

Palladium-Catalyzed Alternating Copolymerization of Alkenes and Carbon Monoxide

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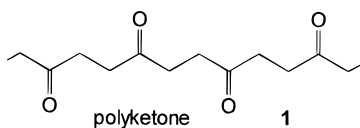
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I. Introduction

The alternating copolymerization of ethene and carbon monoxide has attracted considerable interest from both academia and industry over the last decades.^{1,2} The base materials are readily available, while the product “polyketone” (poly-3-oxotrimethylene, **1**) is predicted to have interesting engineering-plastic type properties, typical for polymers with a high density of heteroatom functionalities. Also, the carbonyl group can be used for derivatization to a variety of interesting new materials.



Nearly 40 years of research have evolved between the first discovery by Reppe of metal-catalyzed alternating ethene/CO copolymerization and the discovery at Shell of a class of highly active, high-yield palladium catalysts for this reaction. These catalysts made possible the essential technological advances in the synthesis and processing of alternating polyketones which enabled Shell to move these polymers to commercial reality.³



Peter Budzelaar was born in Amersfoort, The Netherlands, in 1957. He completed his Ph.D. degree under G. J. M. van der Kerk in Utrecht, 1983, on cyclopentadienylzinc–transition metal complexes. In 1983–1984 he was a postdoctoral fellow with Paul von Ragué Schleyer in Erlangen, Germany. He then worked for a year with R. Prins at the Technical University of Eindhoven, The Netherlands, before joining Shell in 1985. His current research interests are in experimental and theoretical homogeneous catalysis.

Nickel was the first transition metal used to catalyze the copolymerization of CO and ethene. In the late 1940s, Reppe and Magin⁴ showed that $K_2Ni(CN)_4$ in water produced low-melting oligomers of ethene and carbon monoxide in addition to diethyl

ketone and propionic acid. In the early 1970s, workers at Shell Development (Houston) succeeded⁵ in improving the catalyst by the addition of strong acids such as HOTf and HOTs in solvents such as HFIPA. They obtained a polymer with a relatively high molecular weight, but the yield of polymer per gram of catalyst was still low. After the high-yield palladium catalysts had been discovered (see below), Klabunde⁶ reported a new nickel catalyst for the alternating CO/ethene copolymerization, based on a bidentate anionic phosphorus–oxygen ligand. Similar catalysts are also used in the Shell process for the oligomerization of ethene (SHOP). Interestingly, the copolymerization has to be *started* with pure ethene, even for polyketone formation. The use of SHOP-type catalysts for polyketone formation has also been claimed by Keim.⁷

Rhodium carbonyls are also active as catalysts for the production of alternating copolymers of ethene and carbon monoxide.⁸ The molecular weights of these polymers are low, as are the rates of formation. Insertion of carbon monoxide may be extremely fast in rhodium catalysts, but it seems that alkene insertion in the rhodium–carbon bond is relatively slow.

Palladium catalysts for alternating polyketone formation were first disclosed by Gough at ICI in 1967.⁹ These catalyst systems were bis(tertiary phosphine)palladium dichloride complexes which yielded polyketone at a rate of around 300 g (g of Pd)⁻¹ h⁻¹. The disadvantage was that severe conditions were required (250 °C, 2000 bar) and that yields in gram of polymer/gram of palladium were low. During the following 15 years, only small advances were made in increasing catalyst efficiency. Research by Fenton^{10a} at Union Oil and Nozaki at Shell Development Company^{10b} uncovered several related palladium chlorides, cyanides, and zerovalent complexes, which in a variety of solvents were also catalysts. These operated under milder conditions than those used by ICI (typically 120 °C, 70 bar), but both activities and yields were still very low. In the early 1980s, Sen and co-workers¹¹ published work which showed that certain tertiary phosphine-modified palladium complexes containing the weakly coordinating tetrafluoroborate anion in dichloromethane produced polyketone under very mild conditions. However, again the reaction rates (~ 4 g (g of Pd)⁻¹ h⁻¹) were very low, as were the yields (in gram of polymer/gram of palladium) and the molecular weights of the polymer.

In the early 1980s two important independent advances occurred. In 1980, workers at Shell Development Company in Houston could demonstrate melt processability of polyketone produced by palladium cyanide catalysts, after extensive extraction of catalyst residues from the polymers and blending these with other polymers such as styrene/acrylonitrile copolymer. From these studies it was suggested that thermoplastic properties were possible in principle and that the polyketone backbone was not inherently unstable in the melt as previously concluded. However, it was also clear that catalyst extraction did not offer a viable production option from a technical and economic viewpoint.

