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CATALYST SYSTEM AND PROCESS FOR THE PREPARATION OF COPOLYMERS OF
CARBON MONOXIDE AND OLEFINICALLY UNSATURATED COMPOUNDS

The invention relates to a process for the preparation of copolymers of carbon monoxide and one or more ethylenically unsaturated compounds.

Linear copolymers of carbon monoxide with one or more
5 ethylenically unsaturated compounds, in which copolymers the units originating from carbon monoxide on the one hand and the units originating from the ethylenically unsaturated compound(s) on the other hand occur in a substantially alternating arrangement, can be prepared by reacting the monomers under polymerization conditions in
10 the presence of a suitable palladium comprising catalyst system.

The linear copolymers, thus prepared, are eminently suitable for use in various outlets for thermoplastics. They may be further processed by means of conventional techniques into films, sheets, plates, fibres and shaped articles for domestic use and for parts in
15 the car industry. A suitable method for the preparation of the said copolymer which is usually performed in batch operation, is described in EP-A-181014 and EP-A-121965.

In this process, use is made of a catalyst, obtained by reaction of, in particular, a palladium compound, an anion of a
20 carboxylic acid with a pKa lower than 2 and a bidentate ligand of the general formula $Q^1Q^2M-X-MQ^3Q^4$, wherein M represents phosphorus, arsenic or antimony, X represents a divalent organic bridging group having at least two carbon atoms in the bridge, none of which carries steric hindrance causing substituents, and Q^1 , Q^2 , Q^3 and Q^4
25 are similar or dissimilar hydrocarbon groups.

It was of course appreciated that in the preparation of the copolymers, the catalyst and the polymerization conditions had to be selected such that copolymers with high molecular weights are formed, since in general products with higher molecular weights are
30 more suitable for the above-mentioned uses.

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The formation of high molecular weight copolymers is enhanced by performing the reaction at a low reaction temperature. Unfortunately, at the low reaction temperatures suitable for preparing copolymers with sufficiently high molecular weight, the activity of the initially used catalysts often proved to be inadequate for achieving a viable production rate. By increasing the temperature, the rate of copolymer formation could be improved, but the molecular weight of the copolymers will then drop.

Many attempts have therefore been made to find a mode for producing copolymers of high molecular weight at an acceptable rate. These attempts have especially focused on modifications of the catalyst system, whereby, in particular, the influence of many different ligands has been investigated. Whilst it was soon evident that the results obtained with bidentate ligands were generally superior to those obtainable with monodentate ligands and that phosphine ligands were usually more suitable than the corresponding arsine and stibine ligands, the effects resulting from changes in the various groups Q^1 , Q^2 , Q^3 , Q^4 and X in the ligands of the above formula, were by no means predictable.

From the results hitherto obtained, it would appear that the reaction rate is significantly increased by using a bisphosphine ligand of the formula $Q^5Q^6P-X-PQ^7Q^8$, wherein at least one of the groups $Q^5 \dots Q^8$ represents an aryl group containing at least one polar substituent in an ortho-position with respect to phosphorus. A process of this type is disclosed in EP-A-319083 and in EP-A-257663. It would further appear that the activity of catalysts comprising a bidentate ligand of the general formula $Q^1Q^2M-X^1-MQ^3Q^4$ wherein X^1 represents a bivalent bridging group containing three atoms in the bridge, viz. two carbon atoms and a hetero-atom or, more preferably, three carbon atoms, is substantially higher than that of catalysts comprising a similar ligand wherein the bridging group consists of only two, or four bridging atoms (cf. EP-A-121965).

Whilst it thus proved indeed possible to select ligands for incorporation in catalyst compositions of adequate activity for

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preparing the envisaged copolymers, it was observed that the bulk density of the obtained products still formed a problem.

Apart from the molecular weight, the bulk density, expressed in kg copolymers per m³ reaction medium, represents an important property of the copolymers at issue. The bulk density plays an important role both in the preparation of the copolymers and in the treatment, storage, transport and processing thereof.

