

A PROCESS FOR THE PREPARATION OF COPOLYMERS

The invention relates to a process for the preparation of copolymers of carbon monoxide with an olefinically unsaturated compound, and to a catalyst composition.

5 Processes for the polymerization of carbon monoxide with an olefinically unsaturated compound catalysed with a Group VIII metal containing catalyst composition are well known in the art, for example from EP-A-121965, EP-A-248483 and EP-A-254343. The copolymers so prepared are
10 linear copolymers wherein the monomer units originating from carbon monoxide and the monomer units originating from the olefinically unsaturated compounds occur in alternating or substantially alternating order.

 EP-A-254343 discloses in particular processes which
15 make use of catalyst compositions which are based upon (a) a salt of a Group VIII metal, and (b) a tetrahydrocarbylammonium or a tetrahydrocarbyl-phosphonium cation. It appears, however, that in these processes the yield of polymer was sometimes very low.

20 It has now unexpectedly been found that a substantial improvement of the performance of the catalyst compositions of EP-A-254343 can be achieved by replacing in the catalyst composition the tetrahydrocarbylammonium or -phosphonium cation by another cation, as specified
25 hereinafter.

 The invention therefore relates to a process for the preparation of copolymers of carbon monoxide with an olefinically unsaturated compound comprising
30 copolymerizing the monomers in the presence of a catalyst composition based upon (a) a salt of a Group VIII metal, and



(b) a cation which is selected from cationic oxidants and cations of the general formulae $R_nH_{4-n}N^+$, $R_mH_{3-m}C^+$ and $R_mH_{3-m}O^+$, wherein n is 0, 1, 2, 3 or 4, m is 2 or 3, and R represents a hydrocarbyl group and/or two or three of R together with the atom carrying a positive charge represent a ring structure comprising carbon atoms in the ring, on the understanding that when n is 3, at most two of R together with nitrogen represent a heterocyclic ring structure, and when n is 4, three of R together with nitrogen represent an aromatic heterocyclic ring structure.

The invention also relates to catalyst compositions based upon

(a) a salt of a Group VIII metal, and
(b) a cation which is selected from cations of the general formulae $R_nH_{4-n}N^+$, $R_mH_{3-m}C^+$ and $R_mH_{3-m}O^+$, wherein n is 1, 2, 3 or 4, m is 2 or 3, and R represents a hydrocarbyl group and/or two or three of R together with the atom carrying a positive charge represent a ring structure comprising carbon atoms in the ring, on the understanding that when n is 3, at most two of R together with nitrogen represent a heterocyclic ring structure, and when n is 4, three of R together with nitrogen represent an aromatic heterocyclic ring structure.

In addition, the invention relates to catalyst compositions based upon

(a) a salt of a Group VIII metal,
(b) a cation which is selected from cationic oxidants and cations of the general formulae $R_nH_{4-n}N^+$, $R_mH_{3-m}C^+$ and $R_mH_{3-m}O^+$, wherein n is 0, 1, 2, 3 or 4, m is 2 or 3, and R represents a hydrocarbyl group and/or two or three of R together with the atom carrying a positive charge represent a ring structure comprising carbon atoms in the ring, on the understanding that when n is 3, at most two of R together with nitrogen represent a heterocyclic ring



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structure, and when n is 4, three of R together with nitrogen represent an aromatic heterocyclic ring structure, and

5 (c) a ligand which contains at least two dentate groups which can form a complex with the Group VIII metal.

Brookhart et al., J. Am. Chem. Soc., 114 (1992) 5894/5 disclosed the conversion of a zerovalent dimethylpalladium complex into a cationic monomethylpalladium complex by reaction with an equimolar
10 quantity of dimethyloxonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. The dimethyloxonium cations were thereby converted to dimethylether, so that no oxonium cations were present in the composition thus obtained and in the subsequent copolymerization of carbon monoxide
15 with tert.-butylstyrene which was catalyzed with the composition. This renders the present invention novel and inventive over the disclosure.

Similar chemistry is taught in the non-prepublished patent application EP-95202473.5, in this case
20 diphenylmethyllumonium cations being converted to diphenylmethylaniline. EP-95202473.5 further teaches a copolymerization process in which the catalyst composition is based upon a cation of a Group VIII metal and a boron containing anion. It teaches in particular
25 that trihydrocarbylboranes can function as a source of boron containing anions when the catalyst composition further includes a tertiary amine or a tertiary phosphine, and water, an alcohol, an oxime or a mercaptan. The neutral amine or phosphine is thought to
30 be converted thereby into a tertiary ammonium or phosphonium cation.

GB-A-2247890 discloses that oxidizing compounds, in particular nitrosyl tetrafluoroborate, can assist in the extraction of palladium residues from copolymers of
35 carbon monoxide with an alkene. This document, however,

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does not teach the copolymerization of carbon monoxide and an alkene in the presence of palladium and a cationic oxidizing species. Thus, the present invention as defined above is novel and inventive over the disclosure.

5 Examples of suitable Group VIII metals for use in the process according to this invention are nickel and cobalt. The Group VIII metal is preferably a noble Group VIII metal, of which palladium is most preferred.

10 Suitable salts of a Group VIII metal include salts of mineral acids such as sulphuric acid, nitric acid, phosphoric acid and perchloric acid, and organic salts, such as acetylacetonates and salts of sulphonic acids. Preferably, a salt of a carboxylic acid is used, for example a carboxylic acid with up to 8 carbon atoms, such as acetic acid, trifluoroacetic acid, trichloroacetic acid, propionic acid, benzoic acid and citric acid. The Group VIII metal salt may be a complex salt. Palladium (II) acetate is a particularly preferred palladium salt.