During this period, at Shell Research in Amsterdam, cationic palladium complexes containing tertiary phosphine ligands and weakly coordinating anions (e.g. sulfonates), similar to those studied by Sen,¹¹ were studied in methanol as catalysts for the methoxycarbonylation of ethene to give methyl propionate. In experiments using *bidentate* tertiary phosphine ligands, it was surprisingly observed that no methyl propionate product was formed; instead, high molecular weight polyketone was formed at very high rates (~ 6000 g (g of Pd)⁻¹ h⁻¹). These catalysts are very active, and yields (in gram of polymer/gram of palladium) above 10⁶ have been achieved under economically attractive mild reaction conditions (90 °C, 45 bar). Also, the catalysts are easy to prepare either separately or *in situ*.^{12,13}

This discovery of the combined importance of bidentate ligands and weakly coordinating anions for high catalyst activity and yield, has—for the first time—opened the way for efficient synthesis of polyketone. Equally important, these catalysts provided more stable polymers with catalyst residues now measured by parts per million rather than percent. Collaborative research efforts within Shell have subsequently provided further advances in synthesis processes and polymer stabilization. Polyketone thermoplastics have been developed to be easily melt processable and could thus be shown to exhibit a unique set of desirable engineering thermoplastic properties.³ Moreover, the new family of catalysts is active for the copolymerization or terpolymerization with alkenes other than ethene (both simple aliphatic and heteroatom functionalized), thus providing access to a complete family of new polymers.

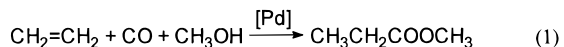
After a decade of fundamental research by a number of groups, several aspects of the chemistry of palladium-catalyzed polyketone formation are now reasonably well understood. Therefore, we feel that this is a good time to review the key points of scientific interest in “polyketone catalysis”. It is not our intention to deal with the great variety of ligands that has been studied. Nor will we attempt to treat all the substrate alkene combinations that may lead to interesting polymers. Instead we will focus on three alkenes: ethene, propene and styrene. In the first part, we will discuss why the cationic palladium complexes containing *cis*-chelating ligands lead to such active catalysts for copolymerization. Initiation, propagation, termination, and the effect of oxidants will be reviewed, and the perfectly alternating character of the polymerization process will be explained. In the second part the regio- and stereoselectivity of the polymerization of carbon monoxide and higher alkenes will be outlined. In the last section we will describe the formation of spiroketal isomers of polyketones and discuss the mechanistic implications.

The “real” polyketone catalytic systems are highly active, and intermediates are usually too reactive to isolate or even detect. Therefore, several groups have studied model systems using other ligands (mainly dinitrogen systems) and olefins (styrene, norbornene, norbornadiene) for which intermediates can be detected (by e.g. NMR or IR) or sometimes isolated. While such model studies provide valuable back-

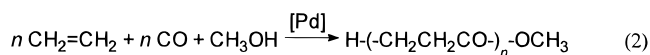
ground information, it is often difficult to translate the results to the "real" catalytic systems. Therefore, we will not discuss these studies in detail but just mention a few of their most relevant conclusions.

II. Copolymerization of CO and Ethene

The discovery of efficient catalysts for the copolymerization of CO with olefins originated from a study of the alkoxycarbonylation of ethylene to methylpropionate (eq 1).



The catalysts were cationic palladium phosphine systems prepared from palladium acetate, an excess of triphenylphosphine (PPh_3), and a Brønsted acid of a weakly or noncoordinating anion (e.g., OTs^-); methanol was used both as a solvent and a reactant. A surprising and remarkable change in selectivity was observed upon replacement of the excess of PPh_3 by a stoichiometric amount of the *bidentate* ligand *dppp*. Under the same conditions, these modified catalysts led to the production of a perfectly alternating CO/ethylene copolymer with essentially 100% selectivity (eq 2).¹²⁻¹⁴



A typical reaction rate would be $\sim 10^4$ mol of converted ethene (mol of Pd)⁻¹ h⁻¹ to give a polymer with an average molecular weight (M_n) of $\sim 20\,000$ (*dppp*/HOTs/MeOH, 65 °C).¹³ Under suitable conditions, the catalysts are highly stable and *total* conversions of more than 10^6 mol of ethene per mole of Pd can be obtained. The product has a high melting point (~ 260 °C) and is insoluble in most organic solvents (the most important exception being HFIPA); it precipitates during copolymerization as a snow-white solid.

