1. General introduction

1.1 Organometallic chemistry and homogeneous catalysis

Organometallic compounds are defined as materials which possess direct, more or less polar bonds between metal and carbon atoms.[1] Since Zeise synthesized in 1827 the first organometallic compound, $K[PtCl_3(CH_2=CH_2)]$, the organometallic chemistry has grown enormously although most of its applications have only been developed in recent decades. Some of the key points in the fast expansion of organometallic chemistry are the selectivity of organometallic complexes in organic synthesis (discovered with Grignard reagents at the end of the 19th century),[2,3] and the interesting role that metals play in biological systems (e.g. enzymes, hemoglobin, etc.).[4]

One of the most interesting things about organometallic compounds is that they can be used as homogeneous catalysts in processes where all the reacting partners are present in one phase, usually the liquid one.[5] Transition metal complexes act in different ways within the catalytic reaction: they bring the substrates together, activate the substrates by coordinating to the metal and lower the activation energy of the reaction between substrates. In general the use of a homogeneous catalyst in a reaction provides a new pathway, because the reactants interact with the metallic complex. These interactions make it possible for thermodynamically favored reactions, which need long times to reach equilibrium, to be accomplished within hours. Therefore, homogeneous

catalysts can be used to synthesize compounds which can hardly be obtained by conventional methods.

Although heterogeneous catalysts are widely used, particularly in oil processes, homogeneous transition metal catalysts are increasingly being applied in industrial processes[6] to obtain fine chemicals and polymers. Some of these processes are: toluene and xylene oxidation to acids, oxidation of ethene to aldehyde, ester condensation to polyesters, carbonylation of methanol and of methyl acetate, polymerization of dienes to unsaturated polymers, hydroformylation of alkenes, oligomerization of ethene and propene, hydrocyanation of 1,3-butadiene, cyclodi(tri)-merization of 1,3-butadiene, asymmetric hydrogenation, asymmetric isomerization, asymmetric epoxidation, codimerization of 1,3-butadiene and ethene, hydrosilylation of alkenes, ring opening metathesis polymerization of dicyclopentadiene and norbornene, alternating copolymerization of ethene and carbon monoxide, etc.[5-7]

One interesting application of homogeneous catalysis is enantioselective (asymmetric) catalysis. It deals with the synthesis of enantiopure compounds, which are active ingredients of pharmatheuticals, agricultural products, flavors, fragrances and some advanced materials.[8-10] Life itself depends on chiral recognition because living systems identify the enantiomers as different substances and interact with them in different ways. For example, for many drugs only one of these enantiomers has a beneficial effect, being the other enantiomer either inactive or even toxic. Although the resolution of racemates is a way of obtaining enantiopure compounds, enantioselective synthesis enables just a single enantiomer to

be obtained. The advantage that enantioselective catalysis has over stoichiometric synthesis is that one organometallic catalyst molecule can generate millions of chiral product molecules. Catalytic synthesis also generates smaller amounts of chemical waste than stoichiometric organic synthesis. Therefore the search for homogeneous enantioselective catalysts that selectively react to give the desired product is one of the most interesting trends in organometallic chemistry.[11]

The success of organometallic catalysts lies in the easy modification of their environment by ligand exchange. A very large number of different types of ligands can coordinate to transition metal ions. Once the ligands are coordinated, the reactivity of the metals may change dramatically. In fact the rate and selectivity of a given process can be optimized to the desired level by controlling the ligand environment. Understanding the role played by the different ligands coordinated to a metal is one of the main themes in homogeneous catalysis.[12] Because organometallic complexes are highly soluble in organic solvents their behavior throughout the catalytic reaction can be studied using different techniques to do *in-situ* measurements. Fundamental knowledge about the catalytic systems and studies about the steps of the catalytic processes can help to improve the efficiency of the catalysts. In this respect kinetic studies and stoichiometric model reactions with well-defined transition metal complexes are used to elucidate the steps of the catalytic cycle. The use of labeled compounds allows the spectroscopic identification of intermediates.