Unexpectedly, it has now been found that by using a catalyst system comprising a specific type of bisphosphine ligand wherein the two phosphorous atoms are separated by an ethylene bridge, copolymers with a high bulk density are obtained at an acceptable and in many cases high reaction rate.

US-A-5010170 disclosed that in the palladium/bidentate ligand catalyzed copolymerization of carbon monoxide with olefins the use of a mixture of phosphorus bidentate ligands leads to a decrease of reactor fouling. The ligand mixture comprises a bidentate ligand carrying at the phosphorus atoms four ortho-alkoxy substituted aryl groups and a bidentate ligand carrying at the phosphorus atoms four aryl groups which are free of alkoxy substitution. An example of a ligand with ortho-alkoxy substitution is 1,2-bis[bis(2,4-diethoxy-phenyl)phosphino]ethane. This document does not provide any teaching which could bring the skilled person to the present invention.

The present invention relates to a catalyst system suitable for the copolymerization of carbon monoxide with an ethylenically unsaturated compound which catalyst system is based on

(a) a source of palladium cations, and

(b) a bidentate ligand of the general formula $R^1R^2P-CH_2-CH_2-PR^3R^4$

(I) wherein R^1 represents a phenyl group substituted with a polar group at one or both ortho-positions and/or the para-position with respect to the phosphorus atom to which the said phenyl group is linked, and R^2 , R^3 and R^4 independently represent a substituted or non-substituted hydrocarbyl group.

When the catalyst system is based on a mixture of bidentate ligands, the quantity of bidentate ligands of the general

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formula (I) in the ligand mixture is preferably at least 95 %-mole, in particular more than 98 %-mole, relative to the total quantity of the bidentate ligands. Such a ligand mixture may comprise a bidentate ligand of the general formula (I) wherein each of R^1 , R^2 , R^3 and R^4 carries an alkoxy group at an ortho-position with respect to the phosphorus atom and a bidentate ligand of the general formula $R^5R^6P-X^2-PR^7R^8$ wherein R^5 , R^6 , R^7 and R^8 independently represent aryl groups, typically of up to 10 carbon atoms, which are free of alkoxy substituents and X^2 represents a divalent hydrocarbyl group typically having 2-4 carbon atoms in the bridge. Such a ligand mixture is typically present in a quantity of 0.5 - 2 mole per gram atom of palladium, and may be used in the catalyst system which is in addition based on an anion of an acid having a pKa of less than 4, typically in a quantity of 0.5 - 50 equivalents per gram atom palladium.

Bidentate ligands of the general formula (I) are preferably applied as the sole ligands.

In addition, the invention relates to a process for the preparation of copolymers of carbon monoxide and an ethylenically unsaturated compound by reacting the monomers in the presence of a catalyst system according to this invention.

As source of palladium cations, i.e. component (a) of the catalyst system, conveniently a palladium salt is used. Suitable salts include salts of mineral acids such as sulphuric acid, nitric acid, phosphoric acid and sulphonic acids. Preferably, a palladium 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 and citric acid. Palladium-(II)-acetate represents a particularly preferred source of palladium cations.

In the bidentate ligands of formula (I), component (b) of the catalyst system, R^1 represents a phenyl group substituted with one or more polar groups. The polar group(s) may be located at an ortho position with respect to the phosphorus atom to which R^1 is linked, at the para-position, or, in the event of more than one polar group,

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at both ortho-positions, or at an ortho- and the para-position. A single polar substituent, located at an ortho-position is preferred.

Suitable polar groups include alkoxy groups and thio-alkyl groups such as a thiomethyl group.

5 Alkoxy groups are preferred, in particular C₁-C₄ alkoxy groups, C₁-C₄ having its usual meaning, indicating methyl, ethyl, propyl, isopropyl, n-butyl, sec.butyl, isobutyl and tertiary butyl.

The presence of a methoxy group in R¹ at an ortho-position with respect to the phosphorus atom, is most preferred.

