

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 olefinically unsaturated compounds.

From European Patent Application No. 0,460,743 a process for
5 the preparation of copolymers of carbon monoxide and one or more
olefinically unsaturated compounds is known, which process
comprises contacting the monomers at an elevated temperature and
pressure in the presence of hydrogen and one or more aprotic polar
diluent, such as tetrahydrofuran (THF) or methyl ethyl ketone. The
10 most suitable catalyst is a catalyst composition containing a
Group VIII metal, preferably palladium, and a phosphorus bidentate
ligand. It was a generally accepted conception that this bidentate
ligand forms a complex with the Group VIII metal and that the molar
ratio of bidentate ligand to Group VIII metal should not exceed 1.5
15 and preferably should be about 1 in order to obtain optimum
activity of the catalyst. Moreover, it was generally believed that
at bidentate ligand/Group VIII metal molar ratios in excess of 1.5,
most or all of the catalytically active sites of the Group VIII
metal will have formed complexes with the phosphorus bidentate
20 ligand. This improves the stability of the catalyst composition,
but is detrimental to the catalytic activity.

It is therefore an object of the present invention to provide
a process for the preparation of copolymers of carbon monoxide and
olefinically unsaturated compounds, wherein a stable catalyst
25 composition comprising a Group VIII metal and a phosphorus
bidentate ligand is used and wherein the copolymer is prepared at
an excellent polymerization rate and with high selectivity.

Surprisingly, it was found that excellent polymerization rates
could be accomplished when using a catalyst composition comprising

a phosphorus bidentate ligand and a Group VIII metal in a molar ratio of more than one in the presence of hydrogen.

Accordingly, the present invention relates to a process for the preparation of copolymers of carbon monoxide and olefinically unsaturated compounds in the presence of an aprotic solvent and a catalyst system based on

- (a) a Group VIII metal,
- (b) an acid or an anion thereof having a pK_A of less than 2, and
- (c) a phosphorus bidentate ligand of the general formula $R^1R^2P-R-P-R^1R^2$, wherein R^1 and R^2 represent identical or different aliphatic alkyl groups and R is a divalent organic bridging group containing at least two carbon atoms in the bridge connecting the two phosphorus atoms,

characterized in that the copolymerization is carried out in the additional presence of hydrogen, while the molar ratio of catalyst component (c) to catalyst component (a) is in the range of from 1.5 to 10.

In principle, any olefinically unsaturated compound can be copolymerized with carbon monoxide according to the process of the present invention. The invention is particularly suitable for copolymerizing carbon monoxide and olefinically unsaturated compounds containing three or more carbon atoms. Hence, suitable unsaturated compounds are α -olefins, such as ethene, propene, 1-butene, 1-hexene, 1-octene, 1-dodecene and 1-hexadecene. However, olefinically unsaturated carboxylic acids, such as 10-undecenoic acid, or derivatives therefrom may also be used as comonomers of carbon monoxide. 1-Octene is a preferred α -olefin comonomer.

It was found that as a result of the hereinbefore specified process strictly alternating copolymers were prepared.

The solvent in which the copolymerization is conducted must be aprotic and may be polar or apolar. Suitable apolar, aprotic solvents are for instance aromatic hydrocarbons such as benzene and toluene. Suitable polar, aprotic solvents are aliphatic ketones such as acetone and methyl ketone, aliphatic carboxylic esters such as methyl acetate, ethyl acetate and methyl propionate, linear

ethers such as diglyme and cyclic ethers such as tetrahydrofuran (THF) and dioxan. Preferably, polar, aprotic solvents are used with THF and diglyme being most preferred.

The catalyst system to be used is based on

- 5 (a) a Group VIII metal,
(b) an acid or an anion thereof having a pK_A of less than 2, and
(c) a phosphorus bidentate ligand.

The Group VIII metals include the noble metals ruthenium, rhodium, palladium, osmium, iridium and platinum, as well as the
10 iron group metals iron, cobalt and nickel. Preferably, the Group VIII metal is selected from palladium, nickel and cobalt, with palladium being particularly preferred. The form in which the Group VIII metal is incorporated in the catalyst composition is not particularly relevant, but preferably said Group VIII metal is in
15 the form of a salt of a carboxylic acid with a Group VIII metal acetate being most preferred.

Component (b) of the catalyst system should be derived from an acid having a pK_A of less than 2. Examples of such acids are mineral acids such as sulphuric acid and perchloric acid, sulphonc
20 acids such as methanesulphonic acid, trifluoromethanesulphonic acid and p-toluenesulphonic acid, and halocarboxylic acids such as trichloroacetic acid, difluoroacetic acid and trifluoroacetic acid.

