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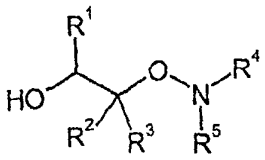
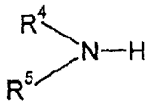
## (54) One-pot process for the preparation of functionalized alkoxyamines

(57) The present invention relates to a new one-pot process for the preparation of functionalized alkoxyamine initiators of the formula (I)



(I)

from amines of the formula (II)



(II)

and to a process of controlled radical polymerization using the functionalized alkoxyamine as initiators. In the above formulae, $R^1$-$R^5$ have the meanings given in the description.

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## Description

**[0001]** The present invention relates to a new process for the preparation of functionalized alkoxyamine initiators and to a process of radical polymerization using the functionalized alkoxyamine initiators as intermediate.

**[0002]** The use of the controlled radical polymerization ("CRP") of vinyl monomers has increased rapidly because it allows the synthesis of a broad range of well-defined (co)polymers under uncomplicated experimental conditions. The polymerization can, for example, be carried out in aqueous media and under moderate polymerization temperatures and purification of the monomer prior to polymerization is not required. Additionally, the main molecular parameters of the polymer chain, for example its polydispersity, molecular weight, polymer architecture or the structure of the chain-ends can be easily controlled and adjusted. The CRP is also called "living" free radical polymerization. The aim of the precise control of free radical polymerization is achieved by reversible chain termination or blocking ("end-capping") after each growth step. The equilibrium concentration of the polymerization-active ("living") chain ends in this case is so low compared with the equilibrium concentration of the blocked ("dormant") chain ends that irreversible termination and transfer reactions are greatly suppressed compared with the growth reaction. Since the end-capping proceeds reversibly, all the chain ends remain "living" if no termination reagent is present. This allows the control of the molecular weight, low polydispersity and controlled functionalization of the chain ends by termination reagents.

**[0003]** Of all the CRP systems presently under investigation, the nitroxyl-mediated polymerization ("NMP") is one of the most attractive and efficient, because this technique provides advantages applicable to a broad range of monomers such as (meth)acrylates, acrylonitrile, styrenes, acrylamides, butadiene or isoprene and can be carried out in a metal-free, colorless and odorless manner.

**[0004]** Numerous publications have shown that alkoxyamines can be used to initiate and control the radical polymerization of vinyl monomers according to an NMP mechanism.

**[0005]** US-A 4,581,429 discloses alkoxyamines which are formed by the reaction of linear or cyclic nitroxides, such as 2,2,6,6-tetra-methylpiperidin-1-oxyl (TEMPO) with organic carbon-based free radicals, and a process for the preparation of vinyl polymers using these compounds as initiators. The reactions typically have a low concentration of free radicals which, in the free radical polymerization of vinyl monomers, means that bimolecular termination reactions are less likely to occur than unimolecular growth reactions.

**[0006]** Other examples are described by *Hawker et al.* (*J. Am. Chem. Soc.* **1994**, 116, 11185 and *J. Am. Chem. Soc.* **1999**, 121, 3904-3920) and in US-A 5,322,912, US-A 5,412,047, US-A 5,449,724, US-A 5,498,679, US-A 6,258,911, DE-A 199 09 767 and EP-A 0 891 986.

**[0007]** The most commonly used method for the synthesis of alkoxyamines consists in coupling an alkyl radical to a nitroxyl radical. The alkyl radical R° can be generated by different methods, for example by decomposition of azo compounds *(Hawker et al.,* Macromolecules 1996, 29, 5245-5254; *Yozu Miura et al.,* Macromolecules 1998, 31, 6727-6729), by hydrogen removal from an appropriate substrate (*Hawker et al.,* Macromolecules 1996, 29, 5245-5254; *Yozu Miura et al.,* Macromolecules 1998, 31, 4659-4661) or by addition of a radical to an olefin (*Hawker et al.,* J. Am. Chem. Soc. 1994, 116, 11185). The alkyl radical can also be generated from an halogenated compound R-X in the presence of a metallic catalyst following an atom transfer radical addition ("ATRA") reaction (WO-A 00/49027; WO-A 00/61544).

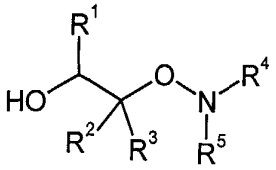
**[0008]** EP-A 1 083 169 discloses a process for the preparation of functionalized alkoxyamine initiators in which hydrogen peroxide is reacted with iron(II) sulfate in the presence of a nitroxyl radical and a vinyl monomer to form the alkoxyamine with a good yield in a one-pot process.

**[0009]** The major disadvantage of the methods described above is that the alkoxyamines have to be synthesised from costly nitroxyl radicals and generally must be purified before they can be used for polymerization.

**[0010]** The object of the present invention was to provide a new synthetic pathway for the synthesis of alkoxyamines in a one-pot process and to use these alkoxyamines as intermediates in a polymerization process which provides homo- and copolymers of narrow polydispersity with a specific molecular weight and which does not have the above-mentioned disadvantages of the prior art.

**[0011]** Surprisingly, it has now been found that hydroxy-functional alkoxyamines can be produced from secondary amines in a one-pot process and used, without intermediate purification, in a controlled, free-radical polymerisation process.

**[0012]** The object of the present invention is a one-pot process for the preparation of functional alkoxyamines of the general formula (I)



(I)

wherein

$R^1$, $R^2$, $R^3$ are independently selected from the group consisting of: hydrogen, $C_1$-$C_{20}$alkyl, $C_1$-$C_{20}$cycloalkyl, $C_6$-$C_{24}$aryl, halogen, cyano, $C_1$-$C_{20}$alkylester $C_1$-$C_{20}$ cycloalkylester, $C_1$-$C_{20}$ alkylamide, $C_1$-$C_{20}$cycloalkylamide $C_6$-$C_{24}$-arylester or $C_6$-$C_{24}$-arylamide;

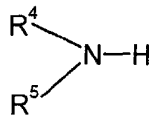
$R^4$ and $R^5$ are independently selected from the group consisting of: $C_1$-$C_{18}$alkyl, $C_2$-$C_{18}$galkenyl, $C_2$-$C_{18}$alkynyl, $C_3$-$C_{12}$cycloalkyl or $C_3$-$C_{12}$-heterocycloalkyl, $C_6$-$C_{24}$-aryl, which are unsubstituted or substituted by $NO_2$, halogen, amino, hydroxy, cyano, carboxy, ketone, $C_1$-$C_4$alkoxy, $C_1$-$C_4$alkylthio, $C_1$-$C_4$alkylamino;

$R^4$ and $R^5$ optionally form, together with the intermediate nitrogen atom, a $C_3$-$C_{12}$cycloalkyl radical, a ($C_4$-$C_{12}$alkanol)yl radical or a $C_2$-$C_{13}$-heterocycloalkyl radical containing oxygen, sulfur or nitrogen atoms;

$R^4$ and $R^5$ together form a residue of a polycyclic ring system or a polycyclic heterocycloaliphatic ring system containing oxygen, sulfur or nitrogen atoms;
wherein the carbon atom of the $R^4$ and $R^5$ radicals directly adjacent to the alkoxyamine nitrogen atom is in each case substituted by 3 further organic substituents and
wherein optionally at least one of the radicals $R^4$ and $R^5$ contains a functional group Y which is capable of further reacting or crosslinking with the functional groups known from the in coatings field;

comprising the reaction steps of

(1) reacting of an oxidizing agent (A) with a sterically hindered secondary amine of the general formula (II),



(II)

wherein

$R^4$ and $R^5$ are independently selected from the group consisting of: $C_1$-$C_{18}$alkyl, $C_2$-$C_{18}$-alkenyl, $C_2$-$C_{18}$alkynyl, $C_3$-$C_{12}$cycloalkyl or $C_3$-$C_{12}$-heterocycloalkyl, $C_6$-$C_{24}$aryl, which are unsubstituted or substituted by $NO_2$, halogen, amino, hydroxy, cyano, carboxy, ketone, $C_1$-$C_4$alkoxy, $C_1$-$C_4$alkylthio, $C_1$-$C_4$alkylamino;

