

PREPARATION OF CO-POLYMERS

The invention relates to a process for the preparation of co-polymers of carbon monoxide with one or more compounds containing an ethylenically unsaturated bond.

The preparation of linear co-polymers wherein units originating from carbon monoxide substantially alternate with units originating from the ethylenically unsaturated compound(s) is known from various publications in the patent literature.

A convenient preparation method is described in EP 181.014. According to this method, a mixture of carbon monoxide and an alkenically unsaturated hydrocarbon is polymerized in the presence of a catalyst, containing one of the Group VIII metals palladium, cobalt or nickel, an anion of a carboxylic acid with a pKa lower than 2 and a bidentate ligand containing two phosphorus, arsenic or antimony atoms.

The co-polymers, prepared according to this method and similar preparation procedures, have relatively high molecular weights and exhibit attractive mechanical properties. They are suitable to be used as thermoplastics for many outlets, such as films, fibres and sheets and shaped articles e.g. tubes, containers and car parts and for applications in the domestic sphere.

For obtaining co-polymers with optimal properties for the intended uses, it is generally preferred that variations in the average molecular weight of the co-polymers produced are kept to a minimum. It would therefore be advantageous to perform the co-polymerization under such conditions that the average molecular weight of the obtained product can be controlled during

the process and substantially maintained at the desired value. The average molecular weight of the co-polymers, calculated as number average (M_n), typically is 10,000 or more.

The higher the molecular weight, the higher will be in general the intrinsic viscosity of the co-polymers.

The intrinsic viscosity can be determined by dissolving the copolymers in m-cresol in different concentrations and measuring the viscosity of each solution at 60 °C. From the relative viscosities the inherent viscosities can be calculated and by extrapolating to a concentration of zero, the intrinsic viscosity in dl/g can be found. Instead of "intrinsic viscosity" the term LVN is used, viz "Limited Viscosity Number". The co-polymers typically have an LVN of between 0.8 and 2.0 dl/g.

In addition to the aforesaid co-polymers oligomers of carbon monoxide and ethylenically unsaturated compounds may be prepared and furthermore co-polymers of these monomers having a considerably lower LVN than the above mentioned thermoplastic co-polymers, e.g. in the range of 0.2 to 0.6 dl/g, have properties which make them useful for other applications than the indicated outlets for thermoplastic products.

They may be used as such, or as starting materials for the preparation of plastics, as blending components or as plasticizers for other polymers. It would therefore also be advantageous, if the co-polymerization process could be performed under such conditions that these products with lower average molecular weights, e.g. of 3000 or less, are the predominant reaction product.

It has been proposed to increase the temperature at which the co-polymerization is carried out. Although the formation of products with lower LVN's is thus enhanced, the stability of the catalyst system often become a



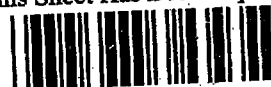
problem.

It has further been proposed to reduce the molecular weight of the produced co-polymers by addition of molecular hydrogen during the reaction. It has appeared, however, that with most catalyst systems, recommended for this process, a significant reduction in molecular weight only occurs by applying large amounts of hydrogen, say of 60 mol% or more, based on carbon monoxide. Apart from the unattractiveness of a high consumption of hydrogen, the use of large quantities of this gas often results in a reduction of the Group VIII metal component of the catalyst system, accompanied by a substantial inactivation thereof. Only in exceptional cases, by selecting specific ligands for the catalyst system, the intended reduction in molecular weight of the co-polymers can be achieved, without impairing the catalytic activity of the system.

According to the co-pending patent application (T 1862) an adequate control of the average molecular weight of the formed co-polymers is achieved and, if desired, products having relatively low molecular weights can be produced, by carrying out the co-polymerization reaction in the presence of a minor amount of a compound containing a hydride moiety.

It has now been found that these aims can also be achieved by using a catalyst system, based on palladium and a bidentate bisphosphine ligand in the additional presence of a compound containing a 1-alkenyl substituted aryl group.

The invention may be defined as relating to a process for the preparation of co-polymers of carbon monoxide and one or more ethylenically unsaturated non-aromatic compounds by contacting the monomers, under polymerization conditions with a catalyst system based on palladium, a bisphosphine ligand and a source of anions,



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being the conjugated base of acids having a pKa of less than 4, in the additional presence of a 1-alkenyl substituted aryl group containing compound (compound A).

The amount of compound A may vary within a relatively wide range. Depending on the prevailing co-polymerization conditions, the optimal amount of compound A can be readily selected by those skilled in the art.

Related to the amount of palladium in the catalyst system the quantity of compound A is usually in the range of 10 to 10^7 moles per gramatom of palladium, preferably in the range of 10^2 to 10^6 on the same basis.

Related to the non-aromatic ethylenically unsaturated compound(s), the amount of compound A may be substantially equimolar or even in excess.

