogen atoms or oxygen atoms, and also hydroxyl groups,

R4, R5, R6, and R7 independently of one another are hydrogen or an aliphatic or aromatic radical, and R5 and R6 may also be part of a cycloaliphatic ring system,

l is the number of Zerewitinoff-active hydrogen atoms in the H-functional starter compound,

m, n, and o are independent of one another and are integral, with n, o = 0 or ≥ 1 and $m \geq 2$, and n and m are preferably 2 to 430, more particularly 3 to 430, more preferably 4 to 430, and o is preferably 1 to 100, more particularly 1 to 50, and more preferably 1 to 10,

where the equivalent molar mass of the structure shown in the formula VII does not exceed the value of 18 900 g/mol.

In the case of the above structure of the formula VII, then, the serial number o may be selected independently for each branch of the compound.

The present invention is directed, moreover, to a polyurethaneurea polymer which is obtainable by reaction of a polyisocyanate with a hydroxy-amino polymer preparable by the process of the invention. For this purpose, the hydroxy-amino polymers obtainable by the process of the invention may be reacted, alone or, optionally, in a mixture with other isocyanate-reactive components, with organic polyisocyanates, optionally in the presence of blowing agents, catalysts, and optionally further adjuvants, such as cell stabilizers, for example, and may accordingly serve as components of solid or foamed polyurethaneureas. Accordingly, polyurethaneureas, preferably solid or foamed polyurethaneureas, more particularly coating systems, comprising the hydroxy-amino polymers of the invention are likewise provided by the invention.

Suitable polyisocyanates are aliphatic, cycloaliphatic, araliphatic, aromatic, and heterocyclic polyisocyanates, of the kind described, for example, by W. Siefken in Justus Liebigs Annalen der Chemie, 562, pages 75 to 136, examples being those of the formula (IX)



in which

$n = 2 - 4$, preferably 2 - 3,

and

5 Q is an aliphatic hydrocarbon radical having 2-18, preferably 6-10 C atoms, a cycloaliphatic hydrocarbon radical having 4-15, preferably 6-13 C atoms, or an araliphatic hydrocarbon radical having 8-15, preferably 8-13 C atoms.

These are, for example, polyisocyanates as described in EP 0 007 502 A1, pages 7-8. Preference is given generally to the polyisocyanates that are readily available industrially, such as to 2,4- and
 10 2,6-tolylene diisocyanate, and also to any desired mixtures of these isomers ("TDI"); to polyphenylpolymethylene polyisocyanates, as are prepared by aniline-formaldehyde condensation and subsequent phosgenation ("crude MID"), and to polyisocyanates containing carbodiimide groups, urethane groups, allophanate groups, isocyanurate groups, urea groups, or biuret groups ("modified polyisocyanates"), more particularly those modified polyisocyanates which derive
 15 from 2,4- and/or 2,6-tolylene diisocyanate and/or from 4,4'- and/or 2,4'-diphenylmethane diisocyanate. The urethane group-containing polyisocyanates (prepolymers) may for example be reaction products of the polyisocyanates with polyricinolic ester polyols or else with any other polyols (for example, conventional polyols). Polyisocyanate used is preferably at least one compound selected from the group consisting of 2,4- and 2,6-tolylene diisocyanate, 4,4'- and
 20 2,4'- and 2,2'-diphenylmethane diisocyanate, and polyphenylpolymethylene polyisocyanate ("polycyclic MDI"); polyisocyanate used is more preferably a mixture comprising 4,4'-diphenylmethane diisocyanate and 2,4'-diphenylmethane diisocyanate and polyphenylpolymethylene polyisocyanate.

Besides the above-stated polyisocyanates, the polyurethane(urea) polymers may also be prepared
 25 using, additionally, conventional polyether polyols. Conventional polyether polyols for the purposes of the invention are compounds which are alkylene oxide adducts of starter compounds having Zerewitinoff-active hydrogen atoms, in other words polyether polyols having a hydroxyl number to DIN 53240 of ≥ 3 mg KOH/g to ≤ 1000 mg KOH/g, preferably of ≥ 5 mg KOH/g to ≤ 600 mg KOH/g. Examples of such polyols are known to the skilled person. They may have a
 30 hydroxyl number to DIN 53240 of ≥ 3 mg KOH/g to ≤ 1000 mg KOH/g, preferably of ≥ 5 mg KOH/g to ≤ 600 mg KOH/g. The starter compounds used for preparing the conventional polyether polyols and having Zerewitinoff-active hydrogen atoms usually have functionalities of 2 to 8, preferably of 3 to 6, more preferably of 3, and the starter compounds are preferably hydroxy-functional. Examples of hydroxy-functional starter compounds are propylene glycol, ethylene
 35 glycol, diethylene glycol, dipropylene glycol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, hexanediol, pentanediol, 3-methyl-1,5-pentanediol, 1,12-dodecanediol, glycerol, trimethylolpropane, triethanolamine, pentaerythritol, sorbitol, sucrose, hydroquinone, pyrocatechol,

resorcinol, bisphenol F, bisphenol A, 1,3,5-trihydroxybenzene, methylol group-containing condensates of formaldehyde and phenol or melamine or urea. Glycerol and/or trimethylolpropane are used with preference as starter compounds.