Palladium is one of the most extensively studied metals in organometallic chemistry because it is versatile and catalyzes a considerable

number of organic reactions. The most important palladium-catalyzed reactions are those leading to C-C bond formation such as oligomerization and polymerization of alkenes, carbonylation of alkenes and organic halides, Wacker oxidation of alkenes, Heck reaction, allylic alkylation, Suzuki reaction, cross coupling reactions, polyamide synthesis, etc.[13] The main steps in the mechanism of reactions catalyzed by palladium complexes are oxidative addition, reductive elimination, ligand substitution, transmetallation and migratory insertion. Migratory insertion is the fundamental step in coordination polymerization reactions such as the copolymerization of alkenes and carbon monoxide which is described in greater detail in the paragraphs below.

1.2. Alkene polymerization reactions

The catalytic conversion of accessible alkenes into high molecular weight polymers is a very important industrial process. The profit generated by this business has made polyolefins the fastest growing part of the polymer industry.[14] In particular, the different types of polyethylene make up more than 50% of the polyolefin production nowadays. Polyethylene, polypropylene and polystyrene are produced commercially using coordination polymerization technology with early transition metals (Ziegler-Natta and metallocene catalysts) or in high-temperature and high-pressure free-radical processes. Copolymers of ethene with polar monomers or functionalized alkenes (methyl(meth)acrylate, vinyl acetate, etc.) are also important commercial polymers. Most functionalized alkenes, particularly the commercially available polar monomers, poison metal catalysts based on early transition metals (titanium, zirconium or chromium), that are

highly oxophilic. For this reason copolymers containing functionalized alkenes with ethene are still produced industrially by free radical polymerization.

Late transition metal catalysts have both low oxophilicity and greater tolerance towards functional groups than early metals. Considering that coordination polymerization provides better selectivity than radical polymerization, the development of polymerization catalysts based on late transition metals is of great interest. The disadvantages of using late-metal polymerization catalysts rather than early-metal catalysts are the lower activity for alkene insertion and the more favoured β-H elimination, which competes with chain growth.[15] For the insertion polymerization of olefins some catalysts have been reported based on iron,[16] cobalt,[16a,17] rhodium,[18] nickel,[19] palladium[20] and platinum. Late-metal catalysts are also used for the polymerization of dienes[21] and for the alternating copolymerization of alkenes with carbon monoxide.

1.3. Alternating copolymerization of alkenes with carbon monoxide

The alternating copolymerization of carbon monoxide with alkenes to yield polyketones is an attractive reaction for various reasons. One of these is that carbon monoxide is an accessible and inexpensive monomer and so the final products are low cost polymers. Moreover, polyketones have interesting properties; they are thermal plastics, they are photo- and biodegradable and they can be starting material for a variety of functionalized polymers due to the chemical transformation of the carbonyl

groups.[22-25] Thermoplastics with high-performance properties are in increasing demand because of their strength, toughness, wear resistance, chemical resistance, UV stability, etc.[26] The applications of these materials include automotive components such as gears, fittings, containers, fibres, packaging, etc.[27] Shell[28] and more recently BP[29] have commercialized polyketones as aliphatic terpolymers (CO/ alkene$_1$/ alkene$_2$) (*Carilon* and *Ketonex*, respectively).

The metal-catalyzed copolymerization reaction started when it was discovered that $K_2[Ni(CN)_4]$ catalyzed the alternating copolymerization of carbon monoxide and ethene.[30] Homogeneous copolymerization catalysts provided greater control of the polymer properties than polymerization initiated via free radicals or γ–rays, and gave a perfect alternation of the alkene and carbon monoxide (Scheme 1). After nickel (II)[31,32] other metal complexes containing rhodium (I)[33,34] and palladium (II)[35] were used as catalysts, always in severe conditions of pressure and temperature. The first catalyst that was active in the copolymerization of carbon monoxide and ethene, in mild conditions, was a palladium complex of formula $[Pd(PR_3)_n(NCMe)_{4-n}][BF_4]_2$ with at least one molecule of phosphine ligand.[36] However, the essential improvement to the efficient synthesis of polyketones at industrial level came with the discovery of the combined importance of using bidentate ligands and weakly coordinating anions in catalytic systems of the type PdX_2(L-L) where (L-L) is a bidentate phosphine and X a weakly or non-coordinating anion.[37]
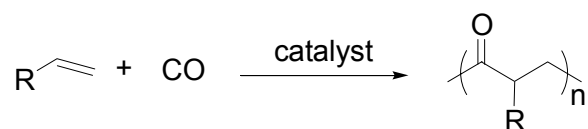
Scheme 1. Alternating CO/alkene copolymerization