10 It is recommended to use a catalyst system comprising a ligand of formula (I) wherein each of R², R³ and R⁴ represents an aryl group, typically having up to 10 carbon atoms, in particular a phenyl group. The aryl groups are preferably substituted with a polar group.

15 Preferably, R², R³ and R⁴ all have the same meaning as R¹. Accordingly, a particularly preferred bidentate ligand of formula (I) is 1,2-bis[di(2-methoxyphenyl)phosphino]ethane.

The amount of bidentate ligand supplied to the catalyst system may vary, but is conveniently selected in the range from 0.5 to 20 2 moles of bidentate ligand per gram atom of palladium. Preferably, the amount is in the range of 0.75 to 1.5 moles of ligand per gramatom of palladium.

The catalyst system may be based on an additional component which is generally thought to function during the copolymerization as a source of anions which are non- or only weakly co-ordinating with palladium. Suitable additional components are, for example, 25 protic acids, salts of protic acids, Lewis acids, combinations of Lewis acids and protic acids, and salts derivable from such combinations. Suitable are strong acids, in particular having a pK_a of less than 3, more in particular less than 2, when measured in 30 aqueous solution at 18 °C. Examples of suitable acids are the above mentioned acids which may also participate in the palladium salts, e.g. trifluoroacetic acid. Other suitable acids are adducts of boric acid and 1,2-diols, catechols or salicylic acids. Salts of 35 these acids may be used as well. Other suitable salts contain one

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or more hydrocarbylborate anions or carborate anions, such as sodium tetrakis[bis-3,5-(trifluoromethyl)phenyl]borate, lithium tetrakis-(perfluorophenyl)borate and cobalt carborate ($\text{Co}(\text{B}_{11}\text{CH}_{12})_2$).

Suitable Lewis acids are, for example, BF_3 , SnCl_2 , SnF_2 and $\text{Sn}(\text{CF}_3\text{SO}_3)_2$, and hydrocarbylboranes, such as triphenylborane, tris-(perfluorophenyl)borane and tris[bis-3,5-(trifluoromethyl)phenyl]-borane. Protic acids with which Lewis acids may be combined are for example sulphonic acids and hydrohalogenic acids, in particular HF. An example of a combination of a Lewis acid with a protic acid is tetrafluoboric acid (HBF_4). Other compounds which may be mentioned in this context are aluminoxanes, in particular methyl aluminoxanes and t-butyl aluminoxanes.

It is in particular advantageous when the additional component on which the catalyst system is based contains boron. It is in particular a boron containing Lewis acid, protic acid or salt. Very good results can be obtained with an boron containing protic acid having a pKa of less than 2 which is tetrafluoboric acid.

The amount of the additional component which is generally thought to function as an anion source is preferably selected in the range of 0.5 to 50 moles per gram atom of palladium, in particular in the range of 1 to 25 moles. However, the aluminoxanes may be used in such a quantity that the molar ratio of aluminium to palladium is in the range of 4000:1-10:1, preferably 2000:1-100:1.

The activity of the catalyst system is such, that amounts in the range from 10^{-8} to 10^{-1} gram atom of palladium per mole of ethylenically unsaturated compound to be copolymerized, are adequate. Preferably, the amount will be between 10^{-7} to 10^{-2} , on the same basis.

As regards the ethylenically unsaturated compound, as starting material for the process of the invention, olefins are preferred, in particular lower olefins, i.e. ethene and propene or mixtures thereof. Ethene is most preferred as monomer for the copolymerization with carbon monoxide, in particular as the sole or substantially sole ethylenically unsaturated compound. By the term "substantially" it is expressed that the presence of a quantity of

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another ethylenically unsaturated compound may be tolerable, in particular such that the other ethylenically unsaturated compound is incorporated in the copolymer in a quantity of less than 2 %mole, preferably less than 1 %mole, calculated on the total of ethylenically unsaturated compounds incorporated. The starting materials are conveniently applied in ratios such that per mole of carbon monoxide 0.25 to 4 moles of ethylenically unsaturated compound(s) is (are) present. Preferably the molar ratio between the two monomers is in the range of 3:1 to 1:3, in particular in the range of 1.5:1 to 1:1.5.