5 Examples of suitable alkylene oxides for the conventional polyether polyols are ethylene oxide, propylene oxide, 1,2-butylene oxide and/or 2,3-butylene oxide, and styrene oxide. Propylene oxide and ethylene oxide are preferably supplied to the reaction mixture individually, in a mixture, or in succession. Where the alkylene oxides are metered in succession, the products prepared comprise polyether chains with block structures. Products with ethylene oxide end blocks are characterized, for example, by elevated concentrations of primary end groups, which
10 endow the systems with an advantageous isocyanate reactivity.

The present invention is lastly directed to the use of a hydroxy-amino polymer of the invention for preparing a polyurethaneurea polymer.

The present invention is elucidated in more detail hereinafter, using working examples.

15 Methods of measurement and determination:

OH number, acid number, amine number, and viscosity

The OH numbers were determined in accordance with the specification of DIN 53240. The acid numbers were determined in accordance with the specification of DIN EN ISO 2114. The amine numbers were determined in accordance with the specification of DIN 53176. The viscosities
20 were determined using a rotational viscometer (Physica MCR 51, manufacturer: Anton Paar) in accordance with the specification of DIN 53018 (spindle type CC27, shear rate range 16-128 s⁻¹).

Molar mass distribution

The molar mass distribution was determined by means of size exclusion chromatography (SEC).

25 The Agilent 1100 series instrument from Agilent was used. Reported is the polydispersity PD for the molecular weight distribution M_w/M_n , where M_w stands for the weight-average molar mass and M_n for the number-average molar mass. Further details:

- Column combination: 1 preliminary column PSS, 5 µl, 8x50mm; 2 PSS SVD, 5 µl, 100 Å, 8x300mm; 2 PSS SVD, 5 µl, 1000 Å, 8x300mm, PSS is the manufacturer of the
30 columns (Polymer Standard Solutions, Mainz)
- Analysis software: WIN GPC from PSS
- Solvent: THF (Merck LiChrosolv)
- Flow rate: 1 ml/min
- Detector type: RI detector (refractive index), Shodex RI 74
- 35 – Calibration standards used: calibrating standard from PSS based on polystyrene.

Raw materials used**Catalyst for the alkylene oxide/acid anhydride addition reaction (DMC catalyst):**

Double metal cyanide catalyst, comprising zinc hexacyanocobaltate, tert-butanol, and polypropylene glycol with a number-average molecular weight of 1000 g/mol; described in WO 01/80994 A1, example 6.

Ambosol®: Precipitated, colloidal, synthetically prepared magnesium silicate, obtained from PQ Europe.

Polyol A: Polyether, obtained by addition reaction of ethylene oxide onto propylene glycol under KOH catalysis; OH number: 190 mg KOH/g, number-average molar mass: 591 g/mol

Example:**A) Preparation of an alkylene oxide/maleic anhydride copolymer via DMC catalysis (prepolymer according to step a))**

A 2 l laboratory autoclave was charged under a nitrogen atmosphere with 233.7 g (396 mmol) of polyol A and 0.25 g of 85% strength phosphoric acid and this initial charge was stirred at room temperature for 30 minutes (propeller stirrer at 800 rpm). Following addition of 0.601 g of DMC catalyst, the contents of the autoclave were stripped for 30 minutes at 130°C with stirring (propeller stirrer) at 450 rpm and at an absolute pressure of 100 to 120 mbar, with introduction of 50 ml of nitrogen per minute via a distributor ring situated beneath the liquid surface. At 130°C and with stirring at 800 rpm, a mixture of 156.5 g of propylene oxide and 469.7 g of ethylene oxide was metered into the headspace of the autoclave over a period of 2.02 hours, the metering being commenced at an absolute pressure of 0.05 bar. After an after-reaction time of 20 minutes, the batch was cooled to room temperature and 0.627 g of vitamin E and also 77.9 g (794 mmol) of maleic anhydride were introduced into the autoclave. After the filling port had been closed, residual oxygen was removed at 25°C by fourfold injection of nitrogen to an absolute pressure of 4 bar with subsequent bleeding of the overpressure to atmospheric pressure. Following heating to 80°C, a mixture of 65.6 g of propylene oxide and 197.0 g of ethylene oxide was metered into the headspace of the autoclave over a period of 2.65 hours. After an after-reaction time of 30 minutes, the product was heated to 80°C for 30 minutes at an absolute pressure of 10 mbar; subsequently, 0.214 g of vitamin E was added.