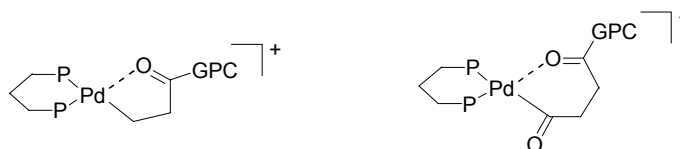### 1.3.1. Copolymerization of ethene with carbon monoxide

In 1996 the copolymerization of ethene and carbon monoxide was extensively reviewed and the complete mechanism, which is applicable to other alkenes, proposed.[23] The alternating copolymerization of alkenes with carbon monoxide consists of the following steps: i) the initiation of the chain growth; ii) the propagation mechanism, with the perfect alternation of monomers; iii) the termination of the chain together with the chain transfer, because of the importance for a polymerization catalyst of making more than one chain per metal center (Scheme 2).[38]

ECT: enolate chain transfer
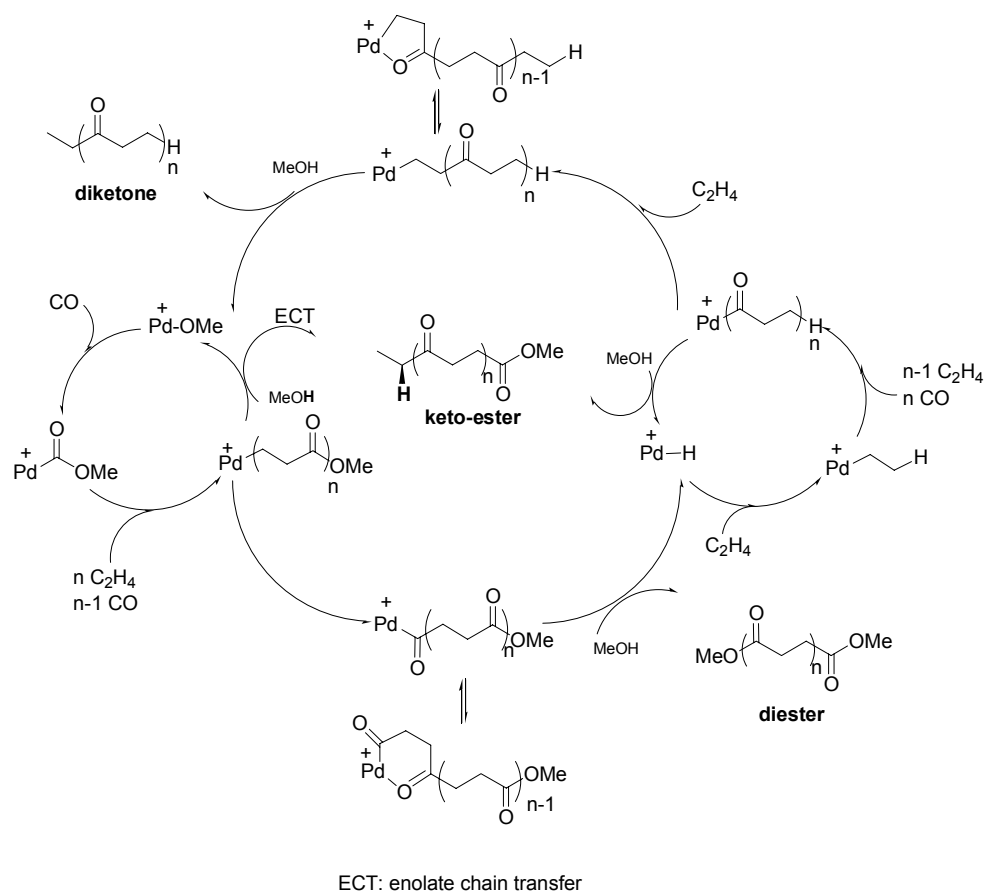
Scheme 2. Proposed mechanism for the copolymerization of
CO/ethene in methanol