15 As indicated hereinbefore, the catalyst compositions according to this invention further comprises a cationic oxidant or a cation according to one or more of the general formulae given. In general, in the formulae given, hydrocarbyl groups R comprise typically up to 20 carbon atoms, more typically 1 to 15 carbon atoms. The hydrocarbyl groups R may represent alkyl, aryl, alkaryl, 20 aralkyl or cycloalkyl groups. The hydrocarbyl groups R may or may not be branched. They may carry substituents, such as hydrocarbyloxy groups or halogen atoms, but they are typically unsubstituted. When there are two or more hydrocarbyl groups R they may be the same or different. 30 When two or three of R together with the atom carrying the positive charge represent a ring structure this ring structure may comprise a 5-, 6- or 7-membered ring, and the ring may or may not be a heterocyclic ring and it may be an aromatic or a non-aromatic ring. Such rings may or 35

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may not carry further substituents, such as hydrocarbyl groups, hydrocarbyloxy groups and halogen atoms and they may or may not be fused with other ring systems, for example aromatic rings. If desired, a heterocyclic ring may comprise more than one heteroatom. The ring structures comprise typically up to 30 carbon atoms, in particular 4 to 25 carbon atoms. Further preferences may depend to some extent on the type of cation involved, as it appears below. The skilled person will appreciate that some of the cations according to this invention may be rather unstable and that in such cases the further preferences relate to the desirability of having cations of sufficient stability. In general, the stability will be determined by electronic and steric factors. A satisfactory level of stability may be accomplished, for example, by the presence of unsaturation, in particular to the extent that there is stabilization by resonance. The stability of cations which do not carry a hydrogen atom at the charged atom may be satisfactory when there are no hydrogen atoms attached to the atoms which are immediately neighbouring the charged atom.

One type of cations is of the general formula $R_nH_{4-n}N^+$, wherein n is 0, 1, 2 or 3 and R represents a hydrocarbyl group and/or two or three of R together with the nitrogen atom represent a heterocyclic ring structure, on the understanding that when n is 3, at most two of R together with nitrogen represent a heterocyclic ring structure. Preferred hydrocarbyl groups R are aryl or alkaryl groups, such as phenyl, 2-tolyl, 2,4-xylyl and 1-naphthyl groups, or alkyl groups, in particular n-alkyl groups, such as methyl, ethyl, 1-propyl or 1-butyl groups. They are most preferably phenyl groups or methyl groups. The ring structures comprise typically a pyrrole, pyrrolidine or piperidine ring. Typical examples of the cations of this type are ammonium

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(i.e. n is 0), diphenylammonium (i.e. n is 2) and trimethylammonium and triethylammonium (i.e. n is 3). It is preferred that at least one, in particular at least two, of the hydrocarbyl groups R is an aryl group.

5 Examples of such preferred cations in which n is 3 are 1-phenylpiperidinium, triphenylammonium and dimethylphenylammonium (i.e. N,N-dimethylanilinium).

Another type of cations is of the general formula $R_nH_{4-n}N^+$, wherein n is 4, three of R together with the
10 nitrogen atom represent an heterocyclic aromatic ring structure and the fourth R represents a hydrocarbyl group. In this type of cation the hydrocarbyl group R is preferably a branched alkyl or aralkyl group, for example a tertiary butyl group or a 2-phenylprop-2-yl group, in
15 particular a triphenylmethyl group. The heterocyclic aromatic ring structure may be that of a pyridine, e.g. pyridine, a substituted pyridine or a fused pyridine. Examples are the ring structures of 2-, 3- or 4-picoline, quinoline, isoquinoline and dibenzopyridine, in
20 particular pyridine. A preferred cation is 1-(triphenylmethyl)pyridinium.

Another type of cations is of the general formula $R_mH_{3-m}C^+$ wherein m is 2 or 3 and R represents a
hydrocarbyl group and/or two or three of R together with
25 the charged carbon atom represent a ring structure comprising carbon atoms in the ring. When m is 3 the hydrocarbyl groups R are preferably aryl groups, such as 2-tolyl, 2,4-xylyl and 1-naphthyl groups, in particular phenyl groups. Thus, an example of a preferred carbonium
30 ion of this type is triphenylcarbonium. When m is 2 it is preferred that the two R together with the charged carbon atom represent a ring structure, for example a 7-membered ring, preferably containing unsaturation. An example of a preferred cation of this type is a tropylium
35 cation, in particular the tropylium cation ($C_7H_7^+$).

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Another type of cations is of the general formula $R_mH_{3-m}O^+$, wherein m is 2 or 3 and R represents a hydrocarbyl group and/or two or three of R together with the oxygen atom represent a heterocyclic ring structure. When all R represent hydrocarbyl groups they are in particular n-alkyl groups, such as methyl, ethyl, 1-propyl and 1-butyl groups. Examples of cations of this type are dimethyloxonium (m is 2) and, in particular, trimethyloxonium (m is 3). In an attractive alternative all three R (m is 3) together with the oxygen atom represent a ring structure, such as an aromatic 6-membered ring which is preferably substituted, for example with one or more (alk)aryl groups, or fused with another aromatic ring. Examples of cations of this type are 2,4,6-triphenylpyrylium, xanthylum and flavylum.

Yet another type of cations which may suitably be used in this invention are cationic oxidants, in particular cations comprising nitrogen and oxygen, more in particular consisting of nitrogen and oxygen. Examples of such cations are nitryl (NO_2^+) and, in particular, nitrosyl (NO^+).