Without wishing to be bound by any theoretical explanation of the reaction mechanism, it is considered likely that during the co-polymerization reaction a molecule of compound A combines with the catalyst thus preventing that a further molecule of the ethylenically unsaturated compound reacts with the catalyst. The growth of the chain of the co-polymer molecule is thereby interrupted and one of the end groups of the resulting reaction product will be derived from compound A.

Compound A can be any compound containing a 1-alkenyl substituted aryl group, such as 1-alkenylbenzenes, 1-alkenylindenes, 1-alkenyl-naphthalenes and 1-alkenyl-anthracenes. Suitable examples include vinylbenzenes, 1-propenylbenzenes, 1-butenylbenzenes and vinyl-naphthalenes. Preferably, compound A is a vinylsubstituted aromatic compound, more preferably a vinyl benzene.

The aryl group of compound A may be substituted by one or more, usually non-bulky substituents. Suitable substituents include halogen atoms, such as fluorine, chlorine and bromine atoms, alkoxy groups having from 1



to 4 carbon atoms, and hydrocarbyl groups, in particular alkyl groups having from 1 to 4 carbon atoms. Two hydrocarbyl substituents linked to adjacent ring carbon atoms of the aryl group may, together with the said ring atoms, form a cyclic structure.

Examples of suitable compounds A are p-chlorostyrene, p-methoxystyrene and p-methylstyrene.

If desired, compound A may be supplied to the reactor separately, or together with any of the other reactants or with the catalyst system. Preferably, compound A is supplied in portions or continuously during the copolymerization reaction, as this facilitates the control of the molecular weight of the final reaction product.

In the catalyst systems used in the process of the invention, palladium is substantially present as palladium cations. Conveniently, palladium is introduced in the form of a palladium-salt, e.g. a salt of a mineral acid such as sulphuric acid or nitric acid or of a sulphonic acid such as methylsulphonic acid or p-toluenesulphonic acid. Preferably a palladium salt of a carboxylic acid is used, e.g. of a carboxylic acid having from 2 to 6 carbon atoms. A preferred palladium-carboxylate is palladium (II) acetate.

The catalyst system further comprises a bisphosphine ligand, whereby two phosphorus atoms can form a complexing bond with palladium. It is considered that the stability of the catalyst system is significantly enhanced by the presence of these two complexing sites.

Preferred bisphosphine ligands may be represented by the formula $R^1R^2PRPR^3R^4$ (I) wherein each of R^1 , R^2 , R^3 and R^4 independently represents a substituted or non-substituted hydrocarbyl group and R represents a bivalent, organic bridging group containing at least two atoms in the bridge.

R^1 , R^2 , R^3 and R^4 may independently represent

optionally substituted aryl, alkaryl, aralkyl or alkyl groups. Preferably they represent aryl groups optionally substituted with one or more polar substituents. Suitable substituents may be selected from the group consisting of halogen atoms, alkoxy groups and (alkyl) amino groups. Preferably at least one of R^1 , R^2 , R^3 and R^4 represents a phenyl group substituted at one or both ortho positions with respect to the phosphorus atom to which the phenyl group is linked, by an alkoxy group, having 1 to 4 carbon atoms in particular a methoxy or ethoxy group.

Ligands in which R^1 , R^2 , R^3 and R^4 have the same meaning, are preferred, inter alia because the preparation is less complicated than that of bisphosphines wherein R^1 , R^2 , R^3 and R^4 are different.

The bivalent organic group, preferably contains from 2 to 4 atoms in the bridge, at least two of which are carbon atoms. Examples of suitable bridging groups are: $-\text{CH}_2-\text{CH}_2-$; $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$; $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$; $-\text{CH}_2-\text{O}-\text{CH}_2-$; $-\text{CH}_2-\text{Si}(\text{CH}_3)_2-\text{CH}_2-$ and $-\text{CH}_2-\text{C}(\text{CH}_3)_2-\text{CH}_2-$.

The catalyst systems of the invention moreover comprise a source of anions, being the conjugated base of acids having a pK_a of less than 4, preferably less than 2.

Examples of suitable acids are mineral acids such as perchloric acid and tetrafluoroboric acid, and sulphonic acids, such as p-toluenesulphonic acid, methanesulphonic acid and trifluoromethanesulphonic acid.

The amount of catalyst used in the process of the invention may vary considerably. Advantageously the catalyst is applied in an amount in the range of 10^{-7} to 10^{-1} gramatoms of palladium per mole of non-aromatic ethylenically unsaturated compound. Preferably this amount is in the range of 10^{-6} to 10^{-2} gramatoms of palladium per mole of ethylenically unsaturated compound.

In the process of the invention the monomers are on

the one hand carbon monoxide and on the other one or more non-aromatic ethylenically unsaturated compounds.

