

The invention relates to a process for the preparation of polymers of carbon monoxide with one or more olefinically unsaturated compounds.

It is known that linear polymers of carbon monoxide with one or more olefinically unsaturated compounds in which polymers the units from carbon monoxide on the one hand and the units from the olefinically unsaturated compounds on the other hand are present in a substantially alternating arrangement, can be prepared by contacting the monomers at elevated temperature and pressure with a catalyst comprising:

- a) a Group VIII metal compound,
- b) an acid, and
- c) a dentate ligand containing at least two phosphorus-, nitrogen- or sulphur-containing dentate groups through which the dentate ligand can complex with the Group VIII metal.

The preparation of the polymers using the above-mentioned catalysts was hitherto mainly carried out as liquid phase polymerization, i.e. the monomers were contacted with a solution of the catalyst in a liquid non-polymerizable diluent in which the polymers are insoluble or virtually insoluble. During the polymerization the polymers are obtained in the form of a suspension in the diluent. After reaching the required degree of polymerization, the polymerization is generally terminated by cooling and releasing the pressure. The polymers are isolated from the suspension, for example by filtration or centrifuging. The pure diluent to be used for a following polymerization is recovered from the remaining liquid, e.g. by distillation.

activity is determined to a large extent by the nature of the acid contained therein as component b). It has been established that catalysts containing as component b) a strong organic acid such as para-toluenesulphonic acid or methylsulphonic acid, exhibit the highest polymerization activity in the above-mentioned liquid phase polymerization. In view of the above, it has hitherto been customary in liquid phase polymerization for the preparation of the present polymers to employ catalysts containing a strong organic acid as component b).

During further investigations by the applicant into the present polymer preparation, it was established that apart by liquid phase polymerization, it could also be carried out by gas phase polymerization. Gas phase polymerization is characterized in that the monomers are contacted with the catalyst substantially in the absence of a liquid non-polymerizable diluent. For the preparation of the polymers on an industrial scale, gas phase polymerization is much to be preferred to liquid phase polymerization on account of the fact that with gas phase polymerization the above-mentioned filtration or centrifuging step, as well as the distillation step, can be omitted. If implemented on an industrial scale, these separation and purification steps involve considerable expense.

The applicant has extensively researched the gas phase polymerization for the preparation of the present polymers using the above-mentioned catalysts. On the assumption that the same rules would apply to the optimum composition of the catalyst for gas phase polymerization as had previously been found for liquid phase poly-

results were disappointing. Contrary to expectations, only low polymerization rates were observed.

Continued research into this subject has now shown that catalysts exhibiting a high activity in gas phase polymerization for the preparation of the present polymers can be obtained by incorporating in catalysts on the basis of components a) and c) a Lewis acid/Brönsted acid mixture as component b). Catalysts on the basis of a Group VIII metal compound, a Lewis acid/Brönsted acid mixture and an N- or S-dentate ligand as described under c) are novel compositions of matter.

The present patent application therefore relates to a process for the preparation of polymers of carbon monoxide with one or more olefinically unsaturated compounds, in which polymers the units from carbon monoxide and the units from the olefinically unsaturated compounds are present in a substantially alternating arrangement, which process comprises contacting the monomers at elevated temperature and pressure and substantially in the absence of a liquid non-polymerizable diluent with a catalyst comprising:

- a) a Group VIII metal compound,
- b) a Lewis acid/Brönsted acid mixture, and
- c) a dentate ligand containing at least two phosphorus-, nitrogen- or sulphur-containing dentate groups whereby the dentate ligand can complex with the Group VIII metal.

The patent application also relates to novel catalysts comprising a Group VIII metal compound, a Lewis acid/Brönsted acid mixture and an N- or S-dentate ligand as described under c).

quantity of diluent and/or hydrogen. In particular, lower aliphatic alcohols are very suitable as alcohols. The use of methanol is particularly preferred.