The process of the invention is conveniently carried out in the presence of a suitable diluent. Since the copolymers of the invention are insoluble or virtually insoluble in many conventional liquid solvents, a large number of these liquids may be used as diluent during the copolymerization reaction. Recommended diluents are polar organic liquids, such as ketones, ethers, esters or amides. Preferably, protic liquids are used, such as monohydric and dihydric alcohols.

It has been observed that by using a lower primary alcohol having at most 4 carbon atoms per molecule, the reaction rate of the copolymerization reaction is generally higher than in a medium whereby the diluent is a tertiary alcohol. Accordingly, lower primary alcohols having at most 4 carbon atoms per molecule are in particular recommended, methanol being an eminently suitable diluent.

Surprisingly, it was found that by using a mixture of a primary alcohol having at most 4 carbon atoms and a tertiary alcohol, having at most 10 carbon atoms per molecule, not only a high reaction rate is obtained, but in addition the resulting copolymers exhibit a high limiting viscosity number (LVN) (The Limiting Viscosity Number, or intrinsic viscosity, is calculated from determined viscosity values, measured for different copolymer concentrations in m-cresol at 60 °C. The primary alcohol and the tertiary alcohol are preferably present at a molar ratio between 30:70 and 70:30.

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A high LVN is indicative of a high molecular weight of the copolymer.

For example, by using a mixture of methanol and tertiary butanol at a 1:1 volume ratio a copolymer having a high LVN is produced at a high reaction rate.

On the other hand, the use of a mixture of a primary and a tertiary alcohol as diluent in a copolymerization process in which a catalyst is used comprising a bidentate ligand of the type exemplified in EP-A-319083, results in a considerably lower reaction rate.

When a diluent is used in the process of this invention it is preferred to have a solid particulate material suspended in the diluent before the monomers are contacted with the catalyst system. Suitable solid particulate materials are silica, polyethene and a copolymer of carbon monoxide and an ethylenically unsaturated compound, preferably a copolymer which is based on the same monomers as the copolymer to be prepared. The quantity of the solid particulate material is preferably in the range of 0.1-20 g, particularly 0.5-10 g per 100 g diluent.

According to a preferred embodiment of the process of the invention, a catalyst system is used which is supported on a solid carrier material.

By using a supported catalyst system of this type, copolymers having a high bulk density are obtained, whereas the use of a supported catalyst system based on a ligand according to EP-A-319083 results in copolymers of lower bulk density.

Suitable solid materials include organic compounds, such as polymers and resins, in particular ion exchanging resins, and inorganic compounds such as zeolites and inorganic oxides, e.g. silica, alumina, titania, zirconia and the like. Inorganic oxides are preferred carrier materials and among these, in particular silica, or a silica containing oxide-mixture.

The amount of carrier material to be used for the supported catalysts may vary considerably. To a large extent the size of the

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carrier material determines the amount required for an optimal performance of the catalyst.

Recommended are in particular carrier materials in which the particle size is in the range of 0.001 to 5 microns, preferably in the range of 0.005 to 4 microns. The said particle sizes are usually indicated as D_{50} values, i.e. the size (in microns) whereby 50% of the particles has a particular diameter. If a particle size range is given, the diameters of substantially all particles are within the said range. Materials having a D_{50} of 0.01 are especially preferred.

If desired, a catalyst system may be used, which additionally comprises an organic oxidant. Examples of suitable oxidants include quinones such as 1,4-benzoquinone, 1,2-naphthoquinone and 1,4-naphthoquinone.

The conditions under which the process of the invention is performed, include the use of elevated temperatures and pressures, such as between 20 and 200 °C, in particular 30 and 130 °C and 1-200 bara, in particular 5-100 bara.

Preferred reaction temperatures are in the range of 70 to 130 °C, temperatures in the range of 80 to 100 °C being most preferred.

