

A POLYMERIZATION PROCESS

The invention relates to a process for the polymerization of ethene and optionally one or more other olefin monomers. The invention is especially related to a polymerization process of ethene, a (functionalized) cyclic olefin monomer and optionally a further olefin monomer in which a cyclic olefin copolymer or a cyclic olefin terpolymer is prepared. The invention is also related to a novel class of functionalized cyclic olefin copolymers which can be prepared by this process. The invention is furthermore directed to various uses of the novel class of functionalized cyclic olefin copolymers obtainable by this process.

In the state of the art are known polymerization processes to prepare cyclic olefin copolymers or cyclic olefin terpolymers of ethylene; nevertheless, oligomeric products having low molecular weight or products with only low amounts of cyclomonomers are often obtained. The term "COC" or "COCs" in this description refers to both cyclic olefin copolymers and cyclic olefin terpolymers; the term "COC" or "COCs" also refers to polymers of four or more different monomers including a cyclic olefin monomer.

Another disadvantage of the prior art processes is that they do not allow the preparation of high number average molecular weight functionalized COCs, containing heteroatoms such as for example halogen, oxygen, nitrogen, phosphorus or sulphur atom. It is difficult with prior art processes to polymerize functionalized monomers, because these monomers will interact with the catalyst resulting in a decrease of catalytic activity and a low number average molecular weight of the polymer.

Both the need for COCs having functional substituents into the hydrocarbon polymer backbones, as well as the difficulty to prepare the same is described for instance in WO-A-9720871, which describes the preparation of addition polymers of (poly)cycloalkenes having pendant silyl functional groups. However, these polymers are made by addition homopolymerization of the cyclic olefin monomer, whereas the non-cyclic monomer mainly acts as a chain transfer agent. The resulting polymer consists almost only of cyclic monomer and will therefore have a high glass transition temperature, which makes the polymer difficult to process.

JP-A-10007736 discloses a method for preparing a cyclic olefin copolymer having improved surface properties, such as adhesive properties. The method involves a polymerization step to obtain a polymer having good chemical reactivity and a subsequent step, such as graft

modification. The disadvantage of this method is that the product having the desired surface properties is obtained in two steps. Another disadvantage is that complex cyclic monomers have to be used in order to obtain a cyclic olefin copolymer having the desired chemical reactivity.

US-A-4 855 399 describes the copolymerization of carbon monoxide and a olefinic hydrocarbon, such as ethene using a catalyst system consisting of palladium and ortho-(diphenylphosphino)benzenesulfonic acid as a ligand. According to the description the phenyl groups could be further substituted. No indication is given in this document that such a further substituted catalyst would be a suitable olefin polymerization catalyst.

The European patent application EP-A-589,527 describes the copolymerization of ethene and 5-norbornene-2,3-dicarboxylic acid anhydride in the presence of a catalyst system consisting of palladiumacetate and ortho-diphenylphosphinobenzene sulphonic acid; the obtained product is an oligomeric product, having a number average molecular weight of 2700, only 5 mol% of the cyclic olefin monomer being built in.

Therefore, it would be desirable to have a catalyst system for the production of copolymers of ethene and cyclic olefins, optionally functionalized with polar groups, having acceptable Number average molecular weights and an acceptable content of cyclic olefin units.

An object of the present invention is a process for the polymerization of ethene and optionally one or more other olefinic monomers, in which a polymerization product is obtained having a higher number average molecular weight and in which the polymerization is performed at a higher rate. This object is achieved by the below described polymerization process.

Therefore, it is an object of the present invention a process for the polymerization of ethene and optionally one or more other olefin monomers comprising contacting they monomer(s) under polymerization conditions with a catalyst system obtainable by combining:

- (a) a palladium, nickel or platinum ion,
- (b) an anion derived from an acid having a pKa of less than 3, and containing an atom of Group V A of the Periodic Table of Elements, wherein the Group V A atom is substituted with at least one aryl group, said aryl group being substituted with a polar group on the ortho position.

In this specification, the expression "polar functionality" or "polar group" is used to indicate

that the bond between the functional group and the remainder of the molecule has a dipole moment that is larger than that of a carbon-hydrogen bond, typically as the result of a bond between a carbon atom and a heteroatom such as a nitrogen, oxygen or sulfur atom.

It has been found that high number average molecular weight polymerization products can be prepared, at a high rate, by using the process according to the invention.

The expression "number average molecular weight", unless otherwise indicated, refers to number average molecular weight (M_n). With "high number average molecular weight" is here meant a number average molecular weight of above about 10,000 (M_n).

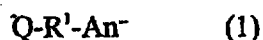
A further advantage of the process of the invention is that it does not require the use of large amounts of co-catalyst or expensive non-coordinating anions, which are commonly used in Ziegler-Natta or metallocene catalyzed polymerization processes known in the state of the art.

It has further been found that the polymerization process according to the present invention can be advantageously used to prepare cyclic olefin copolymers or cyclic olefin terpolymers, having a higher number average molecular weight, starting from ethene, a cyclic olefin monomer and optionally a third olefin monomer.