Without wishing to be bound by a theory, it is believed that, in the cases of cations of which the charged atom carries a hydrogen atom, the pKb value of the conjugated base plays a role in determining the rate of polymerization which can be achieved. This applies in particular to cations of the general formula $R_nH_{4-n}N^+$, wherein n is 0, 1, 2 or 3 and R is as defined hereinbefore. It would appear that the pKb of the conjugated base is preferably at least 2, more preferably at least 4, most preferably at least 6 and in particular at least 8, when determined in aqueous solution at 25 °C. In general the pKb value is below 20, more frequently below 15.

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The quantity of the cation which may be used in the catalyst composition may vary within a wide range. There is a preference for using 0.1 - 50 equivalents of cation per gram atom of Group VIII metal, in particular 0.5 - 25 equivalents in the same basis.

The cations according to this invention may be introduced in the catalyst composition in the form of a salt as the cation source. Very suitable are salts in which they have as a counterion an anion which may function in the catalyst component as a further component, as described hereinafter. Alternatively, the cation may be formed in situ.

The Group VIII metal containing catalyst composition is typically based on an anion as a further catalyst component. The skilled person will appreciate that suitable anions are those which are non- or only weakly co-ordinating with the Group VIII metal under the conditions of the copolymerization. Examples of suitable anions are anions of protic acids, which include acids which are obtainable by combining a Lewis acid and a protic acid, and acids which are adducts of boric acid and a 1,2-diol, a catechol or a salicylic acid. Preferred acids are strong acids, i.e. those which have a pKa of less than 6, in particular less than 4, more in particular less than 2, when measured in aqueous solution at 18 °C. Examples of suitable protic acids are the above mentioned acids which may also participate in the Group VIII salts, e.g. perchloric acid and trifluoroacetic acid. Examples of Lewis acids which can be combined with a protic acid are boron trifluoride, boron pentafluoride, aluminium trifluoride and arsenic pentafluoride. Examples of protic acids which may be combined with a Lewis acid are sulphonic acids and hydrohalogenic acids, in particular hydrogen fluoride. Very suitable combinations of a Lewis acid with a protic

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acid are tetrafluoroboric acid and hexafluoroboric acid (HBF_4 and HBF_6). Other suitable anions are anions of which it appears that there are no stable conjugated acids, such as tetrahydrocarbylborate anions or carborate anions. Borate anions may comprise the same or different hydrocarbyl groups attached to boron, such as alkyl, aryl, aralkyl, alkaryl and cycloalkyl groups. Preferred are tetraarylborates, such as tetraphenylborate, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, tetrakis(4-chlorophenyl)borate and tetrakis(perfluorophenyl)borate, and carborate ($\text{B}_{11}\text{CH}_{12}^-$).

The source of anions may be an acid from which the anions are derivable, or their salts. Suitable salts are, for example, cobalt and nickel salts. A very suitable salt comprises a cation selected as the catalyst component (b) in accordance with this invention. Other sources of anions are suitably Lewis acids, such as halides, in particular fluorides, of boron, tin, antimony, aluminium or arsenic. Boron trifluoride and boron pentafluoride are very suitable. Other suitable Lewis acids are hydrocarbylboranes. The hydrocarbylboranes may comprise one hydrocarbyl group or two or three of the same or different hydrocarbyl groups attached to boron, such as alkyl, aryl, aralkyl, alkaryl and cycloalkyl groups, preferably aryl groups. They may also comprise hydrocarbyloxy or hydroxy groups or halogen atoms attached to boron. Examples of very suitable hydrocarbylboranes are triphenylborane, tris(perfluorophenyl)borane, tris(4-chlorophenyl)borane and tris[3,5-bis(trifluoromethyl)phenyl]borane. Again other suitable compounds which may function as a source of anions are aluminoxanes, in particular methyl aluminoxanes and t-butyl aluminoxanes.

The quantity of the source of anions is preferably selected such that it provides in the range of from 0.1

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The quantity of the source of anions is preferably selected such that it provides in the range of from 0.1 to 50 equivalents of anions per gram atom of Group VIII metal, in particular in the range of from 0.5 to 25 equivalents of anions per gram atom of Group VIII metal. However, the aluminoxanes may be used in such a quantity that the molar ratio of aluminium to the Group VIII metal is in the range of from 4000:1 to 10:1, preferably from 2000:1 to 100:1.

The catalyst composition of the process according to this invention is preferably based, as another additional component, on a ligand which can form a complex with the Group VIII metal. It would appear that the presence of two complexing sites in one ligand molecule significantly contributes to the activity of the catalysts. It is thus preferred to use a ligand containing at least two dentate groups which can complex with the Group VIII metal. Although less preferred, it is also possible to employ a monodentate ligand, i.e. a compound which contains a single dentate group which can complex with the Group VIII metal, in particular a dentate group of phosphorus. Suitably a bidentate ligand is used which contains two phosphorus-, nitrogen- or sulphur containing dentate groups. It is also possible to use a mixed bidentate ligand such as 1-diphenylphosphino-3-ethylthiopropene.

A preferred group of bidentate ligands can be indicated by the general formula



In this formula M^1 and M^2 independently represent a phosphorus, nitrogen, arsenic or antimony atom, R^1 , R^2 , R^3 and R^4 independently represent a non-substituted or polar substituted hydrocarbyl group, in particular of up to 10 carbon atoms, and R^5 represents a bivalent organic bridging group containing at least 1 carbon atom in the bridge.

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In the ligands of formula (I) M^1 and M^2 preferably represent phosphorus atoms. R^1 , R^2 , R^3 and R^4 may independently represent optionally polar substituted alkyl, aryl, alkaryl, aralkyl or cycloalkyl groups. Preferably at least one of R^1 , R^2 , R^3 and R^4 represents an aromatic group, in particular an aromatic group which is polar substituted.