The reaction pressure is preferably selected in the range of 40 to 80 bara, but pressures outside these limits are not precluded.

The invention is illustrated by the following examples.

EXAMPLE 1

A carbon monoxide/ethene copolymer was prepared as follows. A stirred 200 ml autoclave was charged with 90 ml of methanol, 1.58 g of linear alternating carbon monoxide/ethene copolymer (obtained in a previous experiment), and a catalyst solution consisting of 10 ml of methanol, 0.0094 mmol of palladium-II-acetate, 0.188 mmol of fluoboric acid (HBF_4) and 0.0104 mmol of 1,2-bis[di(2-methoxy-phenyl)phosphino]ethane.

The air in the autoclave was displaced by nitrogen (1 bara). The autoclave was then heated to 90 °C and pressurized with an equimolar mixture of carbon monoxide and ethene until a pressure of 50 bar was reached. Accordingly, the polymerization started. During

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the reaction the pressure was maintained by pressurizing with an equimolar carbon monoxide/ethene mixture. After 3 hours the polymerization was terminated by depressurization and subsequent cooling to ambient temperature.

5 The yield was 26.5 g of copolymer having a bulk density of 220 kg/m³. The polymerization rate was 8.3 kg of copolymer per gram of palladium and per hour.

EXAMPLE 2

10 A carbon monoxide/ethene copolymer was prepared, substantially as described in Example 1, with the difference that the reactor was pressurized with a mixture of carbon monoxide and ethene in a molar ratio of 0.40:1 instead of with an equimolar carbon monoxide/ethene mixture.

15 The yield was 36.1 g of copolymer having a bulk density of 315 kg/m³. The polymerization rate was 11.5 kg of copolymer per gram of palladium and per hour.

EXAMPLE 3

20 A carbon monoxide/ethene copolymer was prepared, substantially as described in Example 1, with the difference that the reactor was pressurized with a mixture of carbon monoxide and ethene in a molar ratio of 1.42:1, instead of with an equimolar mixture.

 The yield was 25.6 g of copolymer having a bulk density of 230 kg/m³. The polymerization rate was 8.0 kg of copolymer per gram of palladium and per hour.

25 EXAMPLE 4

 A carbon monoxide/ethene copolymer was prepared, substantially as described in Example 1 with the difference that a reaction temperature of 85 °C, instead of 90 °C was applied.

30 The yield was 20.2 g of copolymer having a bulk density of 195 kg/m³. The polymerization rate was 6.2 kg of copolymer per gram of palladium and per hour.

EXAMPLE 5

35 A carbon monoxide/ethene copolymer was prepared, substantially as described in Example 1 with the difference that the reaction temperature was 95 °C, instead of 90 °C.

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The yield was 30.7 of copolymer having a bulk density of 255 kg/m³. The polymerization rate was 9.7 kg of copolymer per gram of palladium and per hour.

EXAMPLE A (for comparison, not according to the invention)

5 A carbon monoxide/ethene copolymer was prepared, substantially as described in Example 1, with the difference that 0.104 mmol of 1,3-bis[di(2-methoxyphenyl)phosphino]propane was used, instead of 1,2-bis[di(2-methoxyphenyl)phosphino]ethane. The yield was 6.1 g of copolymer having a bulk density of only 70 kg/m³. The polymerization rate was 1.5 kg of copolymer per gram of palladium and per hour.

EXAMPLE 6

15 A carbon monoxide/ethene copolymer was prepared, substantially as described in Example 1, with the difference that 0.188 mmol of trifluoroacetic acid was used, instead of fluo-boric acid. The yield was 16.9 g of copolymer having a bulk density of 107 kg/m³. The polymerization rate was 5.1 kg of copolymer per g of palladium and per hour.

EXAMPLE B (for comparison, not according to the invention)

20 A carbon monoxide/ethene copolymer was prepared, substantially as described in Example 6, with the difference that 0.104 mmol of 1,3-bis[di(2-methoxyphenyl)phosphino]propane was used instead of 1,2-bis[di(2-methoxyphenyl)phosphino]ethane.