$R^4$ and $R^5$ optionally form, together with the intermediate nitrogen atom, a $C_3$-$C_{12}$cycloalkyl radical, a ($C_4$-$C_{12}$alkanol)yl radical or a $C_2$-$C_{13}$heterocycloalkyl radical containing oxygen, sulfur or nitrogen atoms;

$R^4$ and $R^5$ together form a residue of a polycyclic ring system or a polycyclic heterocycloaliphatic ring system containing oxygen, sulfur or nitrogen atoms;
wherein the carbon atom of the $R^4$ and $R^5$ radicals directly adjacent to the alkoxyamine nitrogen atom is in each case substituted by 3 further organic substituents and
wherein optionally at least one of the radicals $R^4$ and $R^5$ contains a functional group Y which is capable of further reacting or crosslinking with functional groups known in the coatings field;

in a water-containing medium,

(2) removing of the aqueous phase and

(3) adding one or more monomer(s) of the general formula (III),

$$HR^1C = CR^2R^3 \qquad (III)$$

wherein

$R^1$, $R^2$, $R^3$ are independently selected from the group consisting of: hydrogen, $C_1$-$C_{20}$alkyl, $C_1$-$C_{20}$cycloalkyl $C_6$-$C_{24}$aryl, halogen, cyano, $C_1$-$C_{20}$alkylester $C_1$-$C_{20}$cycloalkylester, $C_1$-$C_{20}$alkylamide, $C_1$-$C_{20}$cycloalkylamide $C_6$-$C_{24}$-arylester or $C_6$-$C_{24}$-arylamide;

as well as

(B) a system which produces free radicals consisting of

(B1) a reducing agent and
(B2) a molecule able to react with (B1) to form radicals.

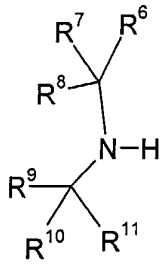
**[0013]** The Y group is capable of reacting further or crosslinking and is for example hydroxyl, carboxy, amino, isocyanate, urethane or epoxide groups.

**[0014]** Suitable oxidizing agents (A) can be all oxidizing agents known from the prior art for the oxidation of secondary amines into nitroxyl radicals. Preferred oxidizing agents are water-soluble oxidizing agents, such as peracids such as peracetic acid, perpropionic acid, m-chloroperbenzoic acid, dimethyldioxirane, perbenzoic acid, or peroxides such as potassium peroxymonosulfate (Oxone®, DuPont Specialty Chemistry, USA), hydrogen peroxide, hydrogen peroxide/sodium tungstate, hydrogen peroxides/titanium containing catalysts, such as for example titanium dioxide and titanium silicalites (EP-A 0 488 403, page 5), phosphotungstic acid and oxidizing gases such as molecular oxygen or ozone. Particularly preferred are peracetic acid, perpropionic acid, m-chloroperbenzoic acid, Oxone® (DuPont Specialty Chemistry, USA) and hydrogen peroxide/sodium tungstate.

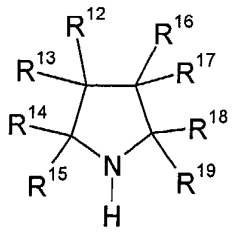
**[0015]** Metal oxides such as silver oxide, lead (IV) oxide and sodium tungstate can also be used, optionally in combination with another oxidizing agent. A mixture of various oxidizing agents can also be used.

**[0016]** The water phase in which the secondary amine is dispersed can contain a basic organic or inorganic buffer or organic or inorganic bases, such as $Na_2CO_3$, $NaHCO_3$, $K_2CO_3$, $KHCO_3$, $Na_3PO_4$, $Na_2HPO_4$, $NaH_2PO_4$, metal salts of carboxylic acids such as acetic acid sodium salt or propionic acid sodium salt, or a mixture thereof. $Na_2CO_3$, $NaHCO_3$, $K_2CO_3$, $KHCO_3$ and the sodium, calcium or potassium salts of acetic acid are preferred.

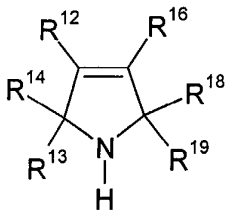
**[0017]** Useful sterically hindered secondary amines of the general formula (II) are for example those of the following formulare (IV) to (XII):



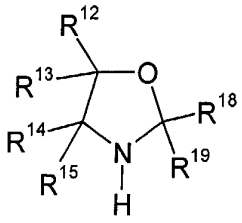

(IV)



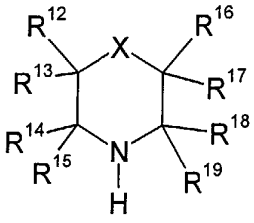

(V)




(VI)



(VII)

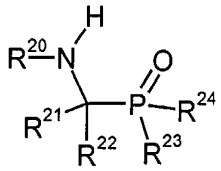


(VIII)

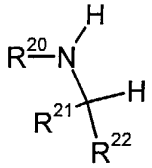
wherein

| | |
|---|---|
| $R^6$, $R^7$, $R^8$, $R^9$,$R^{10}$, $R^{11}$, $R^{12}$, $R^{13}$, $R^{14}$,$R^{15}$,$R^{16}$, $R^{17}$, $R^{18}$, $R^{19}$ | are independently selected from the group consisting of: hydrogen, halogen or cyano-, amide-, ether-, ester-, thioether-, ketone-, amide-, carbomyl-, amidine- or dialkylphosphonyl-containing groups; |
| $R^6$ to $R^{19}$ | are independently selected from the group consisting of: $C_1$-$C_{18}$alkyl, $C_2$-$C_{18}$ alkenyl, $C_2$-$C_{18}$alkynyl, $C_3$-$C_{12}$cycloalkyl or $C_3$-$C_{12}$hetero-cycloalkyl, $C_6$-$C_{24}$aryl, which are unsubstituted or substituted by $NO_2$, halogen, amino, hydroxy, cyano, carboxy, $C_1$-$C_4$alkoxy, $C_1$-$C_4$alkylthio, $C_1$ -$C_4$alkylamino; |
| $R^6$ to $R^{19}$ | can form, together with the intermediate carbon atom, a $C_3$-$C_{12}$-cycloalkyl radical, a ($C_4$-$C_{12}$alkanol)yl radical or a $C_2$-$C_{13}$heterocycloalkyl radical containing oxygen, sulfur or nitrogen atoms; |
| $R^6$ to $R^{19}$ | together form a residue of a polycyclic ring system or a polycyclic heterocycloaliphatic ring system containing oxygen, sulfur or nitrogen atoms; |
| | wherein optionally at least one of the radicals $R^6$ to $R^{19}$ contains a functional group Y which is capable of reacting further or of cross-linking with functional groups known in the coatings field and |
| X | represents a methylene, ketone, ester group or oxygen atom, a hydrocarbon radical, which can be substituted by a cyano, nitro, ether, ester, hydroxy or imido group. |

**[0018]** Other useful secondary amines are for example those of the following formulare (IX) and (X):



(IX)



(X)

wherein

| | |
|---|---|
| $R^{20}$ | is selected from the group consisting of: $C_1$-$C_{18}$alkyl, $C_2$-$C_{18}$alkenyl, $C_2$-$C_{18}$alkynyl, $C_3$-$C_{12}$cycloalkyl or $C_3$-$C_{12}$heterocycloalkyl, $C_6$-$C_{24}$aryl, which are unsubstituted or substituted by $NO_2$, halogen, amino, hy- |

droxy, cyano, carboxy, $C_1$-$C_4$alkoxy, $C_1$-$C_4$alkylthio, $C_1$-$C_4$alkylamino;

$R^{20}$ optionally contain a functional group Y which is capable of reacting further or of crosslinking with the functional groups known from the coatings field;

$R^{21}$, $R^{22}$ are independently selected from the group consisting of: hydrogen, halogen or cyano-, amide-, ether-, ester-, thioether-, ketone-, amide-, carbomyl-, amidine- or dialkylphosphonyl-containing groups;