The analysis of the end groups of the polyketones enabled the
initiation and termination steps of the mechanism to be understood.
Depending on the reaction conditions and on the nature of the alkene, the
chain initiation process has different possibilities. It is generally accepted
that for catalysts of the type PdX_2(L-L), made *in-situ*, or for the preformed
ones $[Pd(L-L)(S)_2][X_2]$ (S = solvent molecule), in alcoholic medium and

under CO pressure, the mechanism starts with CO being inserted into a Pd-OMe bond or the alkene being inserted into a Pd-H species.[23] Reaction of the palladium precatalyst in methanol with carbon monoxide generates the Pd-carbometoxy species (Pd-COOMe).[22,23] The starting palladium hydride species might be formed by β-hydride elimination from a palladium methoxy species[36] although the traces of water present in the reaction medium also lead to the formation of Pd-H species by β-H elimination of the Pd-COOH species formed (shift reaction).[39] β-H elimination reaction from a Pd-methoxyethyl complex (formed by a Wacker type reaction) also generates the Pd-H species.[38] When the precatalyst is an alkyl complex, the insertion of CO into the Pd-alkyl bond is the initiation step. This alkyl complex is only the initiator species, and is not regenerated after the first copolymer molecule is made. Generally, precatalysts of the type [PdR(L-L)(S)][X] (where R is a methyl group) have been used,[40] although recently it has been shown that an *in-situ* system formed by PdX_2(L-L) and a borane BR_3 (where R is the aryl group C_6F_5) is a good catalyst precursor due to the formation of the Pd-C_6F_5 species which inserts CO.[41] When the copolymerization reaction is performed in non-protic solvents an alkylpalladium species is necessary so that the first monomer can be inserted (Scheme 3).

chain initiation   chain termination

GPC: growing polymer chain

Scheme 3. Initiation and termination steps using an alkylpalladium catalyst
in a non-protic solvent

The propagation mechanism consists of the successive migratory insertion of carbonyl into an alkylpalladium complex and of alkene into an acylpalladium complex, in an alternating way (Scheme 2).[42] Cationic complexes with non-coordinating anions ensure the presence of accessible coordination sites and chelate ligands cause *cis*-coordination of the monomers and, thus, enable migratory insertion reactions.[43] Errors in the alternation of the insertions have never been observed and it has been stated that they are not possible. The CO insertion into a Pd-acyl bond is thermodynamically not favored and the insertion of an alkene into an alkylpalladium bond, although thermodynamically possible, is avoided because CO is more strongly coordinated and inserts faster in a Pd-alkyl bond than the alkene.[22,44] It has been shown that the growing polymer chain, σ-bonded to palladium, also coordinates internally to the metal by the last inserted carbonyl to form 5- or 6-membered ring metallacycles (Scheme 4).[23,45,46] This seems to help to the perfect alternation.

Scheme 4. β- and γ- chelates formed during CO/ethene copolymerization

Several studies have been made about the detection and isolation of carbon monoxide and alkene insertion intermediates in the copolymerization reaction.[42,47-50] Theoretical calculations have shown that there is a correlation with the experimental data in the perfect alternation of comonomers.[51,52]