The reaction had to be terminated after 1 h, because fluffy product was formed, hindering proper mixing of the reactor contents. The yield was 8.7 g of copolymer having a bulk density of 80 kg/m³. The polymerization rate was 8.1 kg of copolymer/g palladium and per hour.

EXAMPLE 7

30 A carbon monoxide/ethene copolymer was prepared as follows. A stirred 300 ml autoclave was charged with 100 ml of methanol. Air was removed by pressurizing with carbon monoxide and subsequently the pressure was increased to 50 bar by pressurizing with a mixture of carbon monoxide and ethene in a molar ratio of 1.5:1.

35 The temperature was raised to 96 °C and subsequently a catalyst solution was injected with the carbon monoxide stream at an

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additional pressure of 5 bar. The catalyst solution consisted of 0.01 mmol of palladium (II) acetate 0.012 mmol of 1,2-bis[di(2-methoxyphenyl)phosphino]ethane and 0.2 mmol of fluoboric acid in 10 ml of methanol. Accordingly, the reaction started and was terminated after 1 hour.

The yield of copolymer was 13 g. The polymerization rate was 13 kg of copolymer per gram of palladium and per hour. The Limiting Viscosity Number (LVN) of the copolymer was 0.7 ml/g.

EXAMPLE 8

A carbon monoxide/ethene copolymer was prepared, substantially as described in Example 7, with the difference that a mixture of 50 ml of tertiary butanol and 50 ml of methanol was used, instead of 100 ml of methanol.

The yield of copolymer was 10 g. The polymerization rate was still 10 kg of copolymer per gram of palladium and per hour. The LVN of the copolymer had increased to 4.5 dl/g.

In a similar experiment, in which 100 ml of tertiary butanol and no methanol was used as diluent, the polymerization rate was 1.5 kg of copolymer per gram of palladium and per hour.

EXAMPLE C (for comparison, not according to the invention)

A copolymer of carbon monoxide and ethene was prepared, substantially as described in Example 7, with the difference that 0.012 mmol of 1,3-bis[di-(2-methoxyphenyl)phosphino]propane was used instead of 1,2-bis[di(2-methoxyphenyl)phosphino]ethane. The copolymer obtained had a LVN of 2.0 dl/g and was produced with a polymerization rate of 10 kg of copolymer per gram of palladium and per hour.

In a similar experiment, whereby as diluent 100 ml of tertiary butanol and no methanol was used, the polymerization rate was 0.5 kg of copolymer per gram of palladium and per hour.

In another similar experiment, whereby as diluent 50 ml of tertiary butanol and 50 ml of methanol was used 5 g of copolymer was obtained in 2 hours. The LVN of the copolymer was 6.0 dl/g, but the polymerization rate had dropped from 10 to 2.5 kg of copolymer per gram of palladium and per hour.

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EXAMPLE 9

A copolymer of carbon monoxide and ethene was prepared as follows. A 300 ml autoclave was charged with 5 g of CLA 27252 (a commercially available silica having a particle size (D_{50}) of 3.5 micron), palladium-II-acetate (1.5 mg Pd), 1,2-bis[di(2-methoxyphenyl)phosphino]ethane and fluoboric acid-dimethylether such that the molar ratio palladium compound: bidentate ligand: acid anion was 1.0:1.1:5.0 and 150 ml of methanol. Air was removed and the autoclave was pressurized with an equimolar mixture of carbon monoxide and ethene up to a pressure of 50 bara. The temperature of the contents of the autoclave was raised to 90 °C, whereupon the polymerization started. The reaction was terminated after a runtime of 5 hours.

The polymerization rate was 2.1 kg of copolymer per g of palladium and per hour. The bulk density of the copolymer was 290 kg/m³.

EXAMPLE D (for comparison, not according to the invention)

A copolymer of carbon monoxide and ethene was prepared, substantially as described in Example 9, with the difference that 1,3-bis[di(2-methoxyphenyl)phosphino]propane was used instead of 1,2-bis[di(2-methoxyphenyl)phosphino]ethane. The polymerization rate was 8.2 kg of copolymer per g of palladium and per hour. The bulk density of the copolymer was 123 kg/m³.