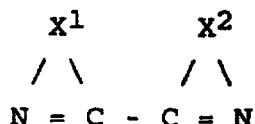
Suitable polar groups include halogen atoms, such as fluorine and chlorine, alkoxy groups such as methoxy and ethoxy groups and alkylamino groups such as methylamino-, dimethylamino- and diethylamino groups. Alkoxy groups and alkylamino groups contain in particular up to 5 carbon atoms in each of their alkyl groups.

It is preferred that one or more, in particular each of R^1 , R^2 , R^3 and R^4 represents an aryl group, preferably a phenyl group, substituted at an ortho position with respect to M^1 or M^2 with an alkoxy group, especially a methoxy group.

In the ligands of formula (I), R^5 preferably represents a bivalent organic bridging group containing from 2 to 4 bridging atoms, at least two of which are carbon atoms. Examples of such groups R^5 are $-\text{CH}_2-\text{CH}_2-$, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$, $-\text{CH}_2-\text{C}(\text{CH}_3)_2-\text{CH}_2-$, $-\text{CH}_2-\text{Si}(\text{CH}_3)_2-\text{CH}_2-$, and $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$. Preferably R^5 is a trimethylene group.

Preferred ligands are 1,3-bis[bis(2,4-dimethoxyphenyl)phosphino]propane, 1,3-bis[bis(2,4,6-trimethoxyphenyl)phosphino]propane and, more preferred, 1,3-bis[bis(2-methoxyphenyl)phosphino]propane.

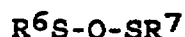
Other suitable bidentate ligands are nitrogen containing compounds of the general formula



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wherein X^1 and X^2 independently represent organic bridging groups each containing 3 or 4 atoms in the bridge at least 2 of which are carbon atoms. There may be an additional bridging group connecting the bridging groups X^1 and X^2 . Examples of such compounds are 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine, 4,4'-dimethoxy-2,2'-bipyridine, 1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline and 4,7-dimethyl-1,10-phenanthroline. Preferred compounds are 2,2'-bipyridine and 1,10-phenanthroline.

Again other suitable bidentate ligands are sulphur containing compounds of the general formula



wherein R^6 and R^7 independently represent a non-substituted or polar substituted hydrocarbyl group and Q represents a bivalent bridging group containing 2 to 4 carbon atoms in the bridge. The groups R^6 and R^7 are preferably alkyl groups, each having in particular up to 10 carbon atoms. Very suitable bis thio compounds are 1,2-bis(ethylthio)ethane and 1,2-bis(propylthio)ethene.

The amount of ligand supplied may vary considerably, but is usually dependent on the amount of Group VIII metal present in the catalyst composition. Preferred amounts of bidentate ligands are in the range of from 0.5 to 8, more preferably in the range of from 0.5 to 2 moles per gram atom of Group VIII metal, unless the bidentate ligand is a nitrogen bidentate ligand, in which case the bidentate ligand is preferably present in an amount of from 0.5 to 200 and in particular 1 to 50 moles per gram atom of Group VIII metal. The monodentate ligands are preferably present in an amount of from 0.5 to 50 and in particular 1 to 25 moles per gram atom of Group VIII metal.

The amount of catalyst composition used in the process of the invention may vary between wide limits.

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Recommended quantities of catalyst composition are in the range of 10^{-8} to 10^{-2} , calculated as gram atoms of Group VIII metal per mole of olefinically unsaturated compound to be copolymerized with carbon monoxide. Preferred quantities are in the range of 10^{-7} to 10^{-3} on the same basis.

The performance of Group VIII metal catalyst compositions in the copolymerization process may be improved by introducing an organic oxidant, such as a quinone or an aromatic nitro compound. Preferred oxidants are quinones selected from the group consisting of benzoquinone, naphthoquinone and anthraquinone. The quantity of oxidant is advantageously in the range of from 1 to 50, preferably in the range of from 1 to 20 mole per gram atom of metal of Group VIII.

Olefinically unsaturated compounds which can be used as monomers in the copolymerization process of the invention include compounds consisting exclusively of carbon and hydrogen and compounds which in addition comprise hetero atoms, such as unsaturated esters, ethers and amides. Unsaturated hydrocarbons are preferred. Examples of suitable olefinic monomers are lower olefins, such as ethene, propene and butene-1, cyclic olefins such as cyclopentene, aromatic compounds, such as styrene and α -methylstyrene and vinyl esters, such as vinyl acetate and vinyl propionate. Most preference is given to ethene and mixtures of ethene with another olefinically unsaturated compound, in particular an α -olefin, such as propene or butene-1. The term "lower" used in this document to specify an organic compound has the meaning that the organic compound contains up to 6 carbon atoms.

The molar ratio of on the one hand carbon monoxide and on the other hand the olefinically unsaturated compound(s) used as monomer is typically selected in the range of 1:5 to 5:1. Preferably the molar ratio is in

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the range of 1:2 to 2:1, substantially equimolar ratios being preferred most.

5 The copolymerization process of this invention may be carried out in the presence of a liquid diluent, but it may also be carried out as a gas phase process. If it is carried out in the presence of a liquid diluent pre-ferably a liquid diluent is used in which the copolymer to be prepared forms a suspension, in which case a diluent may be selected in which the copolymer is
10 insoluble or virtually insoluble. Examples of liquid diluents are ketones (e.g. acetone or methylethylketone), esters (e.g. ethyl acetate), ethers (e.g. diethylether, tetrahydrofuran or diethylene glycol dimethyl ether), chlorinated hydrocarbons (e.g. chloroform or
15 dichloromethane), aromatics (e.g. toluene, benzene, chlorobenzene) and protic diluents, such as lower alcohols (e.g. methanol and ethanol). Protic diluents are preferred. Mixtures of liquid diluents may be used as well, for example protic diluents may comprise an
20 aprotic diluent. Further, according to the teaching of EP-A-254343, ethers, ketones and esters may increase the rate of polymerization.