$R^{21}$, $R^{22}$ are independently selected from the group consisting of: $C_1$-$C_{18}$alkyl, $C_2$-$C_{18}$alkenyl, $C_2$-$C_{18}$alkynyl, $C_3$-$C_{12}$cycloalkyl or $C_3$-$C_{12}$heterocycloalkyl, $C_6$-$C_{24}$aryl, which are unsubstituted or substituted by $NO_2$, halogen, amino, hydroxy, cyano, carboxy, $C_1$-$C_4$alkoxy, $C_1$-$C_4$alkylthio or $C_1$-$C_4$alkylamino;

wherein $R^{21}$ and $R^{22}$ optionally form, together with the intermediate carbon atom a $C_3$-$C_{12}$cycloalkyl radical, a ($C_4$-$C_{12}$alkanol)yl radical or a $C_2$-$C_{13}$heterocycloalkyl radical containing oxygen, sulfur or nitrogen atoms;

$R^{21}$, $R^{22}$ together form a residue of a polycyclic ring system or a polycyclic heterocycloaliphatic ring system containing oxygen, sulfur or nitrogen atoms;

wherein $R^{23}$ and $R^{24}$ optionally form, together with the intermediate phosphorus atom a $C_3$-$C_{12}$cycloalkyl radical, a ($C_4$-$C_{12}$alkanol)yl radical or a $C_2$-$C_{13}$heterocycloalkyl radical containing oxygen, sulfur or nitrogen atoms;

wherein optionally at least one of the radicals $R^{20}$ to $R^{24}$ contains a functional group Y which is capable of further reacting or of crosslinking with functional groups known from the coatings field;

$R^{23}$, $R^{24}$ are independently selected from the group consisting of: $C_1$-$C_{18}$alkyl, $C_2$-$C_{18}$alkenyl, $C_2$-$C_{18}$alkynyl, $C_3$-$C_{12}$cycloalkyl or $C_3$-$C_{12}$heterocycloalkyl or $C_6$-$C_{24}$aryl, which are unsubstituted or substituted by $NO_2$, halogen, amino, hydroxy, cyano, carboxy, $C_1$-$C_4$alkoxy, $C_1$-$C_4$alkylthio or $C_1$-$C_4$alkylamino;

wherein $R^{23}$ and $R^{24}$ optionally form, together with the intermediate phosphorus atom, a $C_3$-$C_{12}$cycloalkyl radical, a ($C_4$-$C_{12}$alkanol)yl radical or a $C_2$-$C_{13}$heterocycloalkyl radical containing oxygen, sulfur or nitrogen atoms;

wherein at least one of the radicals $R^{23}$ to $R^{24}$ optionally contains a functional group Y which is capable of further reacting or of crosslinking with functional groups is known from the coatings field.

**[0019]** Preferred secondary amines of the general formula (II) are tert-butyl amine; 2,2,6,6-tetramethylpiperidine; 4-hydroxy-2,2,6,6-tetramethylpiperidine; 2,2,6,6-tetramethyl-4-piperidinone; 2,2,6,6-tetramethyl-4-piperidinyl acetate; 2,2,6,6-tetramethyl-4-piperidinyl stearate; 2,2,6,6-tetramethyl-4-piperidinyl benzoate; 2,6-dimethyl-2,6-diethylpiperidine; diethyl 1-(tert-butylamino)-2,2-dimethylpropylphosphonate; dipropyl 1-(tert-butylamino)-2,2-dimethylpropylphosphonate; dibutyl 1-(tert-butylamino)-2,2-dimethylpropylphosphonate; N-(tert-butyl)-1-(diethylphosphoryl)-2,2-dimethyl-1-propylamine; N-(tert-butyl)-1-(dipropylphosphoryl)-2,2-dimethyl-1-propylamine; N-(tert-butyl)-2-methyl-1-phenyl-1-propylamine; 2,2,4,6,6-pentamethyl-1,2,5,6-tetrahydropyrimidine; N-[(3E)-2,2-diphenyl-1,2-dihydro-3H-indol-3-ylidene]-N-phenylamine; 2,6-diethyl-2,3,6-trimethyl-4-piperidinone; 2,6-diethyl-2,3,6-trimethyl-4-piperidinol; 14-oxa-7-azadispiro[5.1.5.2]pentadecane; 2,2,4,4-tetramethyl-1,3-oxazolidine; 2,2,5,5-tetramethyl-1-pyrrolidine; 3-carboxy-2,2,5,5-tetramethyl-1 -pyrrolidine; 2,5-diphenyl-2,5-dimethylpyrrolidine; 3-carboxy-2,5-diphenyl-2,5-dimethylpyrrolidine; 1,1,3,3-tetraethylisoindoline; 1,1,3,3-tetramethylisoindoline; 1,1,3,3-tetrapropylisoindoline.

**[0020]** Particularly preferred are: tert-butyl amine; 2,2,6,6-tetramethylpiperidine; 4-hydroxy-2,2,6,6-tetramethylpiperidine; 2,2,6,6-tetramethyl-4-piperidinone; 2,2,6,6-tetramethyl-4-piperidinyl acetate; diethyl 1-(tert-butylamino)-2,2-dimethylpropyl phosphonate; dipropyl 1-(tert-butylamino)-2,2-dimethylpropyl phosphonate; dibutyl 1-(tert-butylamino)-2,2-dimethylpropyl phosphonate; 2,6-diethyl-2,3,6-trimethyl-4-piperidinone; 2,6-diethyl-2,3,6-trimethyl-4-piperidinol; 2,2,5,5-tetramethyl-1-pyrrolidine; 1,1,3,3-tetramethylisoindoline.

**[0021]** Polyfunctional amines can also be used as compounds of the formula (II) in order to form resins displaying heat reversibility. In the context of the present invention polyfunctional amines are compounds which have more than one secondary amino group. These properties are particularly interesting when low viscosity of the polymer is required during processing.

**[0022]** Some examples of suitable polyfunctional amines are bis(2,2,6,6-tetramethylpiperidine) sebacate; bis (2,2,6,6-tetramethylpiperidine) succinate; bis(2,2,6,6-tetramethylpiperidine) adipate; bis(2,2,6,6-tetramethylpiperidine) phthalate; bis(2,2,6,6-tetramethylpiperidine) isophthalate; bis(2,2,6,6-tetramethylpiperidine) terephthalate; or polymeric multifunctional amines such as poly((6-((1,1,3,3-tetramethylbutyl)-amino)- 1,3,5-triazine-2,4-diyl)((2,2,6,6-tetramethyl-4-piperidinyl)imino)- 1,6-hexanediyl((2,2,6,6-tetramethyl-4-piperidinyl)imino)) (CHIMASSORB® 944, Ciba Specialty Chemicals, D-Lampertheim).

**[0023]** Typical monoethylenically unsaturated monomers which are suitable for the present invention are the alkyl esters of acrylic or methacrylic acids, such as methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and isobutyl methacrylate; the hydroxyalkyl esters of acrylic or methacrylic acids, such as hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate and hydroxypropyl methacrylate; acrylamide, methacrylamide, N-tertiary butylacrylamide, N-methylacrylamide, N,N-dimethylacrylamide; acrylonitrile, methacrylonitrile, allyl alcohol, dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, phosphoethyl methacr-

ylate, N-vinylpyrrolidone, N-vinylformamide, N-vinylimidazole, vinyl acetate, conjugated dienes such as butadiene or isoprene, styrene, styrenesulfonic acid salts, vinylsulfonic acid salts and 2-acrylamido-2-methylpropane-sulfonic acid salts and acryloyl. Also suitable are cis- and trans-stilbene and diphenylethylene.

**[0024]** Examples of comonomers suitable for use in the present invention are $C_3$-$C_6$-ethylenically unsaturated monocarboxylic acids as well as the alkali metal salts and ammonium salts thereof. The $C_3$-$C_6$-ethylenically unsaturated monocarboxylic acids include acrylic acid, methacrylic acid, crotonic acid, vinylacetic acid and acryloxypropionic acid. Acrylic acid and methacrylic acid are the preferred monoethylenically unsaturated monocarboxylic acid monomers.