EXAMPLE 10

A copolymer of carbon monoxide and ethene was prepared, substantially as described in Example 9, with the difference that Organo-silicasol (a commercially available silica with a particle size (D_{50}) of 0.01 micron) was used instead of CLA-27252.

The polymerization rate was 5.8 kg of copolymer per g of palladium and per hour. The bulk density of the copolymer was 320 g/m³.

EXAMPLE E (for comparison, not according to the invention)

A carbon monoxide/ethene copolymer was prepared, substantially as described in Example 10, with the difference that 1,3-bis[di(2-methoxy-phenyl)phosphino]propane was used instead of 1,2-bis[di(2-

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methoxyphenyl)phosphino]ethane. The polymerization rate was 9.6 kg of copolymer per g of palladium and per hour. The bulk density of the copolymer was 120 kg/m³.

EXAMPLE 11

5 A carbon monoxide/ethene copolymer was prepared, substantially as described in Example 10, with the difference that trifluoroacetic acid was used instead of fluoboric acid-dimethylether. The polymerization rate was 5.1 kg of copolymer per g of palladium and per hour. The bulk density of the copolymer was 370 kg/m³.

10 EXAMPLE F (for comparison, not according to the invention)

A carbon monoxide/ethene copolymer was prepared, substantially as described in Example 11, with the difference that 1,3-bis[di(2-methoxyphenyl)phosphino]propane was used instead of 1,2-bis[di(2-methoxyphenyl)phosphino]ethane.

15 The polymerization rate was 8.3 kg of copolymer per g of palladium and per hour. The bulk density of the copolymer was 127 kg/m³.



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C L A I M S

1. A catalyst system suitable for the copolymerization of carbon monoxide with an ethylenically unsaturated compound which catalyst system is based on

(a) a source of palladium cations, and

(b) a bidentate ligand of the general formula $R^1R^2P-CH_2-CH_2-PR^3R^4$

(I) wherein R^1 represents a phenyl group substituted with a polar group at one or both ortho-positions and/or the para-position with respect to the phosphorus atom to which the said phenyl group is linked, and R^2 , R^3 and R^4 independently represent a substituted or non-substituted hydrocarbyl group,

on the understanding that when the catalyst system is based on a ligand mixture which ligand mixture comprises a bidentate ligand of the general formula (I) wherein each of R^1 , R^2 , R^3 and R^4 carries an alkoxy group at an ortho-position with respect to the phosphorus atom and a bidentate ligand of the general formula $R^5R^6P-X^2-PR^7R^8$ wherein R^5 , R^6 , R^7 and R^8 independently represent aryl groups of up to 10 carbon atoms which are free of alkoxy substituents and X^2 represents a divalent hydrocarbyl group having 2-4 carbon atoms in the bridge and which ligand mixture is present in a quantity of 0.5-2 mole per gram atom of palladium, and the catalyst system is in addition based on an anion of an acid having a pKa of less than 4 in a quantity of 0.5-50 equivalents per gram atom palladium, the quantity of the bidentate ligand of the general formula (I) in the ligand mixture being at least 95 %-mole, relative to the total quantity of the two types of bidentate ligands.

2. A catalyst system suitable for the copolymerization of carbon monoxide with an ethylenically unsaturated compound which catalyst system is based on

(a) a source of palladium cations, and

(b) a bidentate ligand of the general formula (I) wherein R^1 represents a phenyl group substituted with a polar group at one or

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both ortho-positions and/or the para-position with respect to the phosphorus atom to which the said phenyl group is linked, and R^2 , R^3 and R^4 independently represent a substituted or non-substituted hydrocarbyl group,

5 and which is supported on a solid carrier, such as silica, preferably having a particle size in the range of 0.005 to 4 microns.