When the process of the invention is carried out as a gas phase process it is preferred to use a catalyst
25 system supported on a solid carrier, usually in order to facilitate the introduction of the catalyst system into the reactor.

Suitable carrier materials may be inorganic, such as silica, alumina or charcoal, or organic such as cellulose
30 or dextrose. Furthermore a polymer material may be used as carrier, such as polyethene, polypropene or, in particular, copolymers of carbon monoxide with an ethylenically unsaturated compound, for example linear alternating copolymers of carbon monoxide with ethene or
35 carbon monoxide with ethene and propene or butene-1.

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Conveniently the carrier is impregnated with a solution of the catalyst system in a suitable liquid. It will be appreciated that the amount of liquid used is relatively small, so that any excess thereof can easily be removed before or during the initial stage of the copolymerization process. On the other hand it has been observed, that the addition of a minor amount of liquid during the copolymerization process has a delaying effect on the catalyst deactivation, if there is any, the quantity of liquid being so small that the gas phase is the continuous phase during the polymerization. The quantity of liquid is in particular selected such that it is 20-80% by weight, more in particular 40-60% by weight, of the quantity which is sufficient to saturate the gas phase under the conditions of the polymerization. Polar liquids are preferred, such as lower alcohols, ethers, ketones and esters. Examples of such liquids are indicated hereinbefore in relation to the diluents which may be used when the process is carried out as a liquid phase polymerization.

The copolymerization process is typically carried out at a temperature between 20 and 200 °C, preferably at a temperature in the range of from 30 to 150 °C, and usually applying a pressure between 0.2 and 20 MPa, pressures in the range of from 1 to 10 MPa being preferred.

The copolymer may be recovered from the polymerization mixture by any suitable conventional technique.

The copolymers obtained according to the invention are particularly suitable as thermoplastics for fibres, films or sheets, or for injection moulding, compression moulding and blow moulding applications. They may be used for applications in the car industry, for the

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manufacture of packaging materials for food and drinks and for various uses in the domestic sphere.

The invention is now illustrated by means of the following examples.

5 Examples 1-21 (Examples 1, 2, 12, 13 and 16 are for comparison)

A linear alternating copolymer of carbon monoxide with ethene was prepared as follows.

10 A catalyst solution was prepared as follows: 57.4 mg (0.11 mmole) of 1,3-bis[bis(ortho-methoxyphenyl)phosphino]propane was dissolved in 2.5 ml of tetrahydrofuran. After complete dissolution, 22.0 mg (0.10 mmole) of palladium (II) acetate was added and the resultant mixture was stirred for 30 minutes. Then 17.5 ml of
15 methanol was added and the mixture was stirred during 1 hour. Subsequently 0.25 mmole of a salt as specified in Table I was dissolved in the mixture and the resulting solution was stirred for another 15 minutes.

20 In a 0.3-l autoclave 1 ml of the resulting catalyst solution, and subsequently 1 ml of methanol, were dribbled over 5 gram of a dried, previously prepared reactor powder of a copolymer of carbon monoxide and ethene. The autoclave was equipped with a helical stirrer and an automatic pressure relief.

25 Subsequently, the autoclave was closed and pressurized at 5.0 MPa with nitrogen. The pressure was released and the autoclave was purged with carbon monoxide (1.0 MPa), after which it was pressurized with carbon monoxide (2.0 MPa) and ethene (2.0 MPa).

30 The contents of the autoclave were heated to 90 °C. At the moment that the temperature reached 55 °C, a supply of carbon monoxide/ethene feed (molar ratio 1:1) was started to maintain the pressure at 4.0 MPa absolute. The beginning of the reaction was defined as the moment

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that the temperature of the reaction mixture reached 60 °C.

5 The copolymerization reaction was stopped by automatic pressure relief after a reaction period of 2 hours. The product was recovered, dried overnight in a vacuum oven under a nitrogen purge at 50 °C and weighed.

10 The average polymerization rate in kg copolymer per gram palladium per hour was calculated from the yield of copolymer. The results are shown in Table I. When applicable, the Table also shows the pK_b value of the conjugate base of the cations, measured at 25 °C in aqueous solution.

15 ¹³C-NMR analysis confirmed that the copolymers obtained were linear polymers of which the chains consisted of monomer units of carbon monoxide and monomer units of ethene arranged in an alternating order.

TABLE I

Example	Salt	pKb	Rate kg/ (g Pd.h)
<u>Tetrafluoroborates:</u>			
1 a)	tetrabutylammonium		< 0.5
2 a)	tetraphenylphosphonium		< 0.5
3	triethylammonium	3	4
4	ammonium	4.8	9
5	dimethylphenylammonium	9	12
6	triphenylammonium	10	12
7	triphenylcarbonium (trityl)		13
8	2,4,6-triphenylpyrylium		9
9	trimethyloxonium		14
10	nitrosyl		16
11	1-(triphenylmethyl)pyridinium		11
<u>Hexafluoroborates:</u>			
12 a)	tetramethylammonium		< 0.5
13 a)	tetrabutylammonium		< 0.5
14	dimethylphenylammonium	9	11
15	tropylium		12
<u>Tetraphenylborates:</u>			
16 a)	tetraphenylphosphonium		< 0.5
17	trimethylammonium	4.2	7
18	ammonium	4.8	6
<u>Tetrakis(perfluorophenyl)borates:</u>			
19	dimethylphenylammonium	9	16
20	triphenylcarbonium (trityl)		10
<u>Perchlorates:</u>			
21	dimethylphenylammonium	9	13
a)	For comparison		