The termination step, like the initiation one, depends on the reaction conditions and on the alkene. When the reaction solvent is an alcohol, it acts as a chain transfer agent leading to two termination ways. The alcoholysis of an acylpalladium species regenerates the Pd-H and gives an ester end-group; while the protonolysis of an alkylpalladium bond regenerates Pd-COMe and forms a ketone end-group (Scheme 2).[23] Recently it has been shown that protonolysis does not imply the expected protonation of the alkylpalladium species. In fact, deuterium experiments have shown that previously hydrogen is β- eliminated from the alkylpalladium species, to form an enolate, and is then reinserted (Scheme 5).[53] The hydrolysis of an alkylpalladium bond, due to the water present in the reaction, has also been observed, giving carboxylic end-groups and regenerating the Pd-H species.[54] Another possible termination pathway is the β-H elimination from an alkylpalladium species forming Pd-H bonds and unsaturated-end groups. This is the termination step in the reactions performed in non-protic

solvents (Scheme 3) and in the case of other alkenes, like propene and styrene, is the main termination reaction.
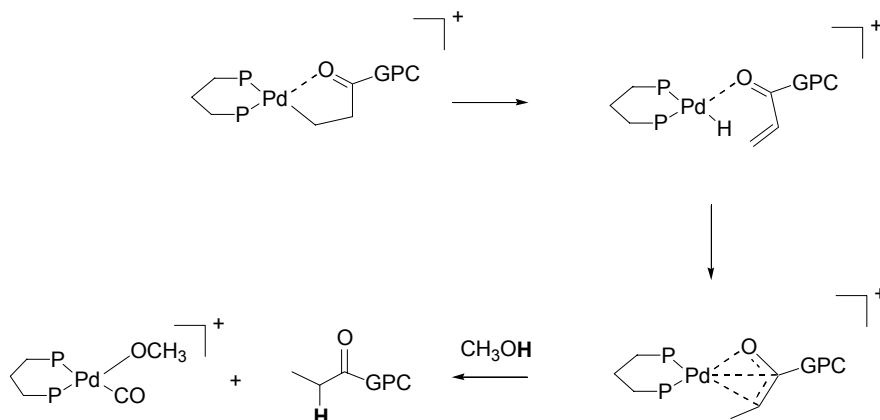

Scheme 5. Enolate chain transfer mechanism

Since the discovery of the efficiency of dppp (1,3-bis(diphenylphosphino)propane) as chelating ligand for the CO/ethene copolymerization reaction,[23] many studies have been made of various diphosphine ligands as well as of modifications to the dppp backbone. An interesting observation concerning diphosphines is that the size of the chelate ring dramatically affects productivity.[55,56] Although it was stated that the most productive catalysts were those with a diphosphine containing a three-carbon backbone (Scheme 6a),[23,39] it has been shown that four-membered diphosphine chelates may indeed lead to efficient catalysts if the ligands are sterically demanding enough (Scheme 6b).[57]

Additionally modifications on the (1,3-bis-(diphenylphosphino)-propane) backbone creating chirality in the 1- and 3-centers by introduction of a methyl group (2,4-bis(diphenylphosphino)pentane) have led to a

considerable increase of productivity.[58] It has also been found that *meso*-diphosphines lead to higher activities than catalysts with similar ligands but without the *meso* structure (Scheme 6c).[59-61] The explanation seems to be that catalysts containing *meso*-diphosphines are more active since the metallacycles formed during the catalytic reaction are less stable. In agreement with this, calculations on the CO migratory insertion barriers for catalysts containing diphosphines with different chelate ring sizes showed that the larger the chelate ring size is, the faster the migratory insertion. Likewise, when the steric bulk of the ligand is increased the migratory insertion is accelerated.[62]
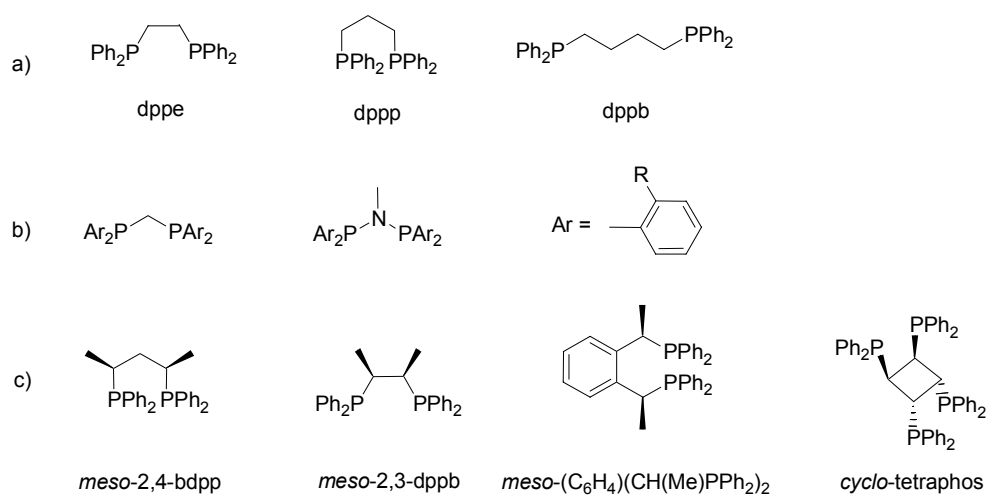
Scheme 6. Diphosphines used in CO/ethene copolymerization