Variation of the bidentate ligand results in significant changes in both the reaction rate and the molecular weight of the product. For example, Figure 1 shows the effect of changing the chain length n of the diphosphine $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ on the rate and molecular weight. Many patents deal with more subtle variations of the diphosphine ligands. In addition, several other types of *chelating* ligands (e.g. bipyridines, dithioethers, bisoxazolines) can be used. The counterions also affect the reaction rate; the best results are obtained with very weakly or noncoordinating anions (OTs^- , OTf^- , TFA^- , BF_4^- , and "organic"

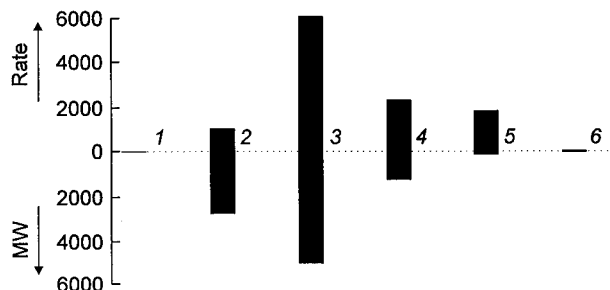
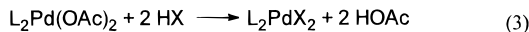


Figure 1. Influence of chain length of ligand $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ on rate and molecular weight of polyketone.

anions, such as certain tetraarylborates). The anions can conveniently be introduced by adding a Brønsted or Lewis acid as the anion source to the palladium acetate (eq 3).



Finally, polyketone catalysis can be carried out in a wide variety of solvents, including water (using sulfonated ligands¹⁵), aprotic solvents (in which aluminoxanes can be used as cocatalysts¹⁶), or even in solvent-free systems,¹⁷ although methanol remains the solvent of choice.

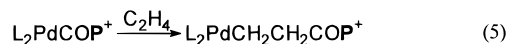
Instead of the free acid, it is sometimes advantageous to use a metal salt (e.g. of Cu^{II} or Ni^{II}) to introduce the anions. Preformed complexes of the type L_2PdX_2 , where L_2 represents a chelating ligand and X a weakly coordinating anion, have also been applied as catalysts. The results are very similar to those obtained with catalysts prepared *in situ*.¹⁸⁻²⁰

A. Mechanism

1. Propagation

The catalytically active species in polyketone formation is thought to be a d^8 square-planar cationic palladium complex L_2PdP^+ , where L_2 represents the bidentate ligand and P is the growing polymer chain. The fourth coordination site at palladium may be filled by an anion, a solvent molecule, a carbonyl group of the chain (*vide infra*), or a monomer molecule. Model studies indicate that having a strongly coordinating group at this position strongly reduces the rates of the insertion steps.^{21,22} Thus, competition for the vacant site appears to be an important factor affecting catalysis, and this explains the sensitivity of the system to the choice of solvent and counterion.

The two alternating *propagation* steps are migratory insertion of CO into the palladium-alkyl (eq 4) bond²³ and migratory insertion of ethene into the resulting palladium-acyl bond (eq 5). Propagation "errors" (double CO or ethene insertion) are not observed.

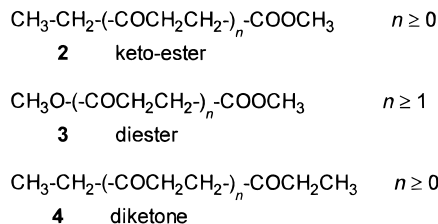


Carbon monoxide insertion in a palladium-carbon bond is a fairly common reaction.²⁴ Under polymerization conditions, CO insertion is thought to be rapid and reversible.²⁵ *Olefin* insertion in palladium-carbon bonds is not as common, but insertions in palladium-acyl bonds appear to be particularly facile.^{22,26,27} Nevertheless, it is likely that olefin insertion is the slowest (rate-determining) step in polyketone formation.