A special feature of the invention is that COCs containing an heteroatom, for example a halogen, oxygen, nitrogen, phosphorus or sulphur atom, with a high number average molecular weight, can be prepared with this polymerization process. As already mentioned above, by means of the polymerization processes known in the state of the art it was not possible to prepare high number average molecular weight functionalized COCs.

The catalyst system used in the process of the invention comprises a palladium, nickel or platinum ion; preferably a palladium ion is used. Suitable sources of these ions are the corresponding salts or acids; suitable palladium cations are described for instance in EP-A-0,589,527. The catalyst will be described below in more detail for the preferred metal palladium; it should be evident that for palladium also nickel and/or platinum can be read.

A preferred class of anions, as defined under b) can be indicated by the general formula (1):



Wherein Q is a group containing an atom of Group V A of the Periodic Table, wherein said atom of Group V A is further substituted with one or two aryl groups, said aryl groups being

substituted with a polar group on the ortho position; An^- is an anionic moiety; and R^1 is a bridging group connecting the said atom of Group V A with said An^- .

Suitable anionic moieties $-An^-$ are for example $-SO_3^-$, $-COO^-$, $-PO_3^-$ and $-AsO_3^-$ groups. Of these, the $-SO_3^-$ group is particularly preferred.

In order to fulfill the requirement of a pK_a of less than 3, in some cases acidity-promoting bridging groups R^1 are present, for example haloalkylidene or haloaryl groups, in particular a $-CCl_2-$ group, a $-CF_2-$ group or a divalent phenyl group substituted with fluoro atoms. Examples of acids containing acidity-promoting groups are acids of formula (1), wherein R^1An^- is $-CCl_2-COO^-$, $CF_2-SO_3^-$, $-CClF-SO_3^-$, 2-carboxylato 3,4,5,6-tetrafluoro-phenyl and $-CF_2-COO^-$.

The anion as defined above under b) contains an atom of Group V A of the Periodic Table, suitably nitrogen, phosphorus, arsenic or antimony; preferably the anion contains a phosphorus atom. If desired, anions may be used containing more than 1 atom of Group V A, for example a phosphorus and a nitrogen atom, or two phosphorus atoms; it is essential, however, that the anion contains one atom of Group V A which is capable of complexing with palladium in the catalyst system, while preferably the other atom of Group V A is not capable of complexing with the same palladium metal ion.

The Group V A atom, in particular the phosphorus atom, is linked via a bridging group R^1 to An^- . In order to fulfill the requirement that the Group V A atom is indeed capable of complexing with palladium in the catalyst system, the size and structure of the bridging group R^1 has been found to be important. Here below an anion wherein the Group V A atom is phosphorus will be further described. It should be evident that for phosphorus also nitrogen, arsenic and antimony can be read.

It is recommended that the bridging group R^1 of the anion according to formula (1) comprises from 1 to 3 atoms, preferably at most two atoms, in the bridge. With the bridge is here meant the shortest chain of atoms connecting the anionic moiety An^- and the phosphorus atom. In particular bridging groups are recommended containing one or two carbon atoms in the bridge, suitable bridging groups being for example $-CH_2-$, $-CH_2-CH_2-$, $-CF_2-$, $-CHCl-$, $-CCl_2-$, $-C(CH_3)_2-$, $-CH_2-CF_2-$ and $-CF_2-CF_2-$ groups.

The bridging atoms, in particular if one or more bridging atoms are carbon atoms, may form

part of cyclic structures, such as cycloalkyl groups, heterocyclic groups, or preferably aromatic groups, such as phenyl-, naphthyl-, indenyl- or fluorenyl groups. Preferably bridging group R^1 is an aryl group in which a sulphonato group is substituted on one of the two first possible adjacent carbon atoms on the ring relative to the bond between R^1 and the phosphorus atom (Q). Because this enables the phosphorus atom (Q) and the sulphonato group (An^-) to complex readily with the same palladium atom in the catalyst system. When R^1 is a phenylene group the sulphonato group is thus preferably in the ortho position, and when R^1 is a naphthalene group the sulphonato group is thus preferably substituted on the 8 or more preferably on the 2-position. Bridging group R^1 may be further substituted, for example with C_1 - C_{12} alkyl groups or C_1 - C_{12} alkoxy groups.

The phosphorus atom of the anion according to formula (1) is substituted with one or two aryl groups, said aryl groups being substituted with a polar group in the ortho position. These aryl groups, that will be further referred to as R^2 and R^3 , suitably comprise 6-18 carbon atoms. Exemplary aryl groups are phenyl, naphthyl, phenanthrenyl or anthracenyl. Preferably R^2 and/or R^3 are phenyl or naphthyl groups.

If the phosphorus is only substituted with one polar substituted aryl group, the other group may be the corresponding non-substituted aryl group or for example, be an organic group containing nitrogen, phosphorus, arsenic and/or antimony atoms, provided that these atoms are not capable of complexing with the same palladium metal ion as the phosphorus atom (Q) of the anion. Preferably the phosphorus atom (Q) is substituted with two aryl groups which are both substituted with a polar group in the ortho position. With "ortho position" is here meant one of the two first possible positions on the ring adjacent to the carbon atom which is bond to the phosphorus atom (Q). For example when a phenyl group is used the polar group is substituted on the ortho position relative to the phosphorus atom, and when a naphthyl group is used the polar group may be substituted on the 8-position, and preferably on the 2-position.