It has been said that Pd(II) complexes are the best choice for the copolymerization of carbon monoxide not only with ethene, but also with propene and with styrene. These alkenes may be considered as models for more complicated substrates like strained alkenes,[63] α-alkenes substituted

with polar groups,[64-66] carbamates,[67] alkynes,[68,69] imines[70], amines,[71] etc. However, other late-metal catalysts such as nickel[72,73] and rhodium[74] have been used to a lesser extent in the copolymerization of alkenes with carbon monoxide. Monodentate ligands and bidentate ligands with relatively large bite angles are not used to avoid coordination in *trans* position in mono or bimetallic complexes, respectively.[75] Therefore, depending on the alkene involved in the catalysis, different types of chelating ligands are used, containing P-, N-, S-, O- or C- donor atoms.[25]
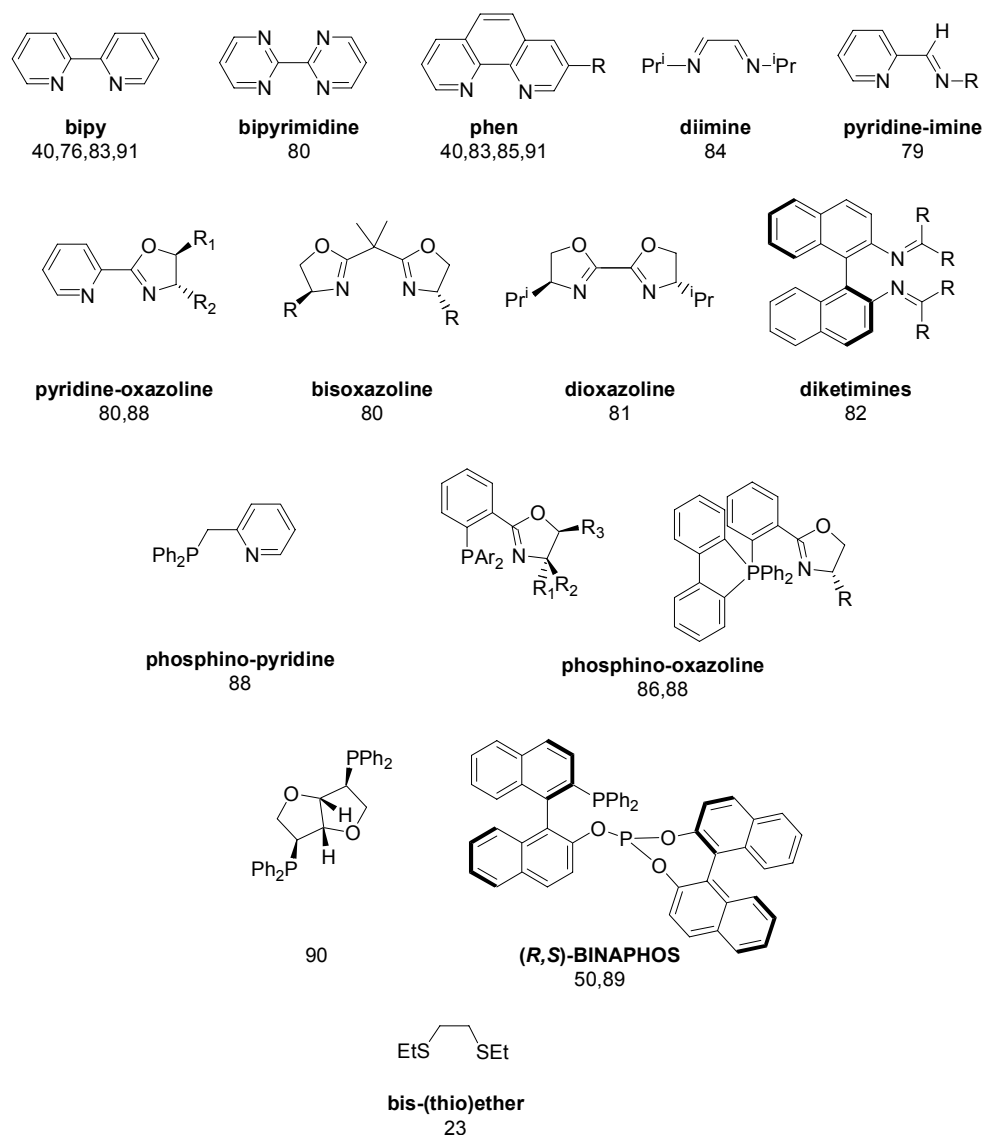
1.3.2. Copolymerization of styrene with carbon monoxide