As regards the way in which, during the gas phase polymerization, the catalyst is presented to the monomer mixture to be polymerized, several different possibilities can be distinguished. Firstly, the catalyst as such, i.e. without carrier material, can be introduced into the polymerization reactor. If desired, the catalyst can be dissolved beforehand or suspended in a liquid diluent and, after the solution or suspension has been introduced into the reactor, for example by spraying, the diluent can be substantially removed. Preferably an alcohol, and in particular methanol, is used as diluent. If an alcohol is used, its removal is carried out such that a small quantity remains behind in the catalyst. The gas phase polymerization is preferably carried out using the catalyst deposited on a carrier material. The deposition of the catalyst on the carrier material can be accomplished very suitably by contacting the carrier material with a solution or suspension of the catalyst in a liquid diluent and then substantially removing the diluent. As diluents, preferably alcohols and in particular methanol are used. If an alcohol is used as diluent, its removal is preferably carried out such that a small quantity remains behind in the catalyst on the carrier. As carrier material, a porous carrier material is preferably chosen. Both inorganic and organic carrier materials are eligible as catalyst carrier materials. Examples of suitable carrier materials are silica, alumina, talc, charcoal, cellulose, dextrose and dextran gel. Polymers such as polyethylene,

in products in which the prepared polymer occurs together with the carrier material used. Depending on the nature and quantity used of the carrier material, products with a very wide range of properties and applications can be prepared. If desired, the carrier material can be wholly or partly removed from the product at the end of the polymerization by treating the product with a solvent in which the carrier material is soluble but the prepared polymer is insoluble.

In the gas phase polymerization according to the invention, a polymer whose structure and composition corresponds substantially to that of the polymer to be prepared is preferably used as carrier material for the catalyst. Polymers prepared both by liquid phase polymerization and by gas phase polymerization are eligible for this purpose.

In this patent application, Group VIII metals are understood to be the noble metals ruthenium, rhodium, palladium, osmium, iridium and platinum, as well as the iron group metals iron, cobalt and nickel. In the process according to the invention, catalysts containing a Group VIII metal selected from palladium, nickel and cobalt are preferably used. Palladium is particularly preferred as Group VIII metal. The incorporation of the Group VIII metal in the catalyst preferably takes place in the form of a salt of a carboxylic acid, in particular in the form of an acetate.

The catalysts used in the process according to the invention should contain a Lewis acid/Brönsted acid mixture as component b). These mixtures preferably contain 0.1-10 and in particular 0.5-5 mol Brönsted acid per mol Lewis acid. Examples of suitable Lewis acids are

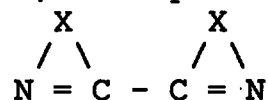
bromides, among others, are suitable as Lewis acid: aluminium tribromide, boron tribromide, gallium tribromide, germanium tetrabromide and phosphorus pentabromide. Finally, the following fluorides, among others, are suitable as Lewis acid: mercury difluoride, aluminium trifluoride, boron trifluoride, gallium trifluoride, indium trifluoride, silicon tetrafluoride, germanium tetrafluoride, titanium tetrafluoride, antimony pentafluoride, arsenic pentafluoride, tantalum pentafluoride, niobium pentafluoride and phosphorus pentafluoride. In the Lewis acid/Brönsted acid mixtures, the Lewis acid is preferably a fluoride and in particular a fluoride selected from boron trifluoride, titanium tetrafluoride, phosphorus pentafluoride and antimony pentafluoride. As examples of suitable Brönsted acids, hydrochloric acid, hydrobromic acid, hydrofluoric acid, fluorosulphurous acid and sulphuric acid can be mentioned. In the Lewis acid/Brönsted acid mixtures, the Brönsted acid is preferably hydrofluoric acid. Catalysts with high polymerization activity were prepared, inter alia, by incorporating therein tetrafluoroboric acid, (which may be seen as a 1:1 mixture of boron trifluoride and hydrofluoric acid) hexafluorotitanic acid ($2\text{HF}\cdot\text{TiF}_4$), hexafluorophosphoric acid ($\text{HF}\cdot\text{PF}_5$) or hexafluoroantimonic acid ($\text{HF}\cdot\text{SbF}_5$) as the component b). Component b) is preferably present in the catalysts in such a quantity that they contain 0.5 to 200 and in particular 1.0 to 100 mol of the Lewis acid per g. atom Group VIII metal.

In addition to components a) and b), the catalyst used in the process according to the invention should include as component c) a dentate ligand containing at

containing more than two dentate groups are also eligible for this purpose, such as the tetradentate ligand 1,8-bis[bis-(2-methoxyphenyl)phosphino]-2,7-bis-[bis(2-methoxyphenyl)-phosphinomethyl]octane, bidentate ligands are preferred.