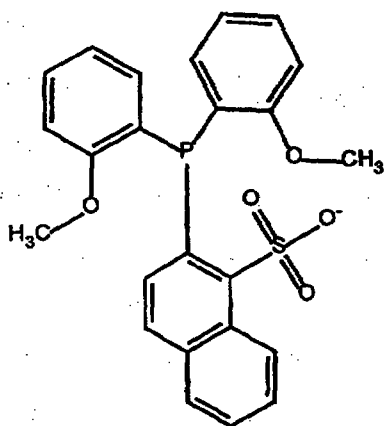
The polar group substituted on the groups R^2 and/or R^3 is preferably hydroxy-, cyano, amino-, alkylamino-, alkoxy-, thio ether- or carbonyl group, for example carboxyl group. Suitably, the afore mentioned organic group may contain 1 to 10 carbon atoms. More preferred is an alkoxy group having preferably 1-10 carbon atoms. Examples are methoxy, ethoxy,

propanoxy and isoproxy. Most preferred polar group is the methoxy group.

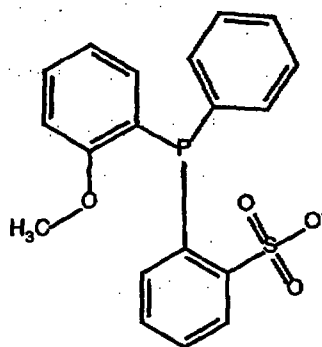
The groups R^1 , R^2 and R^3 may optionally be further substituted, for example with alkyl groups having 1 to 20 carbon atoms or with polar groups. Examples of possible alkyl groups are methyl, ethyl, isopropyl and dodecyl. Examples of suitable polar groups are the earlier described polar groups.

A preferred catalyst system according to the process of the invention comprises palladium and an anion having formula $An^-R^1R^2R^3P$, wherein R^1 is an phenyl group substituted by a sulfonate anion group, and R^2 and R^3 are ortho substituted phenyl groups, or 2- or 8-substituted naphthalene groups, wherein the substituent is a polar group, preferably a methoxy group.

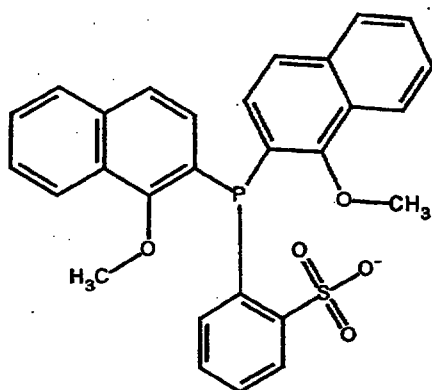
Examples of particularly suitable anions are di(ortho-methoxyphenyl)phosphino-benzenesulfonate and di(ortho-methoxyphenyl)phosphino p-tolylsulfonate. Other examples include:



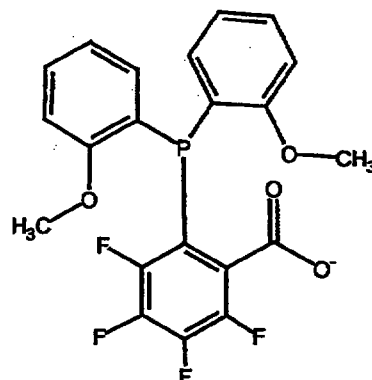
(2)



(3)



(4)



(5)

The anion can be prepared by generally known methods.

The catalyst system of the process according to the present invention may suitably be prepared separately, by combining a source of palladium cations or a precursor thereof and the anions as defined above under b) as a salt or as the acid, if desired in the presence of a suitable solvent, before supplying the monomer(s) to be polymerized. It is also possible to prepare the catalyst in situ, by introducing the catalyst components into the reactor and at the same time adding the monomer(s) and any other compound to be present in the reaction medium.

Examples of suitable metal sources are palladium(II)acetate, palladium(II)decanoate, chloro(1,5-cyclooctadiene)methyl-palladium(II), (1,5-cyclooctadiene)dimethyl-palladium (II), tris(dibenzylideneacetone)palladium(0) or nickel(II)acetate, bis(1,5-cyclooctadiene)nickel(0) and tris(tetramethyl-divinyl-disiloxane)-bis-palladium.

The molar ratio of the palladium, nickel or platinum metal ion and the anion is suitably comprised between 1:1 and 1:100, and more preferably between 1:1 and 1:5.

The process according to the invention can be used for the polymerization of ethene. Preferably ethene is polymerized with one or more other olefinic monomers, optionally functionalized. Examples of said olefinic monomers are propene, butene, styrene, 4-methoxy styrene and 3-buten-1-ol.