Preferably, trifluoromethanesulphonic acid or trifluoroacetic acid is used and most preferably, trifluoromethanesulphonic acid is
25 used. Said component (b) may be incorporated in the catalyst composition in the form of either an acid or a salt containing the anion of said acid.

The phosphorus bidentate ligands used as component (c) of the catalyst composition are of the general formula $R^1R^2P-R-P-R^1R^2$,
30 wherein R^1 and R^2 represent identical or different aliphatic alkyl groups, each alkyl group preferably having from 1 to 10, most preferably 2 to 6, carbon atoms, and R is a divalent organic bridging group containing at least two carbon atoms in the bridge connecting the two phosphorus atoms. Preferably, R^1 and R^2 are
35 primary alkyl groups such as ethyl, propyl or butyl with ethyl

being most preferred. The bridging group R may be any divalent organic group containing at least two carbon atoms. However, those bridging groups containing three or four carbon atoms are preferred. Examples of suitable bridging groups are the

5 -CH₂-CH₂-CH₂- group, the -CH₂-C(CH₃)₂-CH₂- group, the -CH₂-Si(CH₃)₂-CH₂- group, the -CH₂-CH₂-CH₂-CH₂- group and the -CH₂-C(CH₃)₂-C(CH₃)₂-CH₂- group. A very suitable phosphorus bidentate ligand is 1,3-bis(diethylphosphino)-propane.

As already discussed, it was generally accepted up to now that

10 the molar ratio of phosphorus bidentate ligand to Group VIII metal should preferably be less than 1.5 and more preferably about 1, as otherwise the catalytically active site of the Group VIII metal would be blocked by said bidentate ligand. However, it now has been found that excellent polymerization rates are obtained with said

15 molar ratio being in the range of from 1.5 to 10, preferably from 1.5 to 8, more preferably from 1.8 to 6 and most preferably in the range of from 2 to 5, while conducting the copolymerization in the additional presence of hydrogen. Under these conditions polymerization rates of 600 g/g Group VIII metal/hr or higher are

20 readily accomplished.

One of the essential features of the present invention is the fact that the copolymerization is carried out in the presence of hydrogen. Preferably, the hydrogen partial pressure during the copolymerization process is in the range of from 1 to 50 bar, while

25 a hydrogen partial pressure in the range of from 5 to 40 is even more preferred. Hydrogen may be added directly as a gas or may be generated in situ, for instance by the watergas shift reaction. The exact hydrogen partial pressure to be applied is determined by the desired molecular weight of the final copolymer. If a high

30 molecular weight copolymer is desired, the hydrogen partial pressure should be relatively low, while a relatively high hydrogen partial pressure leads to a final copolymer having a low molecular weight due to the terminating effect of hydrogen.

In a preferred embodiment of the present invention, the

35 copolymerization of carbon monoxide and olefinically unsaturated

compound is carried out in the additional presence of a protic compound. Suitable protic compounds are organic acids having a pK_A in the range of from 2 to 7, preferably 4 to 6. Preferred organic acids are carboxylic acids such as benzoic acid, acetic acid, 5 pivalic acid, adipic acid, iso-butyric acid and 2,4,6-trimethylbenzoic acid. Other suitable protic compounds are phenols such as pentachlorophenol and pentafluorophenol. Alcohols such as methanol and ethanol may also be used. Carboxylic acids are preferred and in particular linear carboxylic acids. A particularly preferred 10 carboxylic acid is acetic acid. The molar ratio of protic compound to Group VIII metal may vary within wide limits, but preferably is in the range of from 15 to 10,000, more preferably 25 to 5000 and most preferably 50 to 3500.

The quantity of catalyst composition used for preparing the 15 copolymers of carbon monoxide and the olefinically unsaturated compounds containing at least three carbon atoms may vary over a broad range. Preferably, per mol of olefinically unsaturated compound to be copolymerized, a catalyst composition comprising 10^{-5} - 10^{-1} millimoles (mmol) and in particular 10^{-4} - 10^{-2} mmol of 20 Group VIII metal is used.

The copolymerization is preferably carried out at a temperature of 25-150 °C and a pressure of 2-150 bar, while a temperature of 30-130 °C and a pressure of 5-100 bar is even more preferred.

25 The invention is further illustrated by the following examples without restricting the scope of the invention to these embodiments.