If as component c) in the catalysts a bidentate ligand is used which via two sulphur-containing dentate groups present therein can complex with the Group VIII metal, a component c) is preferred of the general formula $R^1S-R-SR^1$ in which R^1 represents an optionally polar substituted hydrocarbyl group and R represents a divalent organic bridging group containing at least two carbon atoms in the bridge. Examples of such compounds are 1,2-bis(ethylthio)ethane, cis-1,2-bis-(benzylthio)ethene and 1,2-bis(phenylthio)propane.

If as component c) in the catalysts a bidentate ligand is used which via two nitrogen-containing dentate groups present therein can complex with the Group VIII metal, a component c) is preferred of the general formula



in which X represents an organic bridging group containing three or four atoms in the bridge, of which at least two are carbon atoms. Examples of such compounds are 2,2'-dipyridyl and 1,10-phenanthroline.

Preferably, as component c) in the catalysts a bidentate ligand is used which via two phosphorus-containing dentate groups present therein can complex with the Group VIII metal. If such a bidentate ligand is used as component c), a compound of the general formula $(R^1)_2P-R-P(R^1)_2$ is preferred in which R and R^1 have the previously indicated meanings. In that case, there is

alkoxy group as substituent and in which it contains three atoms in the bridge. An example of such a compound is 1,3-bis[bis(2-methoxyphenyl)phosphino]propane.

If as component c) in the catalysts a bidentate ligand is used which via two sulphur- or nitrogen-containing dentate groups present therein can complex with the Group VIII metal, the quantity employed is preferably 0.5-100 and in particular 1-50 mol per g.atom Group VIII metal. If as component c) in the catalysts a bidentate ligand is used which via two phosphorus-containing dentate groups present therein can complex with the Group VIII metal, the quantity employed is preferably 0.5-2 and in particular 0.75-1.5 mol per g.atom Group VIII metal.

To enhance the activity of the catalysts, an organic oxidizing agent can also be incorporated therein as component d). Aromatic nitro compounds such as nitrobenzene are very suitable for this purpose. The quantity of organic oxidizing agent used is preferably 5-5000 and in particular 10-1000 mol per g.atom Group VIII metal.

As olefinically unsaturated compounds which according to the invention can be polymerized with carbon monoxide, compounds are eligible which consist exclusively of carbon and hydrogen, as well as compounds which besides carbon and hydrogen also contain one or more heteroatoms. The process according to the invention is preferably used for the preparation of polymers of carbon monoxide with one or more olefinically unsaturated hydrocarbons. Examples of suitable hydrocarbon monomers are ethene, propene, butene-1, hexene-1, octene-1, styrene, cyclopentene, norbornene and dicyclopentadiene. The process

terpolymers of carbon monoxide with ethene and an α -olefin, in particular propene.

The quantity of catalyst used in the process according to the invention can vary within wide limits. Per mol olefinically unsaturated compound to be polymerized, a quantity of catalyst is preferably used which contains 10^{-7} to 10^{-3} and in particular 10^{-6} to 10^{-4} g.atom Group VIII metal.

The polymerization is preferably carried out at a temperature of 25-150 °C and a pressure of 2-150 bar and in particular at a temperature of 30-130 °C and a pressure of 5-100 bar. The molar ratio of the olefinically unsaturated compounds relative to carbon monoxide is preferably 10:1 to 1:10 and in particular 5:1 to 1:5. The polymer preparation according to the invention can be carried out either batchwise or continuously.

The invention is illustrated further by the following examples.

Example 1

A carbon monoxide/ethene copolymer was prepared as follows. A catalyst was prepared by absorbing a catalyst solution containing
1.5 ml methanol,
0.5 ml tetrahydrofuran,
0.0095 mmol palladium acetate,
0.024 mmol tetrafluoroboric acid, and
0.0104 mmol 1,3-bis[bis(2-methoxyphenyl)phosphino]propane
on 8 g of a linear alternating carbon monoxide/ethene copolymer. The catalyst thus prepared was introduced into a stirred autoclave with a volume of 300 ml. After the air in the autoclave had been displaced by nitrogen,

forced in until a pressure of 55 bar was reached. During the polymerization the pressure was maintained at 55 bar by forcing in a 1:1 carbon monoxide/ethene mixture. After 10 hours the polymerization was terminated by cooling the reaction mixture to room temperature and releasing the pressure.

80.1 g copolymer was obtained. The polymerization rate was 7.1 kg copolymer/(g palladium.hour).