**[0025]** Examples of $C_8$-$C_{16}$-ethylenically unsaturated phenolic compounds which may also be used as comonomers are 4-hydroxy styrene, 4-hydroxy, $\alpha$-methyl styrene, 2,6-ditert-butyl and 4-vinyl phenol.

**[0026]** Another class of carboxylic acid monomers suitable for use as comonomers in this invention are $C_4$-$C_6$-ethylenically unsaturated dicarboxylic acids and the alkali metal and ammonium salts thereof as well as the anhydrides of cis-dicarboxylic acids. Suitable examples include maleic acid, maleic anhydride, itaconic acid, mesaconic acid, fumaric acid and citraconic acid. Maleic anhydride (and itaconic acid) is the preferred monoethylenically unsaturated dicarboxylic acid monomer(s).

**[0027]** The acid monomers suitable for use in the present invention may be in the form of their acids or in the form of the alkali metal salts or ammonium salts of the acid.

**[0028]** Preferred monomers are selected from the group consisting of (meth)acrylic acid esters of $C_1$-$C_{20}$-alcohols, acrylonitrile, cyanoacrylic acid esters of $C_1$-$C_{20}$-alcohols, maleic acid diesters of $C_1$-$C_6$-alcohols, maleic anhydride, vinylpyridines, vinyl-(alkylpyrroles), vinyloxazoles, vinyloxazolines, vinylthiazoles, vinylimidazoles, vinylpyrimidines, vinyl ketones, styrene or styrene derivatives which contain a $C_1$-$C_6$-alkyl radical or halogen in the $\alpha$-position and contain up to 3 additional substituents on the aromatic ring. Nonpolymerizable vinyl monomers such as cis- and trans-stilbene, and diphenylethylene are also preferred.

**[0029]** Particularly preferred monomers are methyl acrylate, methyl methacrylate, butyl acrylate, butyl methacrylate, 2-ethylhexyl acrylate, cyclohexyl methacrylate, isobornyl methacrylate, maleic anhydride, styrene or acrylonitrile.

**[0030]** The compound (B1) is a reducing agent, such as for example transition metal compounds, sulfur compounds of a low degree oxidation or compounds which can be readily enolized. Preferred are sodium hydrogen sulfite, reducing sugars such as a glucose and dextrose, carbonyl compounds which can be readily enolized, such as ascorbic acid and hydroxyacetone, and metal ions, such as $F_e^{2+}$, $Ti^{3+}$ and $Cu^{1+}$. Particularly preferred are $Fe^{2+}$, $Ti^{3+}$ and $Cu^{1+}$ in the form of inorganic salts or organic salts.

**[0031]** Component (B2) is a molecule able to react with (B1) to form one or more free radicals. Hydrogen peroxide is preferably employed as component (B2) in the context of the present invention.

**[0032]** Hydrogen peroxide is a thermodynamically metastable compound in the form of the pure substance and in aqueous solution (e.g. 30% perhydrol). The rate of dissociation of hydrogen peroxide is greatly increased, even at room temperature, by catalysts, (e.g. finely divided metals, manganese dioxide, dust particles, non-metal ions, such as $I^-$, $IO_3^-$ and $OH^-$, or metal ions, such as $Fe^{2+}$, $Fe^{3+}$ and $Cu^{2+}$). Hydroxyl radicals can be generated in a controlled manner from hydrogen peroxide by thermal decomposition of the hydrogen peroxide or by one-electron redox reactions of the hydrogen peroxide with a suitable electron donor. Typical compounds are for example sodium hydrogen sulfite, carbonyl compounds which can be readily enolized, such as ascorbic acid and hydroxyacetone, and metal ions, such as $Fe_2+$, $Ti^{3+}$ and $Cu^{1+}$. The reaction of $Fe^{2+}$ with hydrogen peroxide to give hydroxyl radicals which can be used for oxidation of organic compounds has become known by the name of Fenton's reagent. The hydroxyl anion formed in the redox reaction can also initiate the peroxide dissociation.

**[0033]** In the process according to the invention for the preparation of an alkoxyamine initiator of the formula (I), an hydroxyl radical adds on to a C=C double bond of the monomer of the general formula (III) which can be polymerized by free radicals, and thus introduces a hydroxyl group into the alkoxyamine initiator.

**[0034]** In principle, other compounds of the type R'-O-O-R" which form free radicals can also be used as component (B2). The radicals R' and R" can contain a functional group Y which is capable of further reacting or of crosslinking with the functional groups known from the coatings field, for example OH, $NH_2$, NHR or epoxide.

**[0035]** One way of carrying out the invention is that in the first step the secondary amine of formula (II) is introduced into a reaction vessel containing water. The weight ratio of water to secondary amine is in the range of about 0,1 to 200, preferably about 1 to 50, and more preferably about 2 to 30. It is preferred that the water contains a basic inorganic or organic buffer or inorganic or organic bases. The molar ratio of secondary amine to buffer or base is in the range from about 20 to 0,05, preferably about 10 to 0,1, more preferably about 5 to 0,5.

**[0036]** Preferably the secondary amine of formula (II) is dissolved in a suitable solvent not miscible with water, in order to form a biphasic medium. Preferred solvents are toluene, xylene or dichloromethane. The solvent to secondary amine weight ratio is in the range from about 0,1 to 30, preferably about 0,5 to 10, and more preferably about 1 to 5.

**[0037]** While stirring vigorously, the oxidizing agent (A) is then slowly added in its pure form to the reaction vessel containing the secondary amine of formula (II). It is also possible to add a solution of the oxidizing agent (A) to the reaction vessel. Suitable solvents used for that purpose should be inert towards the various reagents and should not

react during the reaction: they are for example toluene, xylene, dichloromethane. When the oxidizing agent (A) is water-soluble, the preferred solvent is water. The solvent to oxidizing agent weight ratio is in the range from about 0,1 to 30, preferably about 0,5 to 10, and more preferably about 1 to 5.

**[0038]** The temperature of the reaction may range from about -10°C to about 100°C, preferably about 0°C to 80°C, and more preferably about 0°C to 40°C. The reaction time may range from about 10 minutes to about 72 h, preferably about 1h to 36h, and more preferably about 2h to 24 h. The first step of the process of the present invention can be carried out in air or in an inert gas atmosphere such as nitrogen or argon.

**[0039]** In the second step, after the partial or complete oxidation of the secondary amine to form a nitroxyl radical, stirring is terminated and the aqueous phase is removed.

**[0040]** In the third step, the vinyl monomer of formula (III), component (B1) and optionally some additional solvents are added to the organic phase of step two. Suitable solvents for the third step of the process are water, alcohols, preferably methanol, ethanol or isopropanol, ethers, preferably diethylether, oligoethylene glycols or THF, carbonyl compounds, preferably acetaldehyde, acetone or methyl ethyl ketone, or any desired mixtures of the solvents mentioned. While stirring component (B2) is slowly metered in. It is therefore possible to add component (B2) in the form of an aqueous solution.

**[0041]** Component (B2) is used a 0,1- to 20-fold molar excess based on the initial secondary amine. Component (B1) is used in an equimolar amount, but preferably in an up to 20% molar excess, based on the secondary amine initially introduced. The vinyl monomer of formula (III) is used in a 0,2- to 20-fold molar excess, based on the secondary amine initially introduced. The reaction temperature may range from about - 10°C to 150°C, preferably 0°C to 100°C, and more preferably 25°C to 60°C. The reaction can be carried out in air or in an inert gas atmosphere, preferably in an inert gas atmosphere such as in nitrogen or argon. The pH of the reaction solution can optionally be adjusted to a range from 5 to 7 with substances such as $NaHCO_3$.