2. Initiation and Termination

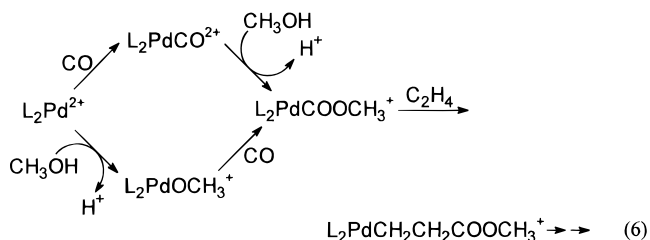
End group analysis of the CO/ethylene copolymer by ¹³C NMR has demonstrated the presence of 50% ester ($-\text{COOCH}_3$) and 50% ketone ($-\text{COCH}_2\text{CH}_3$) groups, in accord with the average overall structure of the polymer molecule as given above in eq 2. It is not *a priori* clear which group is the "head" and which is

the "tail" of the polymer. Moreover, GC and MS analyses of *oligomer fractions* show, in addition to the expected keto ester product **2**, the presence of diester **3** and diketone **4** compounds.¹³



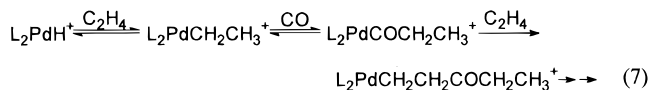
At low temperatures ($\leq 85^\circ\text{C}$), the majority of the products are keto esters, with only small, but balancing, quantities of diesters and diketones. At higher temperatures, the same products are produced in a ratio (**2/3/4**) close to 2:1:1. These observations have been explained¹³ by assuming *two initiation* and *two termination* mechanisms for polyketone formation.

One *initiation* pathway produces ester end groups. It starts with a palladium carbomethoxy species,^{13,18} which can be formed either by CO insertion in a palladium methoxide or by direct attack of methanol on coordinated CO (eq 6).

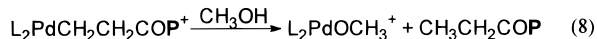


Alternatively, a chain can start by insertion of ethene in a palladium hydride (see below),^{1,13} producing a ketone end group. Ethene insertion in a palladium hydride and CO insertion in the resulting

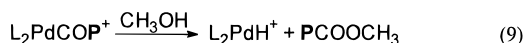
ethyl complex are both rapid and reversible; it is thought that the *second* ethene insertion (in the Pd acyl) is irreversible²⁸ and "traps" the acyl to start the chain (eq 7).



For CO/ethene copolymerization, two relevant *termination* mechanisms have been proposed. One mechanism, protolysis of the palladium-*alkyl* bond, produces a saturated ketone end group (eq 8).



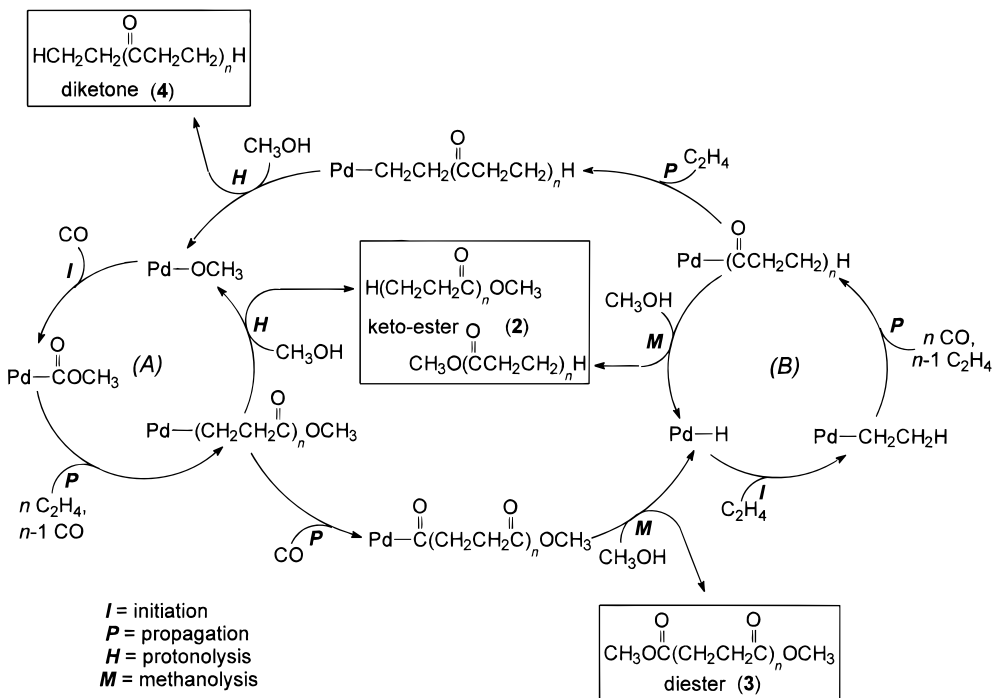
A second mechanism, the alcoholysis of the palladium-*acyl* bond, gives an ester end group (eq 9).