Example 2

A carbon monoxide/ethene copolymer was prepared in substantially the same way as in example 1, but with the following differences:

- a) the catalyst solution contained 0.19 mmol tetrafluoroboric acid instead of 0.024 mmol, and
- b) the reaction time was 4.3 hours instead of 10 hours.

30.2 g copolymer was obtained. The polymerization rate was 5.1 kg copolymer/(g palladium.hour).

Example 3

A carbon monoxide/ethene copolymer was prepared in substantially the same way as in example 1, but with the following differences:

- a) the catalyst solution contained 0.014 mmol hexafluorotitanic acid instead of tetrafluoroboric acid,
- b) the reaction temperature was 82 °C instead of 85 °C, and
- c) the reaction time was 4.3 hours instead of 10 hours.

34.1 g copolymer was obtained. The polymerization rate was 5.9 kg copolymer/(g palladium.hour).

following differences:

- a) the catalyst solution contained 0.19 mmol hexafluorotitanic acid instead of tetrafluoroboric acid, and
- b) the reaction time was 4.2 hours instead of 10 hours. 27.0 g copolymer was obtained. The polymerization rate was 4.5 kg copolymer/(g palladium.hour).

Example 5

A carbon monoxide/ethene copolymer was prepared in substantially the same way as in example 1, but with the following differences:

- a) the catalyst solution contained 0.028 mmol hexafluorophosphoric acid instead of tetrafluoroboric acid, and
- b) the reaction time was 4.5 hours instead of 10 hours. 28.4 g copolymer was obtained. The polymerization rate was 6.1 kg copolymer/(g palladium.hour).

Example 6

A carbon monoxide/ethene copolymer was prepared in substantially the same way as in example 1, but with the following differences:

- a) the catalyst solution contained 0.024 mmol hexafluoroantimonic acid instead of tetrafluoroboric acid, and
- b) the reaction time was 5.4 hours instead of 10 hours. 32.4 g copolymer was obtained. The polymerization rate was 4.5 kg copolymer/(g palladium.hour).

Example 7

A carbon monoxide/ethene copolymer was prepared in substantially the same way as in example 1, but with the following differences:

27. The reaction time was 6 hours instead of 10 hours.
15.6 g copolymer was obtained. The polymerization rate was 1.5 kg copolymer/(g palladium.hour).

Example 8

A carbon monoxide/ethene copolymer was prepared in substantially the same way as in example 1, but with the following differences:

- a) the catalyst solution contained 0.19 mmol methylsulphonic acid instead of tetrafluoroboric acid, and
- b) the reaction time was 4.8 hours instead of 10 hours.

10.9 g copolymer was obtained. The polymerization rate was 0.6 kg copolymer/(g palladium.hour).

Example 9

A carbon monoxide/ethene copolymer was prepared in substantially the same way as in example 1, but with the following differences:

- a) the catalyst solution contained 0.024 mmol para-toluenesulphonic acid instead of tetrafluoroboric acid, and
- b) the reaction time was 4.6 hours instead of 10 hours.

16.8 g copolymer was obtained. The polymerization rate was 1.9 kg copolymer/(g palladium.hour).

Example 10

A carbon monoxide/ethene copolymer was prepared in substantially the same way as in example 1, but with the following differences:

- a) the catalyst solution contained 0.19 mmol para-toluenesulphonic acid instead of tetrafluoroboric acid, and
- b) the reaction time was 4.6 hours instead of 10 hours.

carbon monoxide/ethene copolymer was prepared as follows. Into a stirred autoclave with a volume of 300 ml a catalyst solution was introduced containing 50 ml methanol, 0.1 mmol palladium acetate, 0.2 mmol methylsulphonic acid, and 0.15 mmol 1,3-bis[bis(2-methoxyphenyl)phosphino]propane. After the air in the autoclave had been displaced by nitrogen and the autoclave contents had been brought to 89°C, a 1:1 carbon monoxide/ethene mixture was forced in until a pressure of 55 bar was reached. During the polymerization the pressure was maintained at 55 bar by forcing in a 1:1 carbon monoxide/ethene mixture. After 2 hours the polymerization was terminated by cooling the reaction mixture to room temperature and releasing the pressure. The polymer was filtered off, washed with methanol and dried.

22.3 g copolymer was obtained. The polymerization rate was 10.5 kg copolymer/(g palladium.hour).