EXAMPLE 1

30 Into a stirred autoclave with a volume of 300 ml a catalyst solution was introduced consisting of:
50 ml diglyme,
0.25 mmol palladium acetate,
1.0 mmol trifluoromethanesulphonic acid, and
0.6 mmol 1,3-bis(diethylphosphino)-propane.

35 Subsequently, 260 mmol of 1-octene were introduced.

After air was removed from the autoclave, 30 bar of hydrogen and 30 bar of carbon monoxide were forced into the autoclave. The temperature was raised to 60 °C. After 1.0 hour the polymerization was terminated by cooling the reaction mixture to room temperature and releasing the pressure. The polymer was precipitated by adding methanol, filtrated, washed with methanol and dried.

20 g copolymer was obtained. The polymerization rate was 800 g copolymer/g Pd/hr.

EXAMPLE 2

- 10 A 1-octene/carbon monoxide copolymer was prepared in substantially the same way as in Example 1, but differing in that:
- 160 mmol of acetic acid was additionally introduced, together with the 260 mmol of 1-octene;
 - the hydrogen partial pressure was 10 bar;
 - 15 - the carbon monoxide partial pressure was 50 bar; and
 - the reaction time was 1.5 hours.

30 g copolymer was obtained. The polymerization rate was 900 g copolymer/g Pd/hr.

EXAMPLE 3

- 20 A 1-octene/carbon monoxide copolymer was prepared in substantially the same way as in Example 2, but differing in that:
- the hydrogen partial pressure was 30 bar;
 - the carbon monoxide partial pressure was 30 bar;
 - the temperature during polymerization was 50 °C; and
 - 25 - the reaction time was only 0.5 hour.

17 g copolymer was obtained. The polymerization rate was 1400 g copolymer/g Pd/hr.

EXAMPLE 4

- 30 A 1-octene/carbon monoxide copolymer was prepared in substantially the same way as in Example 2, but differing in that the hydrogen partial pressure was 1 bar and in that the reaction time was 1.0 hour.

19 g copolymer was obtained. The polymerization rate was 750 g copolymer/g Pd/hr.

EXAMPLE 5

A 1-octene/carbon monoxide copolymer was prepared in substantially the same way as in Example 2, but differing in that 89 mmol pivalic acid was added instead of acetic acid.

19 g copolymer was obtained. The polymerization rate was 500 g copolymer/g Pd/hr.

EXAMPLE 6

A 1-octene/carbon monoxide copolymer was prepared in substantially the same way as in Example 2, but differing in that 237 mmol methanol was added instead of acetic acid.

24 g copolymer was obtained. The polymerization rate was 650 g copolymer/g Pd/hr.

COMPARATIVE EXAMPLE 1

This comparative example was carried out in substantially the same way as Example 1, but differing in that no hydrogen was added.

No polymer material was formed after 5 hours.

COMPARATIVE EXAMPLE 2

This comparative example was carried out in substantially the same way as Example 2, but differing in that no hydrogen was added.

No polymer material was formed after 5 hours.

COMPARATIVE EXAMPLE 3

This comparative example was carried out in substantially the same way as Example 2, but differing in that 1,3-bis(diphenylphosphino)propane was used as the phosphorus bidentate ligand.

No polymer material was formed after 5 hours.

EXAMPLE 7

Into a stirred autoclave with a volume of 300 ml a catalyst solution was introduced consisting of:

50 ml toluene,

0.1 mmol palladium acetate,

0.5 mmol trifluoromethanesulphonic acid, and

0.25 mmol 1,3-bis(diethylphosphino)-propane.

Subsequently, 160 mmol of acetic acid and 260 mmol of 1-octene were introduced.

After air was removed from the autoclave, 10 bar of hydrogen and 50 bar of carbon monoxide were forced into the autoclave. The temperature was raised to 60 °C. After 1.5 hours the polymerization was terminated by cooling the reaction mixture to room temperature and releasing the pressure. The polymer was precipitated by adding methanol, filtrated, washed with methanol and dried.

13.5 g copolymer was obtained. The polymerization rate was 900 g copolymer/g Pd/hr.

EXAMPLE 8

A 1-octene/carbon monoxide copolymer was prepared in the same way as in Example 7, but differing in that 147 mmol of 10-undecenoic acid was used as the olefinically unsaturated monomer instead of 1-octene and in that diglyme was used as the solvent and the washing liquid instead of toluene.

22.5 g of copolymer was obtained. The polymerization rate was 1500 g copolymer/g Pd/hr.