**[0042]** After the reaction is complete, the solution can be optionally filtered in order to remove any solid residue such as iron(III) salts. The residual monomer of formula (III), solvents and oxidizing agent (A), if volatile, are removed in vacuo. An organic solvent not miscible with water is added and the organic phase is washed with acidic water (pH ≈ 5-2) in order to remove the residual secondary amine. Optionally, the organic phase can be washed with basic water (pH ≈ 7,5-9,5) in order to remove excess oxidizing agent. The organic phase is then dried under a drying agent such as $Na_2SO_4$ or $MgSO_4$. The elimination of the solvent under vacuum provides the crude alkoxyamines of the formula (I).

**[0043]** Another object of the present invention is to provide a new process for preparing oligomers, cooligomers, polymers or block or random copolymers, which comprises preparing the functional alkoxyamines of formula (I) according to the process of the present invention and adding at least one polymerizable monomer to the unpurified alkoxyamine of formula (I) followed by heating.

**[0044]** An important advantage of the process according to the present invention is that an additional purification step of the alkoxyamines can be dispensed with.

**[0045]** For the preparation of the (co)polymers according to the present invention, all the components such as monomer(s), crude alkoxyamine of the formula (I) are reacted at a temperature ranging from about 0°C to 260°C, preferably about 50°C to 200°C, and more preferably about 70°C to 150°C, for a period of time ranging from about 30 minutes to 72 hours, preferably about 1 hour to 48 hours, more preferably about 2 hours to 24 hours. The polymerization is carried out in an inert gas atmosphere, for example nitrogen or argon.

**[0046]** Optionally, some additives can be added to the polymerization medium before the polymerization or during the polymerization process in order to accelerate the polymerization. Such additives are well-known in the art and are for example camphorsulfonic acid, 2-fluoro-1-methylpyridinium p-toluenesulfonate, acylating compounds such as acetic anhydride (Tetrahedron 1997, 53(45), 15225), glucose, dextrose (Macromolecules 1998, 31, 7559), ascorbic acid (Macromolecules 2001, 34, 6531) or long-life radical initiators as reported in US-A 6,288,186 (column 4, lines 8-24).

**[0047]** Suitable monomers are the water-soluble and water-insoluble polymerizable monomers mentioned above.

**[0048]** The (co)polymers of the present invention may have a number average molecular weight of from 1000 to $2.10^6$, preferably from 2000 to $5\ 10^5$, more preferably from 2000 to $2{,}5 \cdot 10^5$.

**[0049]** The alkoxyamine compound of the formula (I) is introduced in a quantity ranging from about 20 wt% to 0,01 wt%, preferably 10 wt% to 0,05 wt% and more preferably 5 wt% to 0,1 wt%, based on the weight of the monomer(s).

**[0050]** Preferably for the preparation of the (co)polymers only small amounts of organic solvents are used. If organic solvents are required, suitable solvents or mixtures of solvents are typically pure alkanes such as hexane, heptane or cycloalkane, hydrocarbones such as benzene, toluene or xylene, halogenated hydrocarbons such as chlorobenzene, esters such as ethyl acetate, propyl, butyl or hexyl acetate, ethers such as diethyl ether, dibutyl ether or ethylene glycol dimethyl ether, alcohols such as methanol, ethanol, ethylene glycol or monomethyl ether or mixtures thereof of them. The solvent to monomer weight ratio is in the range from about 0 to 5, preferably from about 0 to 2.

**[0051]** The type of polymerization used can be bulk, solution, emulsion, dispersion or suspension polymerization and it can be carried out both batchwise and continuously.

**[0052]** The polymers prepared according to this invention show a low polydispersity ($M_w/M_n$) which is usually lower

than 2 and can be significantly lower.

**[0053]** The number average molecular weight of the polymer chains increases linearly with the monomer conversion, which allows a tailor-made polymer molecular weight to be obtained. Furthermore, the molecular weight of the polymers can be controlled by varying the amount of crude alkoxyamine compared to the amount of monomers. High molecular weight polymers can be formed.

**[0054]** A further advantage of the present invention is that after the removal of the non-polymerized monomers from the (co)polymers or after reaching a conversion rate of 100%, a second polymerization step can be initiated simply by adding to the polymer synthesized in the first step a portion of fresh vinyl monomer or monomer mixture that can be different from the vinyl monomer or monomer mixture used in the first polymerization step. The polymerization of the vinyl monomer or monomer mixture added in the second step is then initiated by the polymer chains synthesized in the first polymerization step and di-block copolymers can be for example produced if the polymer chains synthesized in the first polymerization step consists of linear chains with one single growing chain end. The molecular weight and polydispersity of each block can be controlled independently during the respective polymerization step. This process can be repeated several times and can then provide multiblock copolymers of controlled molecular weight and molecular weight distribution for each block.

**[0055]** The resulting polymers are usually colorless and they can be used in most cases without any further purification.

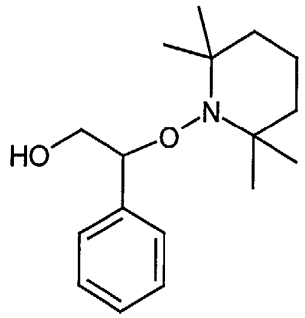
**[0056]** The following Examples illustrate the invention in more detail.

## Examples

**[0057]** The molecular weight was determined by gel permeation chromatography (GPC), equipped with a Shodex RI 74 differential refractometer. A flow rate of 1 ml/min was used and samples were prepared in THF. Polystyrene standards were used for calibration.

### Example 1

**[0058]** Synthesis of 1-phenyl-1-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)-2-hydroxyethane 1 using Oxone® (potassium monopersulfate, DuPont Specialty Chemicals, USA) as the oxidizing agent.




1

**[0059]** In a 500 ml four-necked round bottom flask equipped with a mechanical stirrer, a reflux, a thermometer, a funnel and a septum are added 40 g of water, 10 g $K_2CO_3$ (99 %; 7,24 $10^{-2}$ mol), 5 g 2,2,6,6-tetramethylpiperidine (99 %; 3,53· $10^{-2}$ mol) and 50g toluene. Then, a solution of 21,702 g of Oxone® (Monopersulfate, DuPont Specialty Chemicals, USA) (3,53· $10^{-2}$ mol) in 100 g water is slowly added to the 500 ml flask while stirring vigorously (with a slightly exothermic reaction) and the flask is placed in a water bath at room temperature. After the addition, the reaction medium is stirred at room temperature for 30 minutes, and the organic phase becomes progressively red due to the formation of 2,2,6,6-tetramethylpiperidine-1-oxide (TEMPO). Then, the reaction medium is heated at 40°C for further 30 minutes.

**[0060]** The reaction medium is then cooled at room temperature, the stirring is terminated and the water phase is removed from the reaction flask. The red organic phase is then degassed by bubbling argon for 10 minutes. 11,124 g $FeSO_4 \cdot 7H_2O$ (4 $10^{-2}$ mol) are then slowly added under an argon atmosphere and while stirring vigorously. Then, a degassed mixture of 100 ml methanol and 36,7 g of styrene (3,53 ·$10^{-1}$ mol) are added rapidly to the reaction flask and the temperature is increased to 40°C. Finally, a solution of 13,71 g hydrogen peroxide (35%; 0.1412 mol) in 15 g methanol is added slowly (dropwise) for 28 minutes while keeping the temperature between 30 and 40°C (with an exothermic reaction). When the addition is complete, the reaction mixture is allowed to react while stirring vigorously

by room temperature for 2 h 30 mins.

**[0061]** The brown solution is then filtered and the residual styrene, hydrogen peroxide and methanol are then removed in vacuo at 50°C. To the viscous brown residue obtained is added 100 g of $CH_2Cl_2$ and 30 g of water, and then HCl is added until the pH is 3. The organic phase is then washed 2 times with an acidic solution (pH is 3) in order to remove the excess 2,2,6,6-tetramethylpiperidine. The organic phase is finally dried under $MgSO_4$, filtered and dried in vacuo at 50°C. 2,79 g of a viscous light yellow oil is obtained.

## Example 2

**[0062]** Polymerization of styrene initiated by non-purified 1-phenyl-1-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)-2-hydroxyethane **1** synthesized in example 1 using Oxone® (potassium monopersulfate, DuPont Specialty Chemicals, USA) as the oxidizing agent.