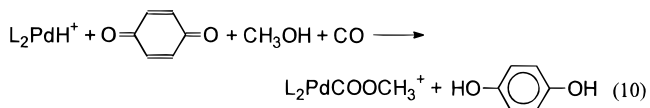
Scheme 1 summarizes the formation of the three possible polymeric products of types **2**, **3**, and **4** by the two initiation-propagation-termination cycles **A** and **B**. Both cycles produce keto ester molecules, but the cycles are connected by the two "cross" termination steps which give diester and diketone products.

The formation of appreciable amounts of **3** and **4** at high temperatures demonstrates that transfer between the cycles is rapid and that both cycles contribute with comparable rates.²⁹ The almost complete absence of the "crossover" products **3** and **4** at *lower* temperatures indicates that *one* initiation and *one* termination mechanism dominate. Rapid protolysis and slow methanolysis would produce product **2** via PdCOOMe⁺ initiation (cycle A). Rapid methanolysis and slow protolysis would produce the same product, but now via PdH⁺ initiation (cycle

Scheme 1. Proposed Mechanism of CO/Ethene Copolymerization



B). Product distribution alone is not sufficient to decide which cycle is responsible for the production of keto esters under these conditions. However, with certain catalysts it has been observed that the addition of a quinone oxidant (at low temperature) increases the proportion of ester end groups (up to 85%) without affecting the molecular weight.¹³ It is thought that quinones are able to convert PdH⁺ initiators into PdCOOCH₃⁺ initiators; the overall reaction can be represented by eq 10. Since the



quinone apparently does not affect the termination under the applied conditions, this implies that *in the absence of quinone* the initiator must have been a palladium hydride, which in turn means that the main termination mechanism must be alcoholysis. It should be realized, however, that the balance between different termination mechanisms may vary with ligand structure and process conditions, so that it is dangerous to draw general conclusions from these experiments.

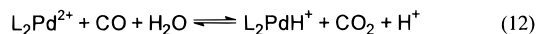
3. Generation of Palladium Hydride Initiators

At the *start* of the catalysis, palladium hydride can be generated in a number of ways:

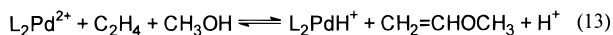
(i) by β -hydrogen elimination from a palladium methoxide



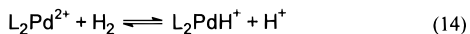
(ii) via the watergas shift reaction



(iii) by a Wacker-type oxidation of ethene



(iv) by hydrogen activation (in the presence of hydrogen)



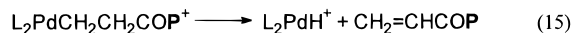
Copolymers with predominantly ketone end groups (i.e., **4**) can be produced either by admitting water to the polymerization or by adding some hydrogen.¹³ In aprotic solvents, *only* diketones are produced. This indicates that palladium hydrides, generated via watergas shift reaction or by heterolytic hydrogen splitting, are indeed efficient initiators and also shows that protolysis and/or hydrogenolysis of palladium alkyls can be efficient termination mechanisms.

During catalysis, hydrides can also be produced by two termination steps:

(v) by alcoholysis

If termination by alcoholysis (eq 9) is the dominating mechanism, termination of the very first chain will always give a palladium hydride, even if that chain started with a carbomethoxy species.

(vi) by β -hydrogen elimination



For CO/ethene copolymerization in methanol, vinyl ketone end groups have never been observed. This indicates that under these conditions β -elimination is not an important termination mechanism. However, polymers containing 50% vinyl ketone and 50% saturated ketone end groups can be obtained in strongly polar but aprotic media.³⁰ Unsaturated end groups are generally observed in the copolymerization of CO with higher olefins (*vide infra*).