1102.4 g of the intermediate were placed in a 2 l three-neck flask. After threefold evacuation and letdown with nitrogen, 88.2 g of Ambosol® were added at 80°C under a countercurrent flow of nitrogen. The contents of the flask were stirred at 80°C over a period of 3 hours, followed by heating at 80°C for a further 3 hours under an absolute pressure of 1 mbar. The Ambosol® was then separated off by filtration on a laboratory suction filter heated using slow steam (about 100°C).

The resulting intermediate had a viscosity of 1854 mPas at 25°C, an OH number of 38 mg

KOH/g, and an acid number of 10 ppm KOH. Size exclusion chromatography found a polydispersity (M_w/M_n) of 1.38. A polydispersity of this low level is unachievable with an unsaturated polyester prepared by polycondensation reaction, since the molar masses of products prepared in that way are subject to the Schultz-Flory distribution, whereas the intermediates prepared via DMC catalysis in accordance with the process of the invention have significantly narrower Poisson distributions.

B) Reaction of the intermediate from A) with N-butylamine (step b))

100 g (33.8 mmol) of the intermediate from step A) were charged to a 500 ml 4-neck flask with top-mounted reflux condenser, internal thermometer, and magnetic stirrer. Following threefold evacuation and letdown with nitrogen, 5.0644 g (69.2 mmol) of N-butylamine were added in a countercurrent stream of nitrogen. Over the course of a few minutes, the internal flask temperature rose from 26°C to 34°C. After 30 minutes, the internal flask temperature was raised to 60°C using a heating jacket, and was held at this temperature for 4 hours with stirring.

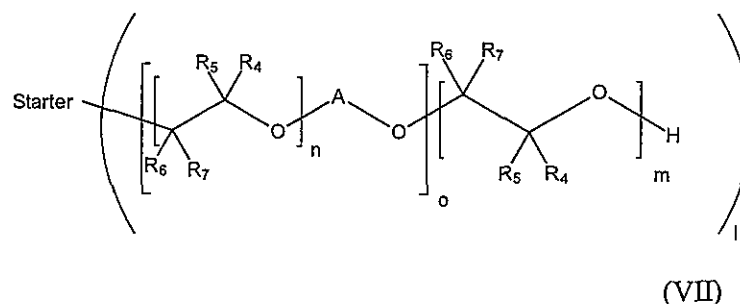
The viscosity of the product at 25°C was 1635 mPas. The measured "OH number" was 73.4 mg KOH/g, the measured "OH number" in this specific case being the sum total of amine number and of the actual OH number. The amine number was 35 mg KOH/g, corresponding approximately to half the measured "OH number". The stoichiometry of the incorporation of MAn in the precursor had been selected so as to insert 1 MAn per OH group. The outcome shows that virtually all of the double bonds have been reacted.

Claims:

1. A process for preparing a hydroxy-amino polymer, comprising the steps of:
 - a) reacting an H-functional starter compound carrying at least one Zerewitinoff-active H atom with an unsaturated cyclic carboxylic anhydride and with at least one alkylene oxide compound, to give a prepolymer carrying hydroxyl groups,
 - b) addition-reacting a primary amine and/or ammonia onto the double bonds of the hydroxyl-carrying prepolymer obtained by step a), to give the hydroxy-amino polymer,where
the reaction of the H-functional starter compound with the unsaturated cyclic carboxylic anhydride and/or the addition reaction of the alkylene oxide compound are/is carried out using a double metal cyanide catalyst (DMC catalyst),
the H-functional starter compound has 1 to 35, more particularly 1 to 8 Zerewitinoff-active H atoms,
the alkylene oxide compound is selected from those having 2 to 24 carbon atoms, more particularly from ethylene oxide and/or propylene oxide,
the amount-of-substance ratio between the alkylene oxide compound and the carboxylic anhydride is at least 1.1:1, preferably at least 2:1, more particularly at least 2.5:1,
and the primary amine is selected from aliphatic, cycloaliphatic and/or araliphatic monoamines and diamines having at least one primary amino group and optionally hydroxyl groups.
2. The process as claimed in claim 1, characterized in that the H-functional starter compound has a number-average molar mass of 17 to 1200 g/mol, more particularly of 62 to 1000 g/mol.
3. The process as claimed in either of the preceding claims, characterized in that the unsaturated cyclic carboxylic anhydride is selected from unsaturated cyclic dicarboxylic anhydrides, such as maleic anhydride, tetrahydrophthalic anhydride, more particularly 3,4,5,6-tetrahydrophthalic anhydride, and also combinations thereof.
4. The process as claimed in any of the preceding claims, characterized in that at least one further comonomer is reacted in step a), and is selected more particularly from lactones, lactides, saturated and/or aromatic cyclic carboxylic anhydrides, cyclic carbonates and/or carbon dioxide, the reaction of the further comonomer preferably being likewise catalyzed by the DMC catalyst.
5. The process as claimed in any of the preceding claims, characterized in that the amount-of-substance ratio between the carboxylic anhydride and the number of Zerewitinoff-active H atoms in the H-functional starter compound is about 1:1 to 1.5:1, more particularly 1:1 to 1.2:1.
6. The process as claimed in any of the preceding claims, characterized in that initially the H-