**[0063]** To a three-necked round bottom flask equipped with a mechanical stirrer, a reflux condenser, a thermometer and a septum are added 0,3 g of non-purified **1** and 50 g of styrene (0,48 mol). The slightly yellow solution is then degassed by bubbling argon for 10 minutes, and is then heated at 125°C. Very rapidly, the solution becomes colorless.

**[0064]** After 7.5 h at 125°C, the polymerization medium is highly viscous and the polymerization is complete. After cooling, the polymer is dissolved with chloroform, transferred to an aluminum bag, dried overnight in air and then for 24 h at 70°C in vacuo. The yield is calculated by gravimetric analysis.

Yield = 80,6 %;

$M_n$ = 23250; $M_w$ = 33110; $M_w/M_n$ = 1,42

## Example 3

**[0065]** Random copolymerization of styrene and acrylonitrile initiated by non-purified 1-phenyl-1-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)-2-hydroxyethane **1** synthesized in example 1 using Oxone® (potassium monopersulfate, DuPont Specialty Chemicals, USA) as the oxidizing agent, and subsequent block copolymerization with a mixture of methylmethacrylate, styrene and acrylonitrile

Synthesis of poly(styrene-co-acrylonitrile)(PSAN)

**[0066]** To a 250 ml three-necked round bottom flask equipped with a mechanical stirrer, a reflux condenser, a thermometer and a septum are added 0,3 g of non-purified **1** (synthesized in example 1), 75 g of styrene (0,72 mol) and 25 g of acrylonitrile (0,471 mol). The slightly yellow solution is then degassed by bubbling argon for 10 minutes, and is then heated at reflux for 9h.

**[0067]** After 9 h under reflux, the polymerization medium is viscous. After cooling, the polymer is dissolved in chloroform, transferred to an aluminum bag, dried overnight in air and then heated for 24 h at 70°C in vacuo. The yield is calculated by gravimetric analysis.

Yield = 45,3 %;

$M_n$ = 53100; $M_w$ = 102960; $M_w/M_n$ = 1,93

Synthesis of poly(styrene-*co*-acrylonitrile)-*b*-poly(methylmethacrylate-co-styrene-*co*-acrylonitrile) block copolymer

**[0068]** To a 500 ml four-necked round bottom flask equipped with a mechanical stirrer, a reflux condenser, a thermometer and a septum are added 20 g of PSAN synthesized in the first step, 75 g of styrene (0,72 mol), 25 g of acrylonitrile (0,471 mol) and 100 g of methylmethacrylate (1 mol). The colorless solution is then degassed by bubbling argon for 10 minutes, and is then heated under reflux for 10h.

**[0069]** After 10 h under reflux, the polymerization medium is highly viscous and the polymerization is stopped. After cooling, the polymer is dissolved in chloroform, transferred to an aluminum bag, dried overnight in air and then heated for 24 h at 70°C in vacuo. The yield is calculated by gravimetric analysis.

Yield = 30%;

$M_n$ = 86570; $M_w$ = 190430; $M_w/M_n$ = 2,19

**[0070]** Chain extension of the starting PSAN is observed which confirms the controlled nature of the SAN (styrene and acrylonitrile) polymerization initiated by the non-purified alkoxyamine **1.**

## Example 4

Synthesis of 1-phenyl-1-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)-2-hydroxyethane **1** using Oxone® (potassium monopersulfate, DuPont Specialty Chemicals, USA) as the oxidizing agent: scale-up

**[0071]** To a 6 l four-necked round bottom flask equipped with a mechanical stirrer, a reflux condenser a thermometer, a funnel and a septum are added 634 g of water, 158,42 g $K_2CO_3$ (99 %; 1,146 mol), 79,21 g 2,2,6,6-tetramethylpiperidine (99%; $5{,}607 \cdot 10^{-1}$ mol) and 792,1 g toluene. Then, a solution of 343,8 g of Oxone® (Monopersulfate, DuPont Specialty Chemicals, USA) ($5{,}59 \cdot 10^{-1}$ mol) in 1584 g water is slowly added (over a period of 1 h 40 mins.) to the 6 l flask while stirring vigorously (slightly exothermic reaction) and the flask is placed in a water bath at room temperature. After the addition is complete, the reaction medium is stirred at room temperature for 30 minutes, and the organic phase becomes progressively red due to the formation of 2,2,6,6-tetramethylpiperidine-1-oxide (TEMPO). Then, the reaction medium is heated at 40°C for a further 30 minutes.

**[0072]** The reaction medium is then cooled at room temperature, the stirring is terminated and the water phase is removed from the reaction flask. The red organic phase is then degassed by bubbling argon for 10 minutes. 176,23 g $FeSO_4 \cdot 7H_2O$ ($6{,}34 \cdot 10^{-1}$ mol) are then slowly added in an argon atmosphere, while stirring vigorously. Then, a degassed mixture of 1584,2 g of methanol and 581,4 g of styrene (5,582 mol) is added rapidly to the reaction flask and the temperature is increased to 30°C. Finally, a solution of 217,19 g hydrogen peroxide (Merck, 35%; 2,235 mol) in 237,63 g methanol is slowly added (dropwise) for 5 h 40 minutes while keeping the temperature at between 30 and 40°C. When the addition is complete, the reaction mixture is allowed to react while stirring vigorously at room temperature for 15 h.

**[0073]** The brown solution is then filtered and the residual styrene, hydrogen peroxide and methanol are then removed in vacuo at 50°C. To the viscous brown residue obtained is added 1500 g of $CH_2Cl_2$ and 475 g of water, and then HCl is added until the pH is 3. The organic phase is then washed twice with an acidic solution (pH = 3) in order to remove the excess 2,2,6,6-tetramethylpiperidine. The organic phase is finally dried under $MgSO_4$, filtered and dried in vacuo at 50°C. 121 g of a viscous light yellow oil is obtained.

**[0074]** In order to remove polystyrene formed during the reaction (optional step), the product is dissolved in chloroform and then precipitated in methanol. After filtration, the methanol phase is dried in vacuo and this operation is repeated once to obtain 71,35 g of a slightly yellow oil. This oil contains **1** and very low molecular weight polystyrene. The alkoxyamine **1** can be purified by flash chromatography or by high vacuum distillation, if necessary. For the controlled radical polymerization of vinyl monomers using alkoxyamine **1**, it is not necessary to purify this alkoxyamine further. The slightly yellow oil can be directly used for polymerization.

## Example 5

**[0075]** Random copolymerization of styrene and acrylonitrile initiated by the non-purified 1-phenyl-1-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)-2-hydroxyethane **1** synthesized in Example 4 using Oxone® (potassium monopersulfate, DuPont Specialty Chemicals, USA) as the oxidizing agent To a 250 ml three-necked round bottom flask equipped with a mechanical stirrer, a reflux condenser, a thermometer and a septum are added 0,3 g of non-purified 1 (obtained in Example 4), 75 g of styrene (0,72 mol) and 25 g of acrylonitrile (0,471 mol). The slightly yellow solution is then degassed by bubbling through argon for 10 minutes and is then heated under reflux for 12h. Samples are taken after 4,5 h, 8,25 h and 12 h and dried in vacuo at 70°C and the conversion is finally calculated gravimetrically.

**[0076]** After 12 h under reflux, the polymerization medium is highly viscous and the polymerization is complete. After cooling, the polymer is dissolved in chloroform, transferred to an aluminum bag, dried overnight in air and heated for 24 h at 70°C in vacuo.

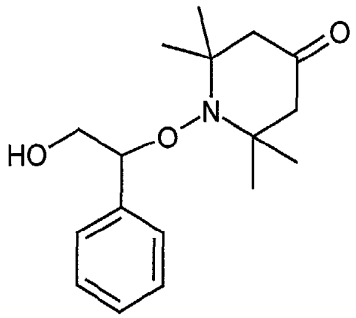
| Sample | Time (h) | Conversion (%) | $M_n$ | $M_w$ | $M_w/M_n$ |
|---|---|---|---|---|---|
| 1 | 4,5 | 26,1 | 59200 | 105800 | 1,78 |
| 2 | 8,25 | 45,7 | 72350 | 122800 | 1,69 |
| 3 | 12 | 57,4 | 91950 | 144700 | 1,57 |

**[0077]** The molecular weight increases with the monomer conversion, as required in a controlled process. The polydispersity is high in the early stages of the polymerization but decreases as the monomer conversion increases. This observation is consistent with a controlled process.