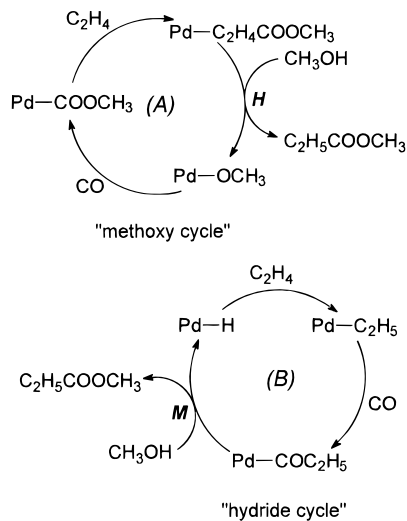
Clearly, the participation of so many reactions makes a full kinetic analysis of polyketone formation a formidable task.

B. Methyl Propionate vs Polyketone: The Role of Bidentate Ligands

Under conditions of polyketone catalysis, cationic palladium(II) catalysts modified with excess *monodentate phosphine* and Brønsted acids of weakly coordinating anions selectively give methyl propionate with high rates (eq 1).¹³

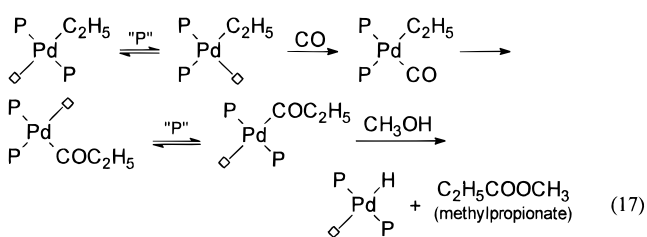
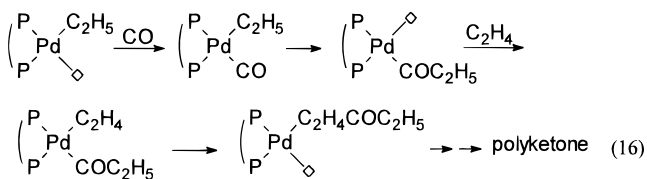
Methyl propionate formation can be considered as a combination of the polyketone initiation and termination steps without the intervening propagation steps. Again, there are two possible catalytic cycles (Scheme 2). There is no *a priori* argument to decide which cycle is actually responsible for methyl propionate formation. The absence of the cycle-transfer products diethyl ketone and dimethyl succinate sug-

Scheme 2. Two Possible Mechanisms for Methyl Propionate Formation



gests that only one cycle is operative, but it is also possible that both cycles operate in isolation.

Although the *reason* for the dramatic ligand effect on chemoselectivity is not known with certainty, we suggest an explanation here. The most obvious difference between monodentate and bidentate ligands is that the latter are always *cis* coordinated, whereas the former can also coordinate in a *trans* fashion. If bidentate phosphines are used, the starting (or growing) polymer chain and the "empty" fourth coordination site are always *cis* to each other, which is the most favorable position for insertion reactions. Therefore, olefin insertion in the palladium-acyl bond is easy in diphosphine complexes. If *monodentate* phosphines are used, both Pd-alkyl and Pd-acyl species prefer a *trans* orientation of the phosphine ligands for steric reasons and probably also because it avoids the unfavorable situation of a Pd-P bond *trans* to a Pd-C bond. At the same time, *cis/trans* isomerization is expected to be rapid because of the presence of excess ligand.³¹ It is reasonable to assume that both the insertion of ethylene in Pd-H and the insertion of CO in Pd-alkyl can *only* occur when the phosphine ligands are *cis*. Immediately after insertion, a *cis/trans* isomerization is likely to occur which places the "chain" and the fourth site *trans* and thus opposes further monomer insertions. Therefore, the palladium acyl will eventually terminate by alcoholysis of the Pd-acyl bond to give methyl propionate. The difference between polyketone and methyl propionate syntheses can then be summarized in eqs 16 and 17.