functional starter compound and the DMC catalyst are introduced and subsequently the alkylene oxide compound, the cyclic unsaturated carboxylic anhydride, and optionally the further comonomer are added.

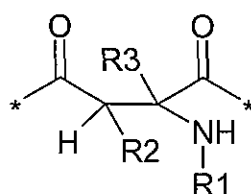
7. The process as claimed in any of claims 1 to 5, characterized in that initially the H-functional starter compound and the DMC catalyst are introduced, alkylene oxide compound and also optionally further comonomer are metered in, and subsequently the unsaturated cyclic carboxylic anhydride is added, the addition of the unsaturated cyclic carboxylic anhydride being followed by further metered addition of alkylene oxide compound and also, optionally, of further comonomer, more particularly more than 1 mol of the alkylene oxide compound per mole of Zerewitinoff-active hydrogen.
8. The process as claimed in any of claims 1 to 5, characterized in that in step a) an H-functional starter polyol and the DMC catalyst are introduced initially and the H-functional starter compound is supplied continuously together with the alkylene oxide and the unsaturated cyclic carboxylic anhydride, with the H-functional starter polyol having an OH number in the range from 3 to 1000 mg KOH/g, preferably in the range from 3 to 300 mg KOH/g.
9. The process as claimed in claim 8, characterized in that an intermediate prepared according to step a) is used as H-functional starter polyol.
10. The process as claimed in either of claims 8 and 9, characterized in that the metering of the cyclic carboxylic anhydride is ended before the metering of the alkylene oxide compound and in a concluding metering, comprising exclusively alkylene oxide and also, if desired, a comonomer, more than 1 mol of alkylene oxide compound per mole of Zerewitinoff-active hydrogen is metered in.
11. The process as claimed in either of claims 8 and 9, characterized in that in step a) a starter polyol and a portion of the DMC catalyst are introduced initially in the reactor system, the H-functional compound and further DMC catalyst are supplied continuously together with the alkylene oxide and the unsaturated cyclic carboxylic anhydride, and the step a) reaction product formed in this procedure is withdrawn continuously from the reactor system after a preselectable average residence time.
12. A hydroxy-amino polymer obtainable by a process as claimed in any of claims 1 to 11, where the amount-of-substance ratio between the alkylene oxide compound and the carboxylic anhydride is at least 1.1:1, preferably at least 2:1, preferably at least 2.5:1, and where the hydroxy-amino polymer with further preference is not subjected to any purification.
13. The hydroxy-amino polymer as claimed in claim 12, characterized in that the hydroxy-amino polymer possesses the general formula (VII)



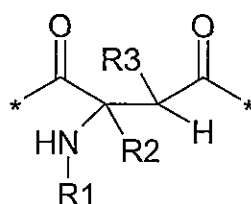
where

"Starter" stands for the radical of the H-functional starter compound,

A is an aspartate group of the following structure, of the formula (VIIIa) or (VIIIb)



(VIIIa)



(VIIIb),

in which

R2 and, R3 independently of one another are hydrogen or an aliphatic or aromatic radical, and R2 and R3 may also be part of a cycloaliphatic ring system,

R1 is hydrogen or an aliphatic, cycloaliphatic, or aromatic radical, which may also contain heteroatoms, more particularly nitrogen atoms or oxygen atoms, and also hydroxyl groups,

R4, R5, R6, and R7 independently of one another are hydrogen or an aliphatic or aromatic radical, and R5 and R6 may also be part of a cycloaliphatic ring system,

l is the number of Zerewitinoff-active hydrogen atoms in the H-functional starter compound,

m, n, and o are independent of one another and are integral, with n, o = 0 or ≥ 1 and $m \geq 2$, and n and m are preferably 2 to 430, more particularly 3 to 430, more preferably 4 to 430, and o is preferably 1 to 100, more particularly 1 to 50, and more preferably 1 to 10,

where the equivalent molar mass of the structure shown in the formula VII does not exceed the value of 18 900 g/mol.

14. A polyurethaneurea polymer obtainable by reacting a polyisocyanate with a hydroxy-amino polymer as claimed in claim 12 or 13.

15. The use of a hydroxy-amino polymer as claimed in claim 12 or 13 for preparing a polyurethaneurea polymer.