C L A I M S

1. A process for the preparation of copolymers of carbon monoxide with an olefinically unsaturated compound comprising copolymerizing the monomers in the presence of a catalyst composition based upon
- 5 (a) a salt of a Group VIII metal, and
(b) a cation which is selected from cationic oxidants and cations of the general formulae $R_nH_{4-n}N^+$, $R_mH_{3-m}C^+$ and $R_mH_{3-m}O^+$, wherein n is 0, 1, 2, 3 or 4, m is 2 or 3, and R represents a hydrocarbyl group and/or two or three of R
- 10 together with the atom carrying a positive charge represent a ring structure comprising carbon atoms in the ring, on the understanding that when n is 3, at most two of R together with nitrogen represent a heterocyclic ring structure, and when n is 4, three of R together with
- 15 nitrogen represent an aromatic heterocyclic ring structure.
2. A process as claimed in claim 1, characterized in that the Group VIII metal salt is a palladium salt of a carboxylic acid.
- 20 3. A process as claimed in claim 1 or 2, characterized in that the cation is of the general formula $R_nH_{4-n}N^+$, with n being 0, 1, 2 or 3, of which the conjugated base has a pKb value of at least 4, preferably at least 6 and most preferably at least 8, when determined in aqueous
- 25 solution at 25 °C.
4. A process as claimed in claim 3, characterized in that at least one, in particular at least two, of the hydrocarbyl groups R is an aryl group.
5. A process as claimed in claim 1 or 2, characterized
- 30 in that the cation is of the general formula $R_nH_{4-n}N^+$, wherein n is 4, three of R together with the nitrogen





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atom represent a pyridine ring and the fourth R represents a hydrocarbyl group, in particular a branched alkyl or aralkyl group.

- 5 6. A process as claimed in claim 1 or 2, characterized in that the cation is of the general formula $R_mH_{3-m}C^+$ wherein m is 3 and R represents aryl groups, in particular phenyl groups, or m is 2 and R together with the charged carbon atom represent a 7-membered ring, preferably containing unsaturation, such as a tropylium cation.
- 10 7. A process as claimed in claim 1 or 2, characterized in that the cation is of the general formula $R_mH_{3-m}O^+$, wherein R represents a hydrocarbyl group, in particular a n-alkyl group, or, if m is 3, three R together with the oxygen atom represent an aromatic 6-membered ring which may be substituted with one or more (alk)aryl groups, or may be fused with another aromatic ring.
- 15 8. A process as claimed in claim 1 or 2, characterized in that the cation is a cationic oxidant containing nitrogen and oxygen, in particular a nitrosyl salt.
- 20 9. A process as claimed in any of claims 1-8, characterized in that the cation is present in a quantity of 0.1 - 50 equivalents per gram atom of Group VIII metal, in particular 0.5 - 25 equivalents in the same basis.
- 25 10. A process as claimed in any of claims 1-9, characterized in that the catalyst composition is based, as an additional component, on a source of anions selected from sources of anions of protic acids, tetrahydrocarbylborate anions and carborate anions, or selected from Lewis acids and aluminoxanes.
- 30 11. A process as claimed in claim 10, characterized in that the anions are applied in a quantity of from 0.5 to 25 equivalents per gram atom of Group VIII metal, on the understanding that aluminoxanes are applied in such a
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quantity that the molar ratio of aluminium to the Group VIII metal is in the range of from 2000:1 to 100:1.

12. A process as claimed in any of claims 1-11, characterized in that the catalyst composition is based, as an additional component, upon a bidentate ligand of the general formula $R^1R^2M^1-R^5-M^2R^3R^4$ (I), wherein M^1 and M^2 independently represent a phosphorus, nitrogen, arsenic or antimony atom, R^1 , R^2 , R^3 and R^4 independently represent a non-substituted or polar substituted hydrocarbyl group and R^5 represents a bivalent organic bridging group containing at least 1 carbon atom in the bridge, which bidentate ligand is typically present in an amount of from 0.5 to 2 moles per gram atom of Group VIII metal.
13. A process as claimed in claim 12, characterized in that M^1 and M^2 represent phosphorus atoms, one or more of R^1 , R^2 , R^3 and R^4 represents a phenyl group substituted at an ortho position with respect to M^1 or M^2 with an alkoxy group, especially a methoxy group, and R^5 contains from 2 to 4 bridging atoms, at least two of which are carbon atoms.
14. A process as claimed in any of claims 1-13, characterized in that it is used for the copolymerization of carbon monoxide with ethene or with a mixture of ethene with another α -olefin, such as propene or butene-1, the molar ratio of on the one hand carbon monoxide and on the other hand the olefinically unsaturated compound(s) used as monomer being in the range of 1:2 to 2:1, the amount of catalyst composition being in the range of 10^{-7} to 10^{-3} , calculated as gram atoms of Group VIII metal per mole of olefinically unsaturated compound to be copolymerized with carbon monoxide, the temperature being between 30 and 150 °C, and the pressure being between 1 and 10 MPa.
15. A catalyst composition based upon