As already stated for the copolymerization of ethene with carbon monoxide, palladium (II) complexes that contain both a non-coordinating anion and a chelating ligand are necessary if catalysts are to be active. Of the different anions tested, the BAr'_4 anion ($Ar' = 3,5-(CF_3)_2C_6H_3$) has been claimed to be the most appropriate because of its combination of bulkiness and low coordinating ability.[40,76] For this anion, multinuclear NMR studies showed the weakest contacts with the cationic part of the catalysts.[76]

Preformed catalysts containing one[40] or two molecules of chelating ligand[77] have generally been used for CO/styrene copolymerization. Bisnitrogen-donating ligands have been mostly used for effective CO/styrene copolymerization (Scheme 7).[40,78-85] The combination of a phosphorous and a nitrogen-donating atom was also found to be active, although severer conditions of pressure and temperature are needed to obtain polyketones.[86] Unlike the co- and terpolymerization of ethene and propene with CO, catalysts containing diphosphine ligands are not active in

the copolymerization of styrene (and its derivatives) with CO since only low molecular weight oligomers are obtained.[23,87] It has been stated that when a phosphine is coordinated to palladium, β-H elimination is more favoured than polymer growth because of the higher electron density existing on the metal.[23] Moreover, the strongly stabilized π-benzylic intermediate formed after styrene insertion prevents subsequent carbon monoxide coordination and insertion.[88]

Surprisingly a palladium complex containing a phosphine-phosphite ligand (BINAPHOS) has also shown activity.[89] This was explained in terms of the reverse regiochemistry observed in the styrene insertion (1,2-insertion) (see below).[50] Very recently a palladium catalyst containing a diphosphine derived from *L*-iditol was reported to be active in the CO/styrene copolymerization, giving polymers with a highly regular microstructure. It seems that the iditol-derived diphosphine coordinates almost in a monodentate fashion (a strong coordination with one phosphorous and a weak one with the other, which can be exchanged during the catalysis) although the system has not been explained clearly (Scheme 7).[90] As well as nitrogen and phosphorous donating ligands, there is an example in the literature with sulfur-donating ligands, yielding polyketones with an irregular microstructure (Scheme 7).[23]

bipy
40,76,83,91

bipyrimidine
80

phen
40,83,85,91

diimine
84

pyridine-imine
79

pyridine-oxazoline
80,88

bisoxazoline
80

dioxazoline
81

diketimines
82

phosphino-pyridine
88

phosphino-oxazoline
86,88

90

(*R,S*)-BINAPHOS
50,89

bis-(thio)ether
23

Scheme 7. Ligands reported for the CO/styrene copolymerization

As well as having an effect on the activity of catalysts, ligands may influence the selectivity in which the copolymerization proceeds. When 1-alkenes are used as monomers, one important goal is the control of the