Preferably the latter are hydrocarbons, in particular alkenes having from 2 to 12 carbon atoms per molecule. Examples are ethene, propene, octene-1, cyclopentene and decene-1.

If desired, monomers, which in addition to carbon and hydrogen atoms, comprise heteroatoms, such as oxygen or nitrogen atoms may be used as well. If a single non-aromatic, ethylenically unsaturated compound is reacted with carbon monoxide, co-polymers are formed in the chains of which two alternating groups occur. In order to modify the properties of the polymeric product, ter-polymers may be prepared whereby carbon monoxide is co-polymerized with two different ethylenically unsaturated compounds (X_1 and X_2). With non-aromatic ethylenically unsaturated compounds, terpolymers are formed whereby the polymer chain is composed of groups $-CO-X_1'-$ and groups $-CO-X_2'-$ which are randomly distributed over the chain, X_1' and X_2' being bivalent moieties derived from the ethylenically unsaturated compounds X_1 and X_2 , respectively. In this connection reference is made to US Patent No. 4,880,903.

It has been established that for preparing ter-polymers, whereby one of the organic monomers contains aromatic unsaturation, as a rule special measures are required such as the use of catalyst systems, containing ligands other than bisphosphines.

In the process of the invention preferred starting materials are lower mono olefins, in particular ethene, and mixtures thereof, in particular a mixture of ethene and propene.

The molar ratio between the monomers, i.e. on the one hand carbon monoxide and on the other the ethylenically unsaturated compound(s), is usually selected in the range

from 1:5 to 5:1. Preferably the molar ratio is in the range of 1:1.5 to 1.5:1, substantially equimolar ratios being most preferred.

The process of the invention is conveniently carried out in the presence of a liquid diluent. A polar as well as polar diluents are suitable, such as pentane and acetone. Protic diluents are preferred, for example lower alcohols having from 1 to 5 carbon atoms such as methanol or 1-butanol.

The temperature at which the co-polymerization reaction is carried out, is generally in the range of 30 to 170 °C. Preferably the temperature is selected in the range of 60 to 130 °C.

Suitable reaction pressures are within the range of 2 to 150 bar, pressures outside this range not being precluded. Preferably the pressure is in the range of 5 to 100 bar.

The invention is further illustrated with the following examples.

Example I

A co-polymer of carbon monoxide and ethene was prepared as follows:

A 250 ml mechanically stirred reactor was charged with 150 ml of methanol and 61.25 mmol of styrene. In order to remove the air, the autoclave was pressurised with a equimolar ethene/carbon monoxide mixture to 40 bar, whereupon the pressure was released. This procedure was repeated twice, Subsequently, the temperature was raised to 95 °C. and an equimolar mixture of ethene and carbon monoxide was supplied until the pressure was 55 bar. Finally, a catalyst solution was added consisting of 0.0123 mmol of palladium (II) acetate, 0.0130 mmol of 1,3-bis(diphenylphosphino)propane and 0.0379 mmol of p-toluenesulphonic acid in 4 ml of acetone.

After a reaction period of 1.02 h the polymerisation was terminated by cooling the reactor contents to ambient temperature and by releasing the pressure. The product was filtered off, washed twice with methanol and once with acetone and dried in vacuo at 50 °C.

10.7 g of polymer was obtained, the average polymerisation rate being 8.0 kg product per g of palladium per hour. The average molecular weight determined by end group analysis using ^{13}C NMR spectrometry was 3100. The end group analysis showed that ethyl, methyl, ester, stytyl and phenethyl end groups had been formed.

The reaction period and the results are shown in the Table.

Example II

A co-polymer of carbon monoxide and ethene was prepared, substantially as described in Example I with the following differences:

- i) 61.44 mmoles of 4-methylstyrene were applied, instead of 61.25 mmoles of styrene;
- ii) the reaction period was 1.03 hours instead of 1.02 hours.

The results are shown in the Table.

Example III

A co-polymer of carbon monoxide and ethene was prepared, substantially as described in Example I with the following differences:

- i) 61.49 mmoles of 4-methoxystyrene were applied, instead of 61.25 mmoles of styrene;
- ii) the reaction period was 1.05 hours, instead of 1.02 hours.

The results are shown in the Table.

Example IV

A co-polymer of carbon monoxide and ethene was prepared, substantially as described in Example I, with

the following differences:

- i) 61.2 mmols of 4-fluorostyrene were applied, instead of 61.25 mmols of styrene;
- ii) 0.0122 mmols of palladium (II) acetate were applied, instead of 0.0123 mmols;
- iii) the amount of p-toluenesulphonic acid was 0.0277 mmols instead of 0.0278 mmols.
- iv) the reaction period was 1.07 hours, instead of 1.02 hours.

The results are shown in the Table.