## Example 6

Synthesis of 1-phenyl-1-(4'-Oxo-2',2',6',6'-tetramethyl- 1'-piperidinyloxy)-2-hydroxyethane **2** using Oxone® (potassium monopersulfate, DuPont Specialty Chemicals, USA) as the oxidizing agent.

**[0078]**



**(2)**

**[0079]** To a 2 1 four-necked round bottom flask equipped with a mechanical stirrer, a reflux, a thermometer, a funnel and a septum are added 160 g of water, 35,40 g $K_2CO_3$ (99 %; 2,56 · $10^{-1}$ mol), 20 g 2,2,6,6-tetramethyl-4-piperidone (95 %; 1,28 · $10^{-1}$mol) and 200 g toluene. Then, a solution of 173,62 g of Oxone (2,82 · $10^{-1}$ mol) in 700 g water is added slowly to the 21 flask while stirring vigorously (with a slightly exothermic reaction) and the flask is placed in a water bath at room temperature. The starting brown-red solution becomes rapidly green when the Oxone® (potassium monopersulfate, DuPont Specialty Chemicals, USA) solution is added. After the addition is complete, the reaction medium is stirred at room temperature for 30 minutes and then at 40°C for 1h.

**[0080]** The reaction medium is then cooled at room temperature, the stirring is terminated and the water phase is removed from the reaction flask. The red organic phase is then degassed by bubbling argon for 10 minutes. 44,5 g $FeSO_4 \cdot 7H_2O$ (1,6 · $10^{-1}$ mol) are then slowly added under an argon atmosphere, while stirring vigorously. Then, a degassed mixture of 400 ml of methanol and 133,3 g of styrene (1,28 mol) are rapidly added to the reaction flask and the temperature is increased to 40°C. Finally, a solution of 49,78 g hydrogen peroxide (Merck, 35%; 5,12 $10^{-1}$ mol) in 60 g methanol is slowly added (dropwise) for 1 h while keeping the temperature between 30 and 40°C. When the addition is complete, the reaction is allowed to react while stirring vigorously at room temperature for 15 h.

**[0081]** The brown solution is then filtered and the residual styrene, hydrogen peroxide and methanol are then removed in vacuo at 50°C. To the viscous brown residue obtained is added 400 g of $CH_2Cl_2$ and 120 g of water, and then HCl is added until the pH is 3. The organic phase is then washed twice with an acidic solution (pH = 3) in order to remove the excess 2,2,6,6-tetramethyl-4-piperidone. The organic phase is finally dried under $MgSO_4$, filtered and dried in vacuo at 50°C. 23,2 g of a viscous brown oil is obtained. This oil contains mainly the alkoxyamine 2, some residual 2,2,6,6-tetramethyl-4-piperidone and other unidentified molecules.

**[0082]** This brown oil can be used directly for polymerization without any intermediate purification.

## Example 7

**[0083]** Random copolymerization of styrene and acrylonitrile initiated by the non-purified 1-phenyl- 1 -(4'-Oxo-2 ' , 2' ,6' ,6' -tetramethyl- 1 '-piperidinyloxy)-2-hydroxyethane **2** synthesized in Example 6 .

**[0084]** To a 250 ml three-necked round bottom flask equipped with a mechanical stirrer, a reflux condenser, a thermometer and a septum are added 0,629 g of non-purified **2**, 75 g of styrene (0,72 mol) and 25 g of acrylonitrile (0,471 mol). The slightly brown solution is then degassed by bubbling argon for 10 minutes and is then heated under reflux for 24h.

**[0085]** After 24 h under reflux, the polymerization medium is solid and the polymerization is complete. After cooling, the polymer is dissolved in chloroform, transferred to an aluminum bag, dried overnight in air and then heated for 24 h at 70°C in vacuo.

Yield = 95,2 %;

$M_n$ = 55760; $M_w$ = 88650; $M_w/M_n$ = 1,59

## Example 8

**[0086]** Polymerization of styrene initiated by the non-purified 1-phenyl-1-(4'-Oxo-2',2',6',6'-tetramethyl-1'-piperidinyloxy)-2-hydroxyethane **2** synthesized in Example 6.

**[0087]** To a 250 ml three-necked round bottom flask equipped with a mechanical stirrer, a reflux condenser, a thermometer and a septum are added 0,629 g of non-purified **2**, and 100 g of styrene (0,96 mol). The slightly brown solution is then degassed by bubbling argon for 10 minutes and is then heated at 125°C for 12h. Samples are taken from the reaction flask after 6 and 12h. The polymer is dried in vacuo at 70°C for 24h and the conversion is calculated by gravimetric analysis.

**[0088]** After 12h at 125°C, the polymerization medium is solid and the polymerization is stopped. After cooling, the polymer is dissolved in chloroform, transferred to an aluminum bag, dried overnight in air and then heated for 24 h at 70°C in vacuo.

| Sample | Time (h) | Conversion (%) | $M_n$ | $M_w$ | $M_w/M_n$ |
|---|---|---|---|---|---|
| 1 | 6 | 59,2 | 24830 | 41450 | 1,66 |
| 2 | 12 | 87,6 | 33620 | 54290 | 1,61 |

**[0089]** The molecular weight increases with the monomer conversion and the polydispersity remains low throughout the polymerization process as required in a controlled process.

## Example 9

Synthesis of 1-phenyl-1-(2',2',6',6 '-tetramethyl-1'-piperidinyloxy)-2-hydroxyethane **1** using peracetic acid as the oxidizing agent.

**[0090]** To a 1 liter four-necked round bottom flask equipped with a mechanical stirrer, a reflux condenser, a thermometer, a funnel and a septum are added 80 g of water, 20 g $K_2CO_3$ (99 %; 0,1448 mol), 10 g 2,2,6,6-tetramethylpiperidine (99 %; 7,079 $10^{-2}$ mol) and 100 g toluene. Then, a solution of 15,34 g of peracetic acid (7,06 · $10^{-2}$ mol) in 80 g water is added slowly to the 1 liter flask while stirring vigorously (with a slightly exothermic reaction) and the flask is placed in a water bath at room temperature. After the addition is complete, the reaction medium is stirred at room temperature overnight and the organic phase becomes red due to the formation of 2,2,6,6-tetramethylpiperidine-1-oxide (TEMPO).

**[0091]** The stirring is terminated and the water phase is removed from the reaction flask. The red organic phase is then degassed by bubbling argon for 10 minutes. 22,25 g $FeSO_4$ · 7H20 (8 · $10^{-2}$ mol) are then slowly added under an argon atmosphere, while stirring vigorously. Then, a degassed mixture of 200 ml methanol and 73,4 g of styrene (7,05 · $10^{-1}$ mol) are added rapidly to the reaction flask and the temperature is increased to 40°C. Finally, a solution of 23,42 g hydrogen peroxide (Merck, 35 %; 0,282 mol) in 30 g methanol is added slowly (dropwise) for 28 minutes while keeping the temperature at between 30 and 40°C (with an exothermic reaction).

**[0092]** When the addition is complete, the reaction mixture is allowed to react while stirring vigorously at 40°C for 3h.

**[0093]** The brown solution is then filtered and the residual styrene, hydrogen peroxide and methanol are then removed in vacuo at 50°C. To the viscous brown residue obtained are added 100 g of $CH_2Cl_2$ and 30 g of water and then HCl is added until the pH is 3. The organic phase is then washed 2 times with an acidic solution (pH = 3) in order to remove the excess 2,2,6,6-tetramethylpiperidine. The organic phase is finally dried under $MgSO_4$, filtered and dried in vacuo at 50°C. 8,57 g of a viscous red oil is obtained. The red coloration is due to some unreacted 2,2,6,6-tetramethylpiperidine-1-oxide (TEMPO) formed by the oxidation of 2,2,6,6-tetramethylpiperidine by peracetic acid.