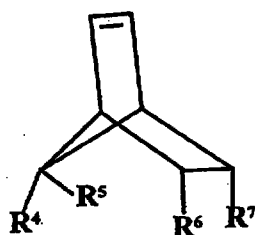
According to a preferred embodiment of the process of the invention, ethene is polymerized with a cyclic olefin monomer. In a most preferred embodiment of the invention, ethene is

polymerized with a functionalized cyclic olefin monomer and optionally with a third olefin monomer. Said third olefin monomer can be for example propene or butene, and preferably is a non-functionalized cyclic olefin; said non-functionalized cyclic olefin preferably corresponds to the functionalized cyclic olefin, without the functional group. An example of non-functionalized cyclic olefin is norbornene.

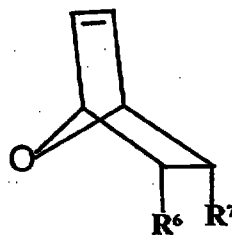
As already reported in the prior art description, it is difficult with prior art processes to polymerize functionalized monomers, because these monomers will interact with the catalyst resulting in a decrease of catalytic activity and a low number average molecular weight of the polymer.

Applicant has now found that ethene and a functionalized cyclic monomer and optionally a third monomer olefin can be polymerized to high number average molecular weight cyclic olefin copolymer products, without such a decrease in catalytic activity. With the process of the invention, high number average molecular weight functionalized polymer products can be obtained, comprising a heteroatoms, for example halogen, oxygen, nitrogen, phosphorus or sulphur atoms.

The functionalized cyclic olefin monomers which are preferably used in the process according to the invention can be described by the following formulas (6) and (7):



(6)



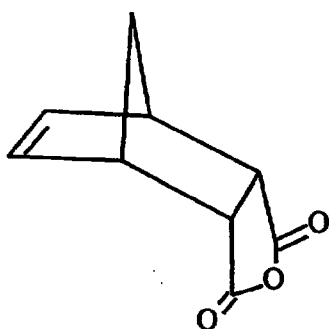
(7)

wherein R^4 , R^5 , R^6 and R^7 , the same or different from each other, are hydrogen, hydrocarbon or heteroatom containing groups, and wherein, in formula (6), at least one of the groups R^4 , R^5 , R^6 and R^7 is a heteroatom containing group.

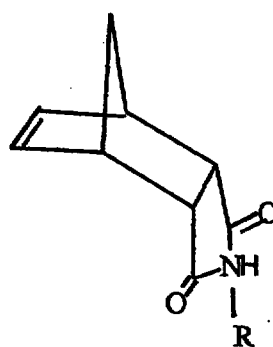
Suitable hydrocarbon groups are C_1 - C_{20} alkyl groups or C_6 - C_{12} aryl groups.

Said heteroatom containing group may contain halogen, oxygen, nitrogen, phosphorus or sulphur atoms as the heteroatom. Examples of suitable heteroatom containing groups are polar groups, for example ester-, ether-, carboxylic acid-, acid-, alcohol-, keto-, carbonyl-, cyano-, amine- or amide groups or halogen atoms.

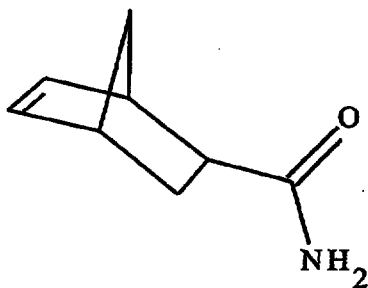
The (functionalized) cyclic olefin can be prepared by the Diels-Alder reaction (a [4+2] cycloaddition) wherein CPD (cyclopentadiene) is used as diene. functionalized cyclic olefins are made in a similar manner, i.e. by cycloaddition of CPD with a heterodienophile. Examples of such heterodienophiles are e.g. diethyl azodicarboxylate, aldehyde, maleic anhydride, dihydrofuran, vinylpyridine, alkyl acrylate or a substituted olefin as mentioned above (cf. "Heterocyclic Chemistry" by TL Gilchrist, Chapter 4.3.3, 1985). Below formulas (8a-8h) are examples of suitable functionalized cyclic olefins wherein $n=1-20$ and R is an alkyl group having 1-20 carbon atoms.



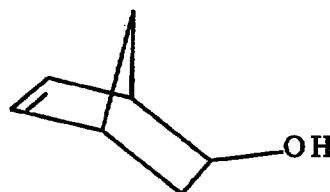
(8a)



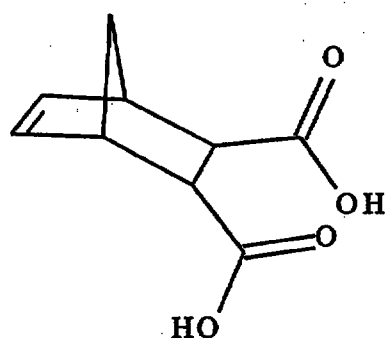
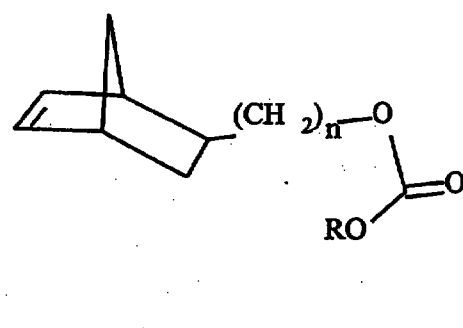
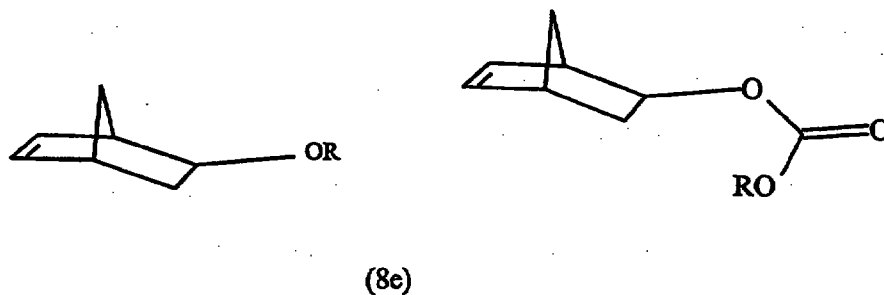
(8b)