EXAMPLE 9

A 1-octene/carbon monoxide copolymer was prepared in the same way as in Example 7, but differing in that 139 mmol of 1-hexadecene was used as the olefinically unsaturated monomer instead of 1-octene and in that tetrahydrofuran was used as the solvent and the washing liquid instead of toluene.

16.5 g of copolymer was obtained. The polymerization rate was 1100 g copolymer/g Pd/hr.

EXAMPLE 10

Into a stirred autoclave with a volume of 300 ml a catalyst solution was introduced consisting of:

50 ml THF,

0.1 mmol palladium acetate,

0.5 mmol trifluoromethanesulphonic acid, and

0.3 mmol 1,3-bis(diethylphosphino)-propane.

Subsequently, 160 mmol of acetic acid and 740 mmol of propene were introduced.

After air was removed from the autoclave, 10 bar of hydrogen and 50 bar of carbon monoxide were forced into the autoclave. The

temperature was raised to 60 °C. After 0.5 hours the polymerization was terminated by cooling the reaction mixture to room temperature and releasing the pressure. The polymer was precipitated by adding methanol, filtrated, washed with methanol and dried.

- 5 12.5 g copolymer was obtained. The polymerization rate was 2500 g copolymer/g Pd/hr.

C L A I M S

1. A process for the preparation of copolymers of carbon monoxide and olefinically unsaturated compounds in the presence of an aprotic solvent and a catalyst system based on
- (a) a Group VIII metal,
- 5 (b) an acid or an anion thereof having a pK_A of less than 2, and
- (c) a phosphorus bidentate ligand of the general formula $R^1R^2P-R-P-R^1R^2$, wherein R^1 and R^2 represent identical or different aliphatic alkyl groups and R is a divalent organic bridging group containing at least two carbon atoms in the
- 10 bridge connecting the two phosphorus atoms,
- characterized in that the copolymerization is carried out in the additional presence of hydrogen, while the molar ratio of catalyst component (c) to catalyst component (a) is in the range of from 1.5 to 10.
- 15 2. A process according to claim 1, characterized in that the hydrogen partial pressure is between 1 and 50 bar.
3. A process according to claim 2, characterized in that the hydrogen partial pressure is between 5 and 40 bar.
4. A process according to any one of the preceding claims,
- 20 characterized in that the molar ratio of catalyst component (c) to catalyst component (a) is in the range of from 1.5 to 8.
5. A process according to claim 4, characterized in that the molar ratio of catalyst component (c) to catalyst component (a) is in the range of from 2 to 5.
- 25 6. A process according to any one of the preceding claims, characterized in that the copolymerization is carried out in the additional presence of an organic acidic compound having a pK_A in the range of from 2 to 7.
7. A process according to claim 6, characterized in that the
- 30 organic acidic compound has a pK_A in the range of from 4 to 6.



8. A process according to claim 7, characterized in that the organic acidic compound is a carboxylic acid.
9. A process according to claim 8, characterized in that the carboxylic acid is acetic acid.
- 5 10. The process according to any one of claims 6 to 9, characterized in that the molar ratio of organic acid to Group VIII metal is in the range of from 25 to 5000.
11. A process as claimed in any one of claims 1 to 10, characterized in that the α -olefin comonomer is 1-octene.

THIS SHEET HAS BEEN
REPLACED

This Sheet Has Been Replaced



* C L M S *

A B S T R A C TPREPARATION OF COPOLYMERS OF CARBON MONOXIDE
AND OLEFINICALLY UNSATURATED COMPOUNDS

A process for the preparation of copolymers of carbon monoxide and olefinically unsaturated compounds in the presence of an aprotic solvent and a catalyst system based on

- (a) a Group VIII metal,
- (b) an acid or an anion thereof having a pK_A of less than 2, and
- (c) a phosphorus bidentate ligand of the general formula $R^1R^2P-R-P-R^1R^2$, wherein R^1 and R^2 represent identical or different aliphatic alkyl groups and R is a divalent organic bridging group containing at least two carbon atoms in the bridge connecting the two phosphorus atoms,

characterized in that the copolymerization is carried out in the additional presence of hydrogen, while the molar ratio of catalyst component (c) to catalyst component (a) is in the range of from 1 to 10.

8. A process according to claim 7, characterized in that the organic acidic compound is a carboxylic acid.
9. A process according to claim 8, characterized in that the carboxylic acid is acetic acid.
10. The process according to any one of claims 6 to 9, characterized in that the molar ratio of organic acid to Group VIII metal is in the range of from 25 to 5000.
11. A process as claimed in any one of claims 1 to 10, characterized in that the olefinically unsaturated compound is 1-octene.