## Example 10

Polymerization of styrene initiated by the non-purified 1-phenyl-1-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)-2-hydroxyethane **1** synthesized in Example 9 using the peracetic acid as the oxidizing agent.

**[0094]** To a three-necked round bottom flask equipped with a mechanical stirrer, a reflux condenser, a thermometer and a septum are added 0,6935 g of non-purified **1** (obtained in Example 9) and 100 g of styrene (0,96 mol). The slightly pink solution is then degassed by bubbling argon for 10 minutes and is then heated at 125°C.

**[0095]** Samples are taken from the reaction flask after 8 and 24h, dried in vacuo at 70°C and analysed by GPC. The conversion is calculated gravimetrically.

| Sample | Time (h) | Conversion (%) | $M_n$ | $M_w$ | $M_w/M_n$ |
|---|---|---|---|---|---|
| 1 | 8 | 25,1 | 9100 | 11570 | 1,27 |
| 2 | 24 | 79,7 | 23090 | 31610 | 1,36 |

**[0096]** The molecular weight increases linearly with the monomer conversion and the polydispersity is narrow as required in a controlled process. Compared to Example 2, the same molecular weights are obtained after about 80 % monomer conversion, but the polymerization of styrene in Example 10 is slower.

**Example 11**

**[0097]** Random copolymerization of styrene and acrylonitrile initiated by the non-purified 1-phenyl-1-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)-2-hydroxyethane **1** synthesized in Example 9 using peracetic acid as the oxidizing agent.

**[0098]** To a 250 ml three-necked round bottom flask equipped with a mechanical stirrer, a reflux condenser, a thermometer and a septum are added 0,3 g of non-purified **1** (obtained in Example 9), 75 g of styrene (0,72 mol) and 25 g of acrylonitrile (0,471 mol). The solution is then degassed by bubbling argon for 10 minutes and is then heated at reflux for 12h. Samples are taken out after 8h and 24h, dried under vacuum at 70°C and the conversion is finally calculated gravimetrically.

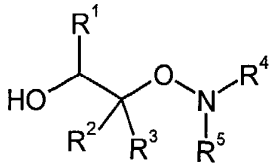
**[0099]** After 24 h under reflux, the polymerization medium is highly viscous and the polymerization is stopped. After cooling, the polymer is dissolved with chloroform, transferred to an aluminum bag, dried overnight in air and then for 24 h by 70°C in vacuo.

| Sample | Time (h) | Conversion (%) | $M_n$ | $M_w$ | $M_w/M_n$ |
|---|---|---|---|---|---|
| 1 | 8 | 18,1 | 24470 | 37530 | 1,53 |
| 2 | 24 | 60,1 | 46290 | 63740 | 1,37 |

**[0100]** The molecular weight increases with the monomer conversion and the polydispersity is narrow as required in a controlled process.

## Claims

**1.** A one-pot process for the preparation of functional alkoxyamines of the general formula (I),



(I)

wherein

$R^1$, $R^2$, $R^3$ are independently selected from the group consisting of: hydrogen, $C_1$-$C_{20}$alkyl, $C_1$-$C_{20}$cycloalkyl, $C_6$-$C_{24}$aryl, halogen, cyano, $C_1$-$C_{20}$alkylester $C_1$-$C_{20}$cycloalkylester, $C_1$-$C_{20}$alkylamide, $C_1$-$C_{20}$cycloalkylamide $C_6$-$C_{24}$-arylester or $C_6$-$C_{24}$-arylamide;

$R^4$ and $R^5$ are independently selected from the group consisting of: $C_1$-$C_{18}$alkyl, $C_2$-$C_{18}$-alkenyl, $C_2$-$C_{18}$alkynyl, $C_3$-$C_{12}$cycloalkyl or $C_3$-$C_{12}$heterocycloalkyl, $C_6$-$C_{24}$aryl, which are unsubstituted or substituted by $NO_2$, halogen, amino, hydroxy, cyano, carboxy, ketone, $C_1$-$C_4$alkoxy, $C_1$-$C_4$alkylthio or $C_1$-$C_4$alkylamino;

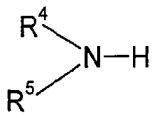
$R^4$ and $R^5$ optionally form together with the intermediate nitrogen atom a $C_3$-$C_{12}$cycloalkyl radical, a ($C_4$-$C_{12}$alkanol)yl radical or a $C_2$-$C_{13}$-heterocycloalkyl radical containing oxygen, sulfur or nitrogen

atoms;

$R^4$ and $R^5$ together form a residue of a polycyclic ring system or a polycyclic heterocycloaliphatic ring system containing oxygen, sulfur or nitrogen atoms;
wherein the carbon atom of the $R^4$ and $R^5$ radicals directly adjacent to the alkoxyamine nitrogen atom is in each case substituted by 3 further organic substituents and
wherein optionally at least one of the radicals $R^4$ and $R^5$ contains a functional group Y which is capable of further reacting or crosslinking with the functional groups known from the coatings field,

comprising the reaction steps of

(1) reacting an oxidizing agent (A) with a sterically hindered secondary amine of the general formula (II),



(II)

wherein

$R^4$ and $R^5$ are independently selected from the group consisting of: $C_1$-$C_{18}$alkyl, $C_2$-$C_{18}$alkenyl, $C_2$-$C_{18}$alkynyl, $C_3$-$C_{12}$cycloalkyl or $C_3$-$C_{12}$-heterocycloalkyl, $C_6$-$C_{24}$aryl, which are unsubstituted or substituted by $NO_2$, halogen, amino, hydroxy, cyano, carboxy, ketone, $C_1$-$C_4$alkoxy, $C_1$-$C_4$alkylthio, $C_1$-$C_4$alkylamino;

$R^4$ and $R^5$ optionally form, together with the intermediate nitrogen atom, a $C_3$-$C_{12}$cycloalkyl radical, a ($C_4$-$C_{12}$alkanol)yl radical or a $C_2$-$C_{13}$heterocycloalkyl radical containing oxygen, sulfur or nitrogen atoms;

$R^4$ and $R^5$ together form a residue of a polycyclic ring system or a polycyclic heterocycloaliphatic ring system containing oxygen, sulfur or nitrogen atoms;
wherein the carbon atom of the $R^4$ and $R^5$ radicals directly adjacent to the alkoxyamine nitrogen atom is in each case substituted by 3 further organic substituents and
wherein optionally at least one of the radicals $R^4$ and $R^5$ contains a functional group Y which is capable of further reacting or crosslinking with functional groups known from the coatings field,

in a water-containing medium,

(2) removing of the aqueous phase and

(3) adding
one or more vinyl monomer(s) of the general formula (III),

$$HR^1C = CR^2R^3 \qquad \text{(III)}$$

wherein

$R^1$, $R^2$, $R^3$ are independently selected from the group consisting of: hydrogen, $C_1$-$C_{20}$alkyl, $C_1$-$C_{20}$cycloalkyl $C_6$-$C_{24}$aryl, halogen, cyano, $C_1$-$C_{20}$alkylester $C_1$-$C_{20}$cycloalkylester, $C_1$-$C_{20}$alkylamide, $C_1$-$C_{20}$cycloalkylamide $C_6$-$C_{24}$-arylester or $C_6$-$C_{24}$-arylamide,

as well as

(B) a system which produces free radicals consisting of

(B1) a reducing agent and
(B2) a molecule able to react with (B1) to form radicals.

**2.** A process for preparing block or random oligomers, cooligomers, polymers or block or random copolymers, which comprises preparing the functional alkoxyamines of formula (I) according to claim 1 and adding at least one polymerizable monomer to the unpurified alkoxyamine of formula (I) followed by heating.

European Patent Office

# EUROPEAN SEARCH REPORT

Application Number
EP 02 01 3949

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C08F

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| MUNICH | 27 November 2002 | Janus, S |

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X : particularly relevant if taken alone
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EPO FORM 1503 03.82 (P04C01)

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