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- (a) a salt of a Group VIII metal, and
(b) a cation which is selected from cations of the
general formulae $R_nH_{4-n}N^+$, $R_mH_{3-m}C^+$ and $R_mH_{3-m}O^+$, wherein
n is 1, 2, 3 or 4, m is 2 or 3, and R represents a
5 hydrocarbyl group and/or two or three of R together with
the atom carrying a positive charge represent a ring
structure comprising carbon atoms in the ring, on the
understanding that when n is 3, at most two of R together
with nitrogen represent a heterocyclic ring structure,
10 and when n is 4, three of R together with nitrogen
represent an aromatic heterocyclic ring structure.
16. A catalyst composition based upon
(a) a salt of a Group VIII metal,
(b) a cation which is selected from cationic oxidants and
15 cations of the general formulae $R_nH_{4-n}N^+$, $R_mH_{3-m}C^+$ and
 $R_mH_{3-m}O^+$, wherein n is 0, 1, 2, 3 or 4, m is 2 or 3, and
R represents a hydrocarbyl group and/or two or three of R
together with the atom carrying a positive charge
represent a ring structure comprising carbon atoms in the
20 ring, on the understanding that when n is 3, at most two
of R together with nitrogen represent a heterocyclic ring
structure, and when n is 4, three of R together with
nitrogen represent an aromatic heterocyclic ring
structure, and
25 (c) a ligand which contains at least two dentate groups
which can form a complex with the Group VIII metal.

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A PROCESS FOR THE PREPARATION OF COPOLYMERS

The invention relates to a process for the preparation of copolymers of carbon monoxide with an olefinically unsaturated compound, and to a catalyst composition.

5 Processes for the polymerization of carbon monoxide with an olefinically unsaturated compound catalysed with a Group VIII metal containing catalyst composition are well known in the art, for example from EP-A-121965, EP-A-248483 and EP-A-254343. The copolymers so prepared
10 are linear copolymers wherein the monomer units originating from carbon monoxide and the monomer units originating from the olefinically unsaturated compounds occur in alternating or substantially alternating order.

EP-A-254343 discloses in particular processes which
15 make use of catalyst compositions which are based upon (a) a salt of a Group VIII metal, and (b) a tetrahydrocarbylammonium or a tetrahydrocarbyl-phosphonium cation. It appears, however, that in these processes the yield of polymer was sometimes very low.

20 It has now unexpectedly been found that a substantial improvement of the performance of the catalyst compositions of EP-A-254343 can be achieved by replacing in the catalyst composition the tetrahydrocarbylammonium or -phosphonium cation by another cation, as specified
25 hereinafter.

The invention therefore relates to a process for the preparation of copolymers of carbon monoxide with an olefinically unsaturated compound comprising copolymerizing the monomers in the presence of a catalyst
30 composition based upon

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(a) a salt of a Group VIII metal with exclusion of $\text{Pd}(\text{O}_2\text{CNEt}_2)_2(\text{NEt}_2)_2$, and

(b) a cation which is selected from cationic oxidants and cations of the general formulae $\text{R}_n\text{H}_{4-n}\text{N}^+$, $\text{R}_m\text{H}_{3-m}\text{C}^+$ and $\text{R}_m\text{H}_{3-m}\text{O}^+$, wherein n is 0, 1, 2, 3 or 4, m is 2 or 3, and R represents a hydrocarbyl group and/or two or three of R together with the atom carrying a positive charge represent a ring structure comprising carbon atoms in the ring, on the understanding that when n is 3, at most two of R together with nitrogen represent a heterocyclic ring structure, and when n is 4, three of R together with nitrogen represent an aromatic heterocyclic ring structure.

The invention also relates to catalyst compositions based upon

(a) a salt of a Group VIII metal with exclusion of $\text{Pd}(\text{O}_2\text{CNEt}_2)_2(\text{NEt}_2)_2$, and

(b) a cation which is selected from cations of the general formulae $\text{R}_n\text{H}_{4-n}\text{N}^+$, $\text{R}_m\text{H}_{3-m}\text{C}^+$ and $\text{R}_m\text{H}_{3-m}\text{O}^+$, wherein n is 1, 2, 3 or 4, m is 2 or 3, and R represents a hydrocarbyl group and/or two or three of R together with the atom carrying a positive charge represent a ring structure comprising carbon atoms in the ring, on the understanding that when n is 3, at most two of R together with nitrogen represent a heterocyclic ring structure, and when n is 4, three of R together with nitrogen represent an aromatic heterocyclic ring structure.

In addition, the invention relates to catalyst compositions based upon

(a) a salt of a Group VIII metal with exclusion of $\text{Pd}(\text{O}_2\text{CNEt}_2)_2(\text{NEt}_2)_2$,

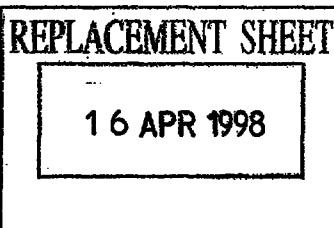
(b) a cation which is selected from cationic oxidants and cations of the general formulae $\text{R}_n\text{H}_{4-n}\text{N}^+$, $\text{R}_m\text{H}_{3-m}\text{C}^+$ and

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$R_mH_{3-m}O^+$, wherein n is 0, 1, 2, 3 or 4, m is 2 or 3, and
R represents a hydrocarbyl group and/or two or three of R
together with the atom carrying a positive charge
represent a ring structure comprising carbon atoms in the
ring, on the understanding that when n is 3, at most two
of R together with nitrogen represent a heterocyclic ring



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1. A process for the preparation of copolymers of carbon monoxide with an olefinically unsaturated compound comprising copolymerizing the monomers in the presence of a catalyst composition based upon