regio- and stereochemistry of the alkene insertion in the growing chain. It has been reported that in complexes containing bisnitrogen ligands, styrene insertion always takes place in a secondary fashion (2,1 insertion),[40,91] because of the stabilization of the π-benzylic intermediates (Scheme 8).[40] However, this situation changes when the ligand is varied: steric modifications in P-N ligands yield regioirregular polyketones containing some 1,2-inserted styrene units,[86b] while only 1,2- insertions were found in the regioregular copolymer obtained with the BINAPHOS ligand. The reverse insertion of styrene, observed with the phosphine-phosphite ligand, prevents the β-H elimination and might explain the activity of this ligand in CO/ styrene copolymerization.[50]
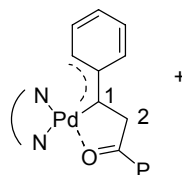
Scheme 8. π-benzylic intermediate formed after 2,1 insertion of styrene in a Pd-acyl bond

The stereochemistry of the alkene insertion along the chain determines the copolymer tacticity: isotactic, syndiotactic or atactic (Scheme 9). Two facts may be responsible for the control of the stereochemistry to give stereoregular (isotactic or syndiotactic) copolymers. On the one hand the enantioselective environment created by the chiral ligand may govern the stereoregularity of the alkene insertion, which is known as *enantiosite control*, and this leads to isotactic polymers. On the other hand the growing polymer chain, which is also chiral because of its successive stereogenic

carbon centers, may lead to a controlled stereoregular insertion of styrene. This control is known as *chain-end control*, and it gives syndiotactic polymers.


isotactic

syndiotactic
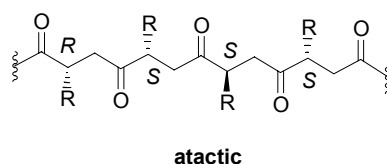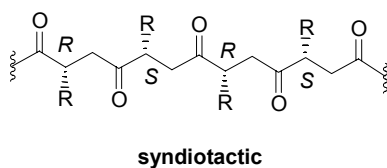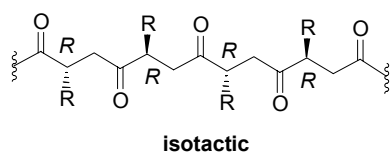
atactic

Scheme 9. Tacticity of CO /alkene copolymers

C_2- and C_{2v}- achiral ligands give completely stereoregular syndiotactic copolymers due to the *chain-end control*.[40,80,83,84,91] For C_2-symmetrical chiral ligands, *enantiosite control* overrides the effect of the growing chain to give isotactic polymers.[80-82] However, for C_1-symmetrical ligands the relative influence of both effects cannot be inferred *a priori*. There are examples reported where the use of C_1-symmetrical ligands led to isotactic,[86,89] syndiotactic[79,80,85,88] or even atactic copolymers.[88]

1.4. Terpolymerization of styrene and ethene with carbon monoxide

The CO/alkene copolymer chains are packed together in an orderly fashion giving highly crystalline materials. This makes polyketones to be very strong but also very brittle. To avoid this problem, another alkene, e.g. propene, can be introduced in the chain to disturb somehow the crystal packing. Inserting a second alkene into the palladium-catalyzed CO/alkene copolymerization reaction gives strictly alternating CO/alkene polyketones in which two different units are obtained (CO/alkene$_1$) and (CO/alkene$_2$) (Scheme 10). The relative amount of both units inside the polymer chain depends on the conditions of the reaction as well as on the different reactivity of each alkene.
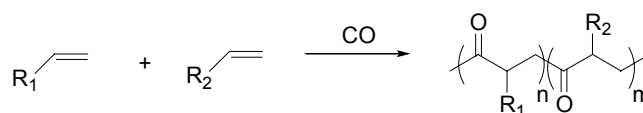
Scheme 10. Terpolymerization reaction of alkenes with CO

Different alkenes have been terpolymerized with CO using cationic palladium catalysts although combinations of ethene and 1-alkenes have been more studied.[59,79,92-94] Recently some reports have appeared on terpolymerization of 1-alkenes and vinylarenes with CO.[95,96]

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