In this scheme, a hydride cycle has been assumed. However, the same reasoning would apply if a palladium methoxide were the initiating species in both methyl propionate and polyketone formation or even if different cycles would be taken for methyl propionate and polyketone formation. If *cis/trans* isomerization is suppressed (by the absence of excess ligand and/or at low temperature), one could expect a higher tendency to form oligomers or polymers. Indeed, it has been shown that at low temperature in methanol $[\text{Pd}(\text{PPh}_3)_2(\text{CH}_3\text{CN})_2]^{2+}$ converts CO and ethylene into methyl propionate and a significant amount of keto ester oligomers.¹¹

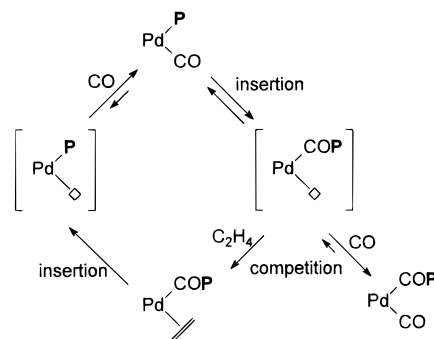
C. Alternation in CO/Ethene Copolymerization

Chain propagation of CO/ethene copolymerization proceeds by a strictly alternating insertion of CO and

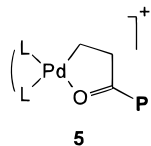
olefin monomers in the growing chain. It seems safe to assume that *double CO* insertion does not occur for thermodynamic reasons.³² However, the complete absence of *double ethene* insertions is remarkable because ethene insertion in a Pd-alkyl species must be exothermic by ~ 20 kcal/mol. The observation of strict alternation is the more surprising since the same palladium catalysts also efficiently dimerize ethene to butenes;³³ certain α -diimine palladium complexes even polymerize ethene to high molecular weights.³⁴ The perfect alternation is maintained even in the presence of very low concentrations of carbon monoxide. This is nicely illustrated by a batch experiment, which was carried out starting with a high ethene/CO ratio (~ 10).¹³ Only error-free copolymers were produced until the carbon monoxide had been consumed; then the system started making butene. Interestingly, the rate of butene formation (in the *absence* of CO) is higher than that of copolymerization (in the *presence* of CO) by a factor of about 2, in particular with dinitrogen (2,2'-bipyridyl) ligand systems. It is reasonable to assume that butene formation starts with a palladium hydride. This inserts ethene twice (the first insertion is probably reversible) and then terminates by β -hydrogen elimination to produce butene and regenerate the hydride. Thus, butene formation shows that olefin insertion and β -elimination are intrinsically rapid reactions. However, the copolymer produced in the above batch experiment shows neither double-olefin insertion errors nor the unsaturated end groups indicative of β -elimination.

One reason for the perfect alternation is probably the stronger coordination of CO to palladium (compared to ethene). Once a palladium alkyl is formed, the stronger CO coordination ensures that the next monomer to insert will usually be a CO molecule.³⁵ Of course, CO also coordinates more strongly to a palladium acyl, but since the CO insertion is now thermodynamically unfavorable there the system will "wait" for an ethene molecule to coordinate and insert (Scheme 3). The necessity of ethene to compete with CO for a coordination site could also be a factor causing the lower rate of copolymer formation compared to dimerization, observed for some catalysts. This explanation seems nice and tidy, but we believe that it is not the whole picture. For one thing, it cannot explain the slow rate of termination by β -elimination. Also, the rate depression by the CO/ethene competition for the coordination site is not large enough (with some catalysts containing phos-

Scheme 3. Competition between CO and Ethene Coordination in Polyketone Formation



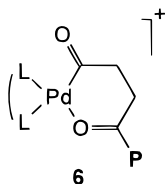
phine ligands a higher rate for copolymerization relative to dimerization is observed) to explain the complete lack of double ethene insertion errors. We suggest that, in addition, internal coordination of the growing polymer chain to palladium might be responsible for the observation of strict alternation. Each time after an ethene insertion, the polymer chain end acts as a chelating ligand, in which the oxygen atom of the β -carbonyl group coordinates to the electrophilic palladium atom (structure 5).



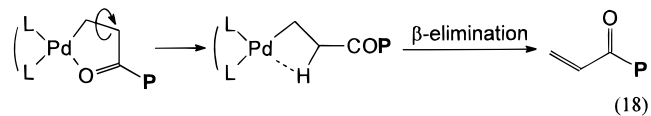
Stable species of this type have recently been observed by spectroscopic techniques in the studies of olefin insertion in palladium acyls,^{21,22,26,27} and the structure of some of such compounds has been determined.^{26,27} The electrostatic interaction between the positive palladium center and the negative oxygen atom is probably the main driving force for chelate formation. The internal coordination may affect the chain propagation in a number of ways.