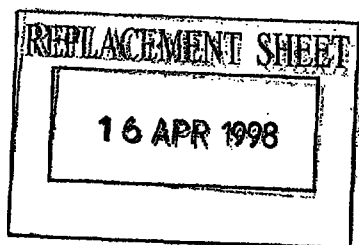
5 (a) a salt of a Group VIII metal with exclusion of $\text{Pd}(\text{O}_2\text{CNEt}_2)_2(\text{NHEt}_2)_2$, and

(b) a cation which is selected from cationic oxidants and cations of the general formulae $\text{R}_n\text{H}_{4-n}\text{N}^+$, $\text{R}_m\text{H}_{3-m}\text{C}^+$ and $\text{R}_m\text{H}_{3-m}\text{O}^+$, wherein n is 0, 1, 2, 3 or 4, m is 2 or 3, and
10 R represents a hydrocarbyl group and/or two or three of R together with the atom carrying a positive charge represent a ring structure comprising carbon atoms in the ring, on the understanding that when n is 3, at most two of R together with nitrogen represent a heterocyclic ring
15 structure, and when n is 4, three of R together with nitrogen represent an aromatic heterocyclic ring structure.

2. A process as claimed in claim 1, characterized in that the Group VIII metal salt is a palladium salt of a
20 carboxylic acid.

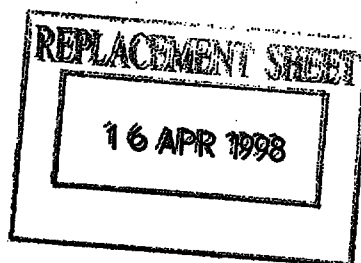
3. A process as claimed in claim 1 or 2, characterized in that the cation is of the general formula $\text{R}_n\text{H}_{4-n}\text{N}^+$, with n being 0, 1, 2 or 3, of which the conjugated base has a pKb value of at least 4, preferably at least 6 and
25 most preferably at least 8, when determined in aqueous solution at 25 °C.

4. A process as claimed in claim 3, characterized in that at least one, in particular at least two, of the hydrocarbyl groups R is an aryl group.





5. A process as claimed in claim 1 or 2, characterized in that the cation is of the general formula $R_nH_{4-n}N^+$, wherein n is 4, three of R together with the nitrogen



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(a) a salt of a Group VIII metal with exclusion of $\text{Pd}(\text{O}_2\text{CNEt}_2)_2(\text{NEt}_2)_2$, and

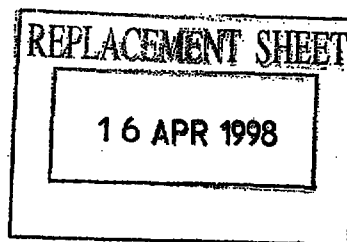
(b) a cation which is selected from cations of the general formulae $\text{R}_n\text{H}_{4-n}\text{N}^+$, $\text{R}_m\text{H}_{3-m}\text{C}^+$ and $\text{R}_m\text{H}_{3-m}\text{O}^+$, wherein n is 1, 2, 3 or 4, m is 2 or 3, and R represents a hydrocarbyl group and/or two or three of R together with the atom carrying a positive charge represent a ring structure comprising carbon atoms in the ring, on the understanding that when n is 3, at most two of R together with nitrogen represent a heterocyclic ring structure, and when n is 4, three of R together with nitrogen represent an aromatic heterocyclic ring structure.

16. A catalyst composition based upon

(a) a salt of a Group VIII metal with exclusion of $\text{Pd}(\text{O}_2\text{CNEt}_2)_2(\text{NEt}_2)_2$,

(b) a cation which is selected from cationic oxidants and cations of the general formulae $\text{R}_n\text{H}_{4-n}\text{N}^+$, $\text{R}_m\text{H}_{3-m}\text{C}^+$ and $\text{R}_m\text{H}_{3-m}\text{O}^+$, wherein n is 0, 1, 2, 3 or 4, m is 2 or 3, and R represents a hydrocarbyl group and/or two or three of R together with the atom carrying a positive charge represent a ring structure comprising carbon atoms in the ring, on the understanding that when n is 3, at most two of R together with nitrogen represent a heterocyclic ring structure, and when n is 4, three of R together with nitrogen represent an aromatic heterocyclic ring structure, and

(c) a ligand which contains at least two dentate groups which can form a complex with the Group VIII metal.



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(21) International Application Number: PCT/EP97/01001 (22) International Filing Date: 27 February 1997 (27.02.97) (30) Priority Data: 96200529.4 29 February 1996 (29.02.96) EP (34) Countries for which the regional or international application was filed: GB et al. (71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). (72) Inventors: BAARDMAN, Frank; Badhuisweg 3, NL-1031 CM Amsterdam (NL). JUBB, Jayne; Badhuisweg 3, NL-1031 CM Amsterdam (NL).		(81) Designated States: AU, CA, CN, JP, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: A PROCESS FOR THE PREPARATION OF COPOLYMERS (57) Abstract A process for the preparation of copolymers of carbon monoxide with an olefinically unsaturated compound comprising copolymerizing the monomers in the presence of a catalyst composition based upon (a) a salt of a Group VIII metal, and (b) a cation which is selected from cationic oxidants and cations of the general formulae $R_nH_{4-n}N^+$, $R_mH_{3-m}C^+$ and $R_mH_{3-m}O^+$, wherein n is 0, 1, 2, 3 or 4, m is 2 or 3, and R represents a hydrocarbyl group and/or two or three of R together with the atom carrying a positive charge represent a ring structure comprising carbon atoms in the ring, on the understanding that when n is 3, at most two of R together with nitrogen represent a heterocyclic ring structure, and when n is 4, three of R together with nitrogen represent an aromatic heterocyclic ring structure.		