3. A catalyst system as claimed in claim 1 or 2, characterized that it is based in addition on a source of anions, in particular an
10 acid with a pKa of less than 2, more in particular tetrafluoboric acid.

4. A catalyst system suitable for the copolymerization of carbon monoxide with an ethylenically unsaturated compound which catalyst system is based on

15 (a) a source of palladium cations,

(b) a bidentate ligand of the general formula (I) wherein R^1 represents a phenyl group substituted with a polar group at one or both ortho-positions and/or the para-position with respect to the phosphorus atom to which the said phenyl group is linked, and R^2 , R^3
20 and R^4 independently represent a substituted or non-substituted hydrocarbyl group, and

(c) a boron containing component.

5. A catalyst system as claimed in claim 4, characterized that the boron containing component is a Lewis acid, a protic acid or a salt,
25 in particular a protic acid which is tetrafluoboric acid.

6. A catalyst system as claimed in any one of claims 1-5, characterized in that, as regards (b), it is based on a bidentate ligand of the formula (I), wherein R^1 represents a phenyl group substituted at an ortho-position with respect to the phosphorus atom
30 to which the phenyl group is linked, by a C_1-C_4 alkoxy group, and wherein R^1 represents in particular an ortho-methoxyphenyl group.

7. A catalyst system as claimed in any one of claims 1-6, characterized in that in the bidentate ligand of formula (I) each of R^2 , R^3 and R^4 have the same meaning as R^1 .



8. A catalyst system as claimed in claim 7, characterized in that in the bidentate ligand of formula (I) is 1,2-bis[di(2-methoxy-phenyl)phosphino]ethane.

9. A catalyst system as claimed in any one of claims 1-8, characterized in that, as regards (a), it is based on a palladium salt of a carboxylic acid, in particular palladium-II-acetate.

10. A catalyst system as claimed in any one of claims 3-9, characterized in that the amount of bidentate ligand of formula (I) is selected in the range of 0.75 to 1.5 moles per gram atom of palladium, and in that the amount of the source of anions or the boron containing component, as the case may be, is selected in the range of 1 to 25 moles per gram atom of palladium.

11. A process for the preparation of copolymers of carbon monoxide with an ethylenically unsaturated compound comprising reacting the monomers in the presence of a catalyst system as claimed in any one of claims 1-10.

12. A process as claimed in claim 11, characterized in that the amount of catalyst is selected such that per mole of ethylenically unsaturated compound to be copolymerized, 10^{-7} to 10^{-2} gram atom of palladium is present, in that the molar ratio between carbon monoxide relative to ethylenically unsaturated compound(s) is in the range of 1.5:1 to 1:1.5, and in that the copolymerization is carried out at a temperature in the range of 30 to 130 °C and a pressure of 50-100 bara.

13. A process as claimed in claim 11 or 12, characterized in that a. ethylenically unsaturated compound ethene is used.

14. A process as claimed in any one of claims 11-13, characterized in that the copolymerization is carried out in the presence of a diluent in which the copolymers are insoluble or virtually insoluble, in particular an organic protic liquid.

15. A process as claimed in claim 14, characterized in that as diluent a primary alcohol having at most 4 carbon atoms per molecule is used, in particular methanol.

16. A process for the preparation of copolymers of carbon monoxide with an ethylenically unsaturated compound comprising reacting the



monomers in the presence of a suitable catalyst system which is based on

(a) a source of palladium cations, and

(b) a bidentate ligand of the general formula (I) wherein R^1

5 represents a phenyl group substituted with a polar group at one or both ortho-positions and/or the para-position with respect to the phosphorus atom to which the said phenyl group is linked, and R^2 , R^3 and R^4 independently represent a substituted or non-substituted hydrocarbyl group,

10 and using as a diluent a primary alcohol having at most 4 carbon atoms per molecule is used, in particular methanol, in the further presence of a tertiary alcohol having at most 10 carbon atoms per molecule, in particular tertiary butanol, the molar ratio between the primary alcohol and the tertiary alcohol preferably being in the
15 range of 30:70 to 70:30.