(8c)



(8d)



If desired, the process of the invention may be carried out in the presence of a suitable solvent; examples of suitable solvents are hydrocarbons, aromatics, alcohols, ethers, esters and ketones. An excess of one of the monomers, provided this monomer is in the liquid phase under the reaction conditions of the process, can also be used as solvent.

Preferably apolar solvents are used, that result in the formation of COCs of relatively high number average molecular weight. Solvents particularly suitable are the dimethylether of

ethylene glycol, diethylether, toluene, cyclohexane and sulfolane.

The amount of catalyst employed in the process according to the invention suitably ranges from 10^{-8} to 10^{-2} gram atom metal (palladium) per mole of cyclic olefinic compound to be polymerized.

The process of the invention may be carried out at moderate reaction conditions. Reaction temperatures suitably ranges from 20 to 180 °C, and preferably ranges from 40 to 130 °C.

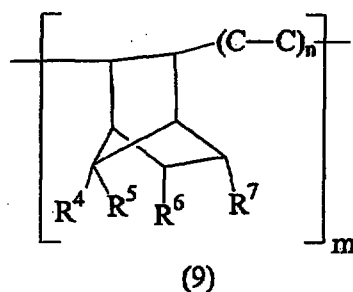
Usually superatmospheric reaction pressures are applied, for example in the range of 1 to 100 bar, pressures outside the indicated range not being precluded. Preferably a pressure in the range of 2 to 60 bar is applied.

Another object of the present invention is a novel COC, consisting of cyclic structures and non-cyclic structures of at least 2 carbon atoms in the backbone of the polymer, having a number average molecular weight greater than 10,000 and having a content of functional group bearing cyclic monomer(s) of at least 0.1 mol%, wherein the COC is obtained by polymerizing ethene, a functional group bearing cyclic monomer(s) and optionally a third olefinic monomer. It has been found that the COC does not contain successive monomeric cyclic structures. The COC preferably comprises 0.1-50 mol% of a functionalized cyclic monomer, 50-99.9 mol% ethene and 0-49.9 mol% of a third monomer.

Possible third monomers are described above.

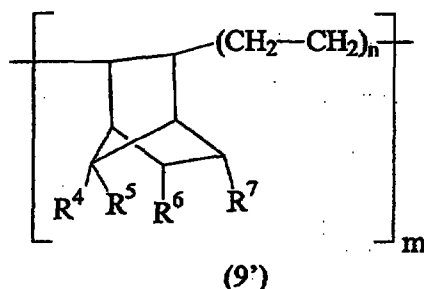
According to an embodiment of the invention, a suitable class of COCs according to the invention are copolymers of ethene and a functional group bearing cyclic monomer, in which the latter is present in a low content, suitably ranging from 0.1 mol% to 10 mol%. This class of copolymers provides a polyethene like polymer, having improved surface properties due to the functional groups incorporated in the polymer backbone.

Preferably the COC contains for the larger part a sequence according to the following formula(9):



in which n is 1-10,000 and in at least 0.1 mol% of the monomer olefin compounds is a cyclic structure in which hydrogen is replaced by a polar group R^4 , R^5 , R^6 and/or R^7 . The values for n and m are at least high enough to results in a number average molecular weight of above 10,000 (M_n). R^4 , R^5 , R^6 and/or R^7 can be the same as described above for formula (6).

Most preferably, the COC comprise a sequence of formula (9'):



wherein m , n , R^4 , R^5 , R^6 and R^7 have the meaning reported above.

At least 0.1 mol% of the monomer units along the sequence of formula (9') is a monomer having cyclic structure wherein at least one of the groups R^4 , R^5 , R^6 and R^7 is a polar group.

The novel functionalized COCs are preferably obtained by the above described polymerization process. The cyclic structure of the cyclic olefin monomers are not (or not substantially) affected during the process of this invention. The content of cyclic structures will therefore be substantially the same as the content of cyclic monomers in the resulting COC.

It will be appreciated that the utility of the COCs depend on the degree of functionalization and number average molecular weight of the products. They may in principle be used for the applications wherein COCs compete with poly(methyl methacrylate) or polycarbonate.