Example 12

A carbon monoxide/ethene copolymer was prepared in substantially the same way as in example 11, but with the following differences:

- a) the catalyst solution contained 0.19 mmol para-toluenesulphonic acid instead of methylsulphonic acid, and
- b) the reaction temperature was 88 °C instead of 89 °C.

19.5 g copolymer was obtained. The polymerization rate was 9.7 kg copolymer/(g palladium.hour).

Of the examples 1-12, examples 1-6 are according to the invention. In these examples, catalysts were used for the gas phase polymerization which contained a Lewis

strong organic acid as component b). In examples 7-10 gas phase polymerization was applied. Examples 11-12 relate to liquid phase polymerization.

Comparison of the results of examples 1-6 with those of examples 7-10 shows the gain in the polymerization rate which occurs if in the gas phase preparation of the polymers a strong organic acid in the catalyst is replaced by a Lewis acid/Brönsted acid mixture according to the invention.

Comparison of the results of examples 7 and 9 with those of examples 11 and 12 shows clearly the large influence that the polymerization method (gas phase or liquid phase) has on the polymerization activity of catalysts containing a strong organic acid as component b).

It was established by NMR analysis that the polymers prepared according to examples 1-12 were built up of linear chains in which the units from carbon monoxide and the units from ethene occurred in an alternating manner.

1. Process for the preparation of polymers of carbon monoxide with one or more olefinically unsaturated compounds in which polymers the units from carbon monoxide and the units from the olefinically unsaturated compounds are present in a substantially alternating arrangement, characterized by contacting the monomers at elevated temperature and pressure and substantially in the absence of a liquid non-polymerizable diluent with a catalyst comprising:

- a) a Group VIII metal compound,
- b) a Lewis acid/Brönsted acid mixture, and
- c) a dentate ligand containing at least two phosphorus-, nitrogen- or sulphur-containing dentate groups whereby the dentate ligand can complex with the Group VIII metal.

2. Process according to claim 1, characterized in that component b) of the catalyst contains 0.1-10 mol Brönsted acid per mol Lewis acid.

3. Process according to claim 1 or 2, characterized in that the Lewis acid in component b) of the catalyst is a fluoride.

4. Process according to claim 3, characterized in that the Lewis acid in component b) of the catalyst is selected from boron trifluoride, titanium tetrafluoride, phosphorus pentafluoride and antimony pentafluoride.

5. Process according to one or more of claims 1-4, characterized in that the Brönsted acid in component b) of the catalyst is hydrofluoric acid.

6. Process according to claim 5, characterized in that component b) of the catalyst is selected from

characterized in that component b, is present in the catalyst in such a quantity that the catalyst contains 0.5-200 mol of the Lewis acid per g.atom Group VIII metal.

8. Process according to one or more of claims 1-7, characterized in that the catalyst contains as component c) a compound of the general formula $(R^1)_2P-R-P(R^1)_2$ in which R^1 represents an optionally polar substituted hydrocarbyl group and R represents a divalent organic bridging group containing at least two carbon atoms in the bridge, in a quantity of 0.5-2 mol per g.atom Group VIII metal.

9. Process according to one or more of claims 1-8, characterized in that per mol of olefinically unsaturated compound to be polymerized a quantity of catalyst is used which contains 10^{-7} - 10^{-3} g.atom Group VIII metal, and that it is carried out at a temperature of 25-150 °C, a pressure of 2-150 bar and a molar ratio of the olefinically unsaturated compounds relative to carbon monoxide of 10:1 to 1:10.

10. Catalysts, characterized in that they comprise:

- a) a Group VIII metal compound,
- b) a Lewis acid/Brönsted acid mixture, and
- c) a dentate ligand containing at least two nitrogen- or sulphur-containing dentate groups through which the dentate ligand can complex with the Group VIII metal.

POLYMER PREPARATION

Process for the preparation of polymers of carbon monoxide with one or more olefinically unsaturated compounds in which polymers the units from carbon monoxide and the units from the olefinically unsaturated compounds are present in a substantially alternating arrangement, comprising contacting the monomers at elevated temperature and pressure and substantially in the absence of a liquid non-polymerizable diluent with a catalyst comprising:

- a) a Group VIII metal compound,
 - b) a Lewis acid/Brönsted acid mixture, and
 - c) a dentate ligand containing at least two phosphorus-, nitrogen- or sulphur-containing dentate groups
- whereby the dentate ligand can complex with the Group VIII metal.

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