Example V

A co-polymer of carbon monoxide and ethene was prepared, substantially as described in Example IV, with the following differences:

- i) 61.19 mmols of 4-bromostyrene were applied, instead of 61.2 mmols of 4-fluorostyrene;
- ii) the reaction period was 0.97 hours, instead of 1.07 hours.

The results are shown in the Table.

Example VI

A co-polymer of carbon monoxide and ethene was prepared, substantially as described in Example I, with the following differences:

- i) 32.5 mmols of 2-vinylnaphthalene were applied, instead of 61.25 mmols of styrene;
- ii) 154 ml of methanol, instead of 150 ml were used;
- iii) 0.0189 mmols of palladium (II) acetate were applied, instead of 0.0123 mmols;
- iv) 0.0203 mmols of 1,3-bis(diphenylphosphino)propane were applied, instead of 0.0130 mmols;
- v) the amount of p-toluenesulphonic acid was 0.0444 mmols, instead of 0.0279 mmols;
- vi) the reaction period was 8.10 hours, instead of 1.02 hours.

The results are shown in the Table.

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

A co-polymer of carbon monoxide and ethene was prepared, substantially as described in Example I, with the following differences:

- i) no 1-alkenylaryl compound was added;
- ii) the reaction period was 0.95 hours, instead of 1.02 hours.

The results are shown in the Table.

TABLE

Example No.	1-Alkenylaryl compound	Reaction time (hrs)	Yield (g)	Rate (Kg/g Pd.h)	Degree of polymerization	Aver. mol. weight (M_n)
I	styrene	1.02	10.7	8.0	54	3100
id (duplo)	"	1.03	11.18	8.3	46	2600
II	4-methylstyrene	1.03	6.64	4.9	42	2400
id (duplo)	"	1.02	5.33	4.0	40	2300
III	4-methoxystyrene	1.05	5.19	3.8	42	2400
id (duplo)	"	1.05	5.58	4.1	43	2500
IV	4-fluorostyrene	1.07	13.55	9.7	48	2700
id (duplo)	"	1.07	11.99	8.6	64	3600
V	4-bromostyrene	0.97	5.86	4.6	52	3000
id (duplo)	"	1.12	9.98	6.8	77	4400
VI	2-vinylnaphthalene	8.10	3.20	0.2	53	3000
A	-	0.95	12.99	10.4	100	5600



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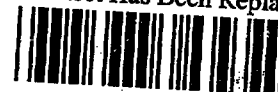
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1. A process for the preparation of co-polymers of carbon monoxide and one or more ethylenically unsaturated non-aromatic compounds by contacting the monomers, under polymerization conditions, with a catalyst system based on palladium, a bisphosphine ligand and a source of anions, being the conjugated base of acids having a pKa of less than 4, in the additional presence of a 1-alkenyl substituted aryl group containing compound (compound A).
2. A process as claimed in claim 1, characterized in that compound A is a vinyl substituted aromatic compound, preferably a vinyl benzene.
3. A process as claimed in claim 2, characterized in that compound A is a vinyl benzene substituted with one or more substituents selected from the group consisting of halogen atoms, alkyl groups with 1 to 4 carbon atoms and alkoxy groups with 1 to 4 carbon atoms, preferably one halogen atom, one alkyl group with 1 to 4 carbon atoms, or one alkoxy group with 1 to 4 carbon atoms.
4. A process as claimed in any one of claims 1 to 3, characterized in that the catalyst system comprises palladium (II) acetate.
5. A process as claimed in any of claims 1-4, characterized in that the catalyst system comprises a bisphosphine ligand of the formula
$$R^1R^2PRPR^3R^4 \quad (I)$$
wherein each of R^1 , R^2 , R^3 and R^4 independently represents a substituted or non-substituted hydrocarbyl group and R represents a bivalent organic bridging group containing at least two atoms in the bridge.
6. A process as claimed in claim 5, characterized in that in the bisphosphine ligand of formula (I) at least

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one of R^1 , R^2 , R^3 and R^4 represents a phenyl group substituted by a polar group, in particular an alkoxy group with 1 or 2 carbon atoms, at one or both ortho positions with respect to the phosphorus atom to which the phenyl group is linked.

7. A process as claimed in any of claims 1 to 6, characterized in that the amount of catalyst is such that per mole of ethylenically unsaturated compound to be copolymerized, 10^{-6} to 10^{-2} gramatoms of palladium are present.

8. A process as claimed in any of claims 1-7, characterized in that as non-aromatic ethylenically unsaturated compounds ethene or a mixture of ethene and propene is used.

9. A process as claimed in any of claims 1-8, characterized in that the molar ratio between carbon monoxide on the one hand and the non-aromatic ethylenically unsaturated compound(s) on the other, is in the range from 1.5:1 to 1:1.5.

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