The functional COCs obtained with the process of this invention can be used in a wide variety of applications. Due to their improved surface adhesive and surface reactive properties, the functionalized COCs according to the invention are particularly suitable for compact discs applications, as a tie-layer between for example polar and non-polar polymer surfaces, compatibilisers or as surface coatings.

The present COCs can also be used in electronic and microelectronic applications, for example planarizing dielectric layers in IC manufacture, passivation layers, as protective coatings and potting compounds, as adhesives, as polymers for printed wire board fabrication.

The present COCs can be transparent and are useful in optical applications. The transparency will depend on the content and nature of the functionalized groups present in the COC. They can be used as coating in optical fibers, lenses and other optical devices.

The COCs can be used as wire coatings, wire wrap film and as protective and anticorrosion coatings. The COCs can also be formed into fibers by methods known in the art, for example wet spinning, dry spinning, gel spinning and extrusion.

The present invention is further illustrated by the following, non-limiting examples. The following abbreviations are used:

Pd(OAc) ₂	Palladium acetate
DPBS	2-diphenylphosphinobenzenesulfonic acid
DOMPBS	2-(di-2-methoxyphenylphosphino)benzenesulfonic acid

Example 1

Synthesis of 2-[di(2-methoxyphenyl)phosphino]benzenesulfonic acid

Lithium benzenesulfonate was made from LiOH and benzenesulfonic acid in a water toluene mixture. The water was removed by azeotropic distillation with toluene. 8.37g (0.051 mol) of lithium benzenesulfonate were suspended in 120 ml of THF (THF = tetrahydrofuran) (under nitrogen) and cooled to 0°C. 32 ml N-butyllithium (1.6 mol/l) were added at 0°C over 1 hour. The mixture was allowed to reach room temperature and subsequently stirred for 18 hours. The mixture was cooled to -30°C and a solution of 14.5g (0.05 mol) of di(2-methoxyphenyl)-methoxyphosphine in 30 ml THF was added slowly. The mixture was allowed to reach room temperature and subsequently stirred for 18 hours. 20 ml of water were added and the THF was removed in vacuum, leaving a yellow oil. Dichloromethane and

hydrochloric acid (10%) were added and the phases were separated. The organic phase was washed with 10% hydrochloric acid and dried with MgSO_4 . The product was dissolved in water/acetone-mixture (1:1). This mixture was extracted with 5 ml of toluene and then the product was crystallized by concentrating in vacuum and cooling to 4°C. The pure product contained water. It was therefore dissolved again in dichloromethane, dried with MgSO_4 and filtered. The solvent was then removed in vacuum. Yield: 7.01 g (33%).

Example 2

Synthesis of 2-[di(2-methoxyphenyl)phosphino)-p-toluenesulfonic acid

The compound was prepared as described in Example 1 from 0.03 mol p-toluenesulfonic acid, 19 ml n-Butyllithium (1.6 mol/l) and 8.7 g di(2-methoxyphenyl)-methoxyphosphine. Yield: 3.8g (30%).

Examples 3-7

2-[di(2-methoxyphenyl)phosphino)benzenesulfonic acid, prepared as described in Example 1, $\text{Pd}(\text{OAc})_2$, the phosphine ligand and the cyclic co-monomer reported in Table 1 were successively introduced in a 250 ml magnetically stirred Hastelloy C autoclave, containing the solvent reported in Table 1 (pre-de-aerated by bubbling through with nitrogen gas), under a nitrogen atmosphere. The autoclave was closed and pressurized with ethene to the desired pressure and subsequently heated to reaction temperature. In Table 1 are reported amounts, process conditions, compounds used and results.

The obtained products were analyzed by Gel Permeation Chromatography (GPC) for molecular weight (Mw) and analyzed by ^1H and ^{13}C -NMR to determine ethene and cyclic monomer contents.

Comparative Experiment A

Example 3 was repeated, except that was used the anion 2-diphenylphosphino-benzenesulfonic acid. In Table 1 are reported amounts, process conditions, compounds used and results.

Table 1

Example	Catalyst (mmol)	T (°C)	Time (hrs)	Solvent amount (ml)	Ethene pressure (bar)	Cyclic monomer (g)	Polymer yield (g)	Mw*	Cyclic monomer in polymer (mol%)
A	Pd(OAc) ₂ (0.025) DPBS (0.05)	90	7	Diglyme 50	40	5-norbor-nene-2-methanol (5 g)	2	2,500	2
3	Pd(OAc) ₂ (0.025) DOMPBS (0.05)	90	3	Diglyme 50	40	5-norbor-nene-2-methanol (5 g)	29	30,000	10
4	ditto	90	0.25	Toluene 50	10	5-norbor-nene-2-yl acetate (10 g)	8	80,000	35
5	ditto	90	1	Toluene 50	5	norbornene (20 g)	14	90,000	48
6	ditto	90	0.5	Toluene 50	30	norbornene (20 g)	26	85,000	35
7	ditto	75	1.5	o-dichloro benzene 50	30	5-norbornene-2-methanol (10 g)	14	90,000	14

* Mw (molecular weight) was determined by GPC, using the polystyrene standard and THF as solvent.

Examples 8-11

A solution of 20g norbornene (and a norbornene derivative as termonomer in Examples 10-11, see Table 2) in 100ml toluene was added under nitrogen into an autoclave of 250ml, containing 20mg of 2-[di(2-methoxyphenyl)-phosphino]benzenesulfonic acid (0.05mmol) and 5mg Pd(OAc)₂ (0.025mmol), maintained under nitrogen. The mixture was pressurized with 5 bar ethylene and heated to 90°C. After reaching the reaction temperature, the pressure was kept constant at the given pressure for one hour, by continuously adding ethene. The autoclave was then depressurized and cooled to room temperature. The toluene solution was diluted to 300ml with toluene and the polymer was precipitated by injection into methanol through a nozzle. The obtained polymer was filtered off and dried at 200 mbar, at 75°C. In Table 2 are reported amounts, process conditions, compounds used and results.

Example 12

Example 11 was repeated, except that 100ml of THF were used as solvent; 17g norbornene and 6.5 g of nadic anhydride as termonomer were used. In Table 2 are reported amounts, process conditions, compounds used and results.

Example 13

Example 8 was repeated, by using as anion 2-[di(2-methoxyphenyl)phosphino)-p-toluenesulfonic acid, prepared as reported in Example 2. The obtained results were very similar to the ones obtained in Example 8.

Table 2

Example	Solvent (ml)	Ethene pressure (bar)	Cyclic Monomer (g)	Cyclic termonomer (g)	Polym. yield (g)	Mw*	Tg (°C)	Cyclic monomer in polymer ** (mol%)	Cyclic termonomer in polymer (mol%)
8	Toluene (100)	12	Norbornene (20 g)	None	19	90,400	109	2	None
9	Toluene (100)	5.5	Norbornene (20 g)	None	2.9	94,000	141	10	None
10	Toluene (100)	12	Norbornene (20 g)	5-norbornene-2-methanol myristyl ester (1.5g)	8	71,000	80	35	~ 3
11	Toluene (100)	12	Norbornene (20 g)	5-norbornene-2-methanol (1.2g)	7	Not measured	113	48	~ 1
12	THF (100)	12	Norbornene (17 g)	nadic anhydride (6.5g)	3.7	Not measured	101	35	5

* Mw (molecular weight) was determined by GPC, using the butadiene standard and cyclohexane as solvent.

** Inclusive the termonomer.

This Sheet Has Been Replaced

**Examples 14-16**

In a first step 2-[di(2-methoxyphenyl)-phosphino]benzene-sulfonic acid was suspended in water and neutralised with a solution of tetrabutylammonium-hydroxide in water until pH 7. Toluene was added to this solution and the water was removed by azeotropic distillation. Then the toluene was removed in vacuum to yield 2-[di(2-methoxyphenyl)-phosphino]benzene-sulfonic acid tetrabutylammonium-salt Bu₄N(DOMPBS).

In a second step Pd₂(tetramethyl-divinyldisiloxane)₂ was prepared according to the literature (J. Krause, K.J. Haack, G. Cestarc, R. Goddard, K.-R. Poerschke, *Chem. Commun.* 1998, 226)

Then a 2 litres autoclave with mechanical stirrer and catalyst injection unit was charged with 100 mg (0.25 mmol) of 2-[di(2-methoxyphenyl)-phosphino]benzene-sulfonic acid and a solution of norbornene, the norbornene derivative and 0.25 mmol acetic acid in 1100 ml toluene. This mixture was saturated with 5 bar of ethylene. The temperature was raised till 90 °C and the final polymerisation pressure was adjusted to 12 bar. Separately 96 mg (0.125 mmol) Pd₂(tetramethyl-divinyldisiloxane)₂ were dissolved in 8 ml cold (-30 °C) toluene under nitrogen and kept at -30 °C. Then 174 mg (0.25 mmol) Bu₄N(DOMPBS) were dissolved in 10 ml toluene under nitrogen and added to the solution of Pd₂(tetramethyl-divinyldisiloxane)₂ at -30 °C. These 18ml of catalyst solution were allowed to reach room temperature within 15 minutes and were subsequently injected into the 2l autoclave. The pressure was kept at 12 bar for one hour by supplying the consumed ethylene. Afterwards the reactor was depressurised and allowed to cool to room temperature. The solution was diluted with toluene and filtered through Celite. The polymers was isolated by precipitation in ethanol and dried at 200 mbar and 75 °C.

See Table 3 for more details on amounts, process conditions, compounds used and results.

Table 3

Example	cyclic monomer (g)	cyclic ter-monomer (g)	yield polymer product (g)	mol weight (Mw) (1)	glass transition temperature - T _g (°C)	Mol % cyclic monomer in polymer product (inclusive the ter-monomer)	mol % cyclic termonomer of the incorporated cyclic monomer
14	norbornene (160)	5-norbornene-2-methanol (52)	130	38000	105	38	10
15	norbornene (160)	5-norbornene-2-yl-acetat (64)	49	117000	113	40	10
16	norbornene (190)	5-norbornene-2-carboxylic acid (14,5)	142	68000	114	42	~2,5

(1) Mw determined by GPC using PS as standard and THF as solvent



Claims

1. A process for the polymerization of ethene and optionally one or more other olefin monomers comprising contacting the monomers under polymerization conditions with a catalyst system obtainable by combining:
 - (a) a palladium, nickel or platinum ion,
 - (b) an anion derived from an acid having a pKa of less than 3, and containing an atom of Group V A of the Periodic Table of Elements, wherein the Group V A atom is substituted with at least one aryl group, said aryl group being substituted with a polar group on the ortho position.
2. The process according to claim 1, wherein said ion as defined under (a) is a palladium ion.
3. The process according to claim 1 or 2, wherein said anion as defined under (b) has the general formula (1):



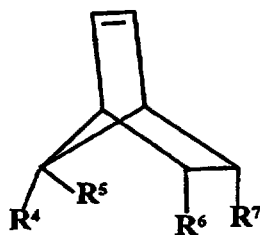
wherein Q is a group containing an atom of Group V A of the Periodic Table, wherein the Group V A atom is substituted with one or two aryl groups, said aryl groups being substituted with a polar group on the ortho position; An^- is an anionic moiety; and R^1 is a bridging group connecting said atom of Group V A and said An^- .

4. The process according to claim 3, wherein said anionic moiety An^- is $-SO_3^-$ group.
5. The process according to any one of claims 1-4, wherein said atom of Group V A is phosphorus.
6. The process according to any one of claims 3-5, wherein said bridging group R^1 is an aryl group in which a sulphonato group (An^-) is substituted on one of the two first possible adjacent carbon atoms on the ring, relative to the bond between R^1 and the phosphorus atom (Q).
7. The process according to any one of claims 1-6, wherein said atom of Group V A is substituted with two aryl groups, said aryl groups being substituted with a polar group on the ortho position.
8. The process according to any one of claims 1-7, wherein said polar group is an ester-, ether-, carboxylic acid-, acid-, alcohol-, keto-, carbonyl-, cyano-, amine- or amide group

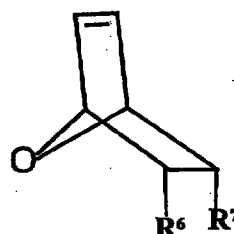




- or a halogen atom, and said aryl groups are phenyl or naphthyl.
9. The process according to claim 8, wherein said polar group is an alkoxy group having 1-10 carbon atoms.
 10. The process according to claim 9, wherein said polar group is methoxy group.
 11. The process according to any one of claims 1-10, wherein said anion is di(ortho-methoxyphenyl)phosphinobenzenesulfonate or di(ortho-methoxyphenyl)phosphino p-tolylsulfonate.
 12. The process according to claim 1, wherein the molar ratio of said palladium, nickel or platinum metal ion (a) and said anion (b) ranges from 1:1 to 1:100.
 13. The process according to claim 12, wherein said molar ratio ranges from 1:1 to 1:5.
 14. The process according to claim 1, wherein ethene is polymerized with a functionalized cyclic olefin monomer and optionally with a third olefin monomer.
 15. The process according to claim 14, wherein said functionalized cyclic olefin monomer has formula (6) or (7):



(6)



(7)

wherein R^4 , R^5 , R^6 and R^7 , the same or different from each other, are hydrogen, hydrocarbon or heteroatom containing groups, and wherein in formula (6) at least one of the groups R^4 , R^5 , R^6 and R^7 is a heteroatom containing group.

16. A cyclic olefin copolymer comprising cyclic structures and non-cyclic structures of at least 2 carbon atoms in the backbone of the polymer, having a number average molecular weight greater than 10,000 and having a content of functional group bearing cyclic monomer(s) of at least 0.1 mol%, said copolymer being obtained by polymerizing ethene, a functional group bearing cyclic monomer(s) and optionally a third olefinic monomer.
17. The cyclic olefin copolymer according claim 16, comprising 0.1-50 mol% of said functional group bearing cyclic monomer, 50-99.9 mol% ethene and 0-49.9 mol% of

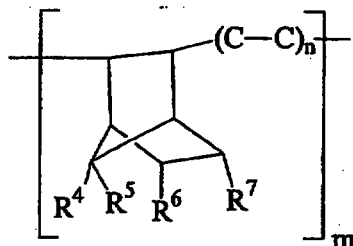




said third olefinic monomer.

18. The cyclic olefin copolymer according to claim 17, containing for the larger part a sequence according to the following formula (9):

(9)



wherein n is 1-10,000, and m and n are at least high enough to results in a number average molecular weight of above 10,000; R^4 , R^5 , R^6 and R^7 , the same or different from each other, are hydrogen, hydrocarbon or a heteroatom containing groups; and at least 0.1 mol% of the monomer olefin compounds is a cyclic structure in which hydrogen is replaced by a polar group R^4 , R^5 , R^6 and/or R^7 .

19. The cyclic olefin copolymer according to any one of claims 16-18, obtainable by a process according to any one of claims 1-15.
20. Use of a cyclic olefin copolymer according to any one of claims 16-19 as a tie-layer, as compatibiliser between different polymers or as surface coatings.
21. Use of a cyclic olefin copolymer according to any one of claims 16-19 as an optical device.

This Sheet Has Been Replaced