Firstly, the stabilization by chelate formation should increase the exothermicity of the olefin insertion step in palladium-acyl. Since part of the stabilization will already be "felt" in the transition state (Hammond postulate), it may considerably reduce the barrier for olefin insertion in a palladium acyl.

However, at the same time, chelate formation opposes insertion of the *next* monomer by blocking the fourth coordination site at palladium. The incoming monomer has to displace the carbonyl group first, and this can increase the insertion barrier. It might well be that olefin coordination to Pd^{II} in this chelate is too weak to displace the carbonyl group in this stable five-membered ring structure. Displacement of the chelate carbonyl by the olefin (and not olefin migratory insertion in the "open" Pd-alkyl) could thus provide the highest barrier for olefin insertion in Pd-alkyl under polyketone synthesis conditions. Carbon monoxide, which binds more strongly to palladium, and probably requires less space than olefins to coordinate, *can* more readily displace the carbonyl group and then insert. This generates a species in which the carbonyl group is now located γ with respect to palladium. This carbonyl group might still coordinate to palladium (structure 6), but the resulting six-membered ring should be less stable than five-membered ring structure 5. Ethene will be able to readily displace the carbonyl group in 6 and then insert to regenerate the next five-membered ring species.



Secondly, chelate formation should also prevent or slow down termination by β -elimination. For β -elimination to occur, the β -H atom has to approach the palladium atom, but that is inhibited by coordination of the carbonyl group to palladium (eq 18). Inhibition of β -H elimination in metallacycles is well-known.³⁶



In the third place, chelate formation could be important by imposing a *cis*-ligated environment around the palladium center. This is, of course, not relevant to systems bearing bidentate ligands, where *cis*-coordination is enforced by the ligand. It could, however, contribute in the reported CO/ethene copolymerization by catalysts based on monodentate phosphines.¹¹ Chelate formation at the chain end should force the monodentate ligands to a *cis* arrangement, which is essential to chain propagation.

To summarize, we have the following picture of alternation in chain propagation. Internal coordination of the chain end to palladium and the CO/ethene competition prevent double ethene insertion, while thermodynamics prevents double CO insertion. The architecture of the copolymer thus assists in its own formation, achieving a perfect chemoselectivity to alternating polyketone.

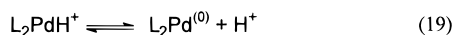
D. The Role of Oxidant Promoters

The copolymerization catalysts generally show a higher activity in the presence of added oxidants like quinones. Rate enhancements vary from 2–15 for catalysts based on diphosphines³⁷ to more than 200 for bipyridine-type ligands.³⁸ These rate enhancements are not due to faster propagation, since chain lengths are not affected by the presence of (low concentrations of) promoters. Therefore, added oxidants must cause the participation of a larger number of active centers. We will try to rationalize this promoting effect of oxidants below.

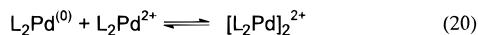
As discussed earlier, a chain can be started either from a palladium hydride or from a carbomethoxy species. Both initiation reactions are rapid, at least for alkyl olefins. Initiation by a hydride gives an alkyl end group, while initiation by a carbomethoxy gives an ester end group. Termination can produce either a hydride (by β -elimination or methanolysis) or a methoxide (by protonolysis) which is rapidly converted to a carbomethoxy species. Addition of low concentrations of oxidants does not affect the chain length (and therefore the propagation or termination steps) but results in a greater proportion of ester end groups. This means that it causes more chains to *start* via carbomethoxy species.

If both hydride and carbomethoxy precursors remained intact until they started a new chain, and (as suggested above) both initiation steps were rapid relative to propagation, oxidants could affect the end groups but should *not* affect the rate. The fact that they do indicates that palladium hydride can "drop

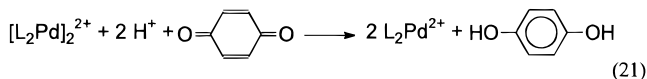
out" of the catalytic cycle. The most obvious way for it to do so is by decomposition to Pd⁽⁰⁾:



For complexes bearing nitrogen ligands, the Pd⁽⁰⁾ may immediately lose its ligand and precipitate as metallic palladium. For diphosphine systems, the Pd⁽⁰⁾ complexes might have a reasonable stability. In the case of *aryldiphosphines*, they could combine with a Pd²⁺ species to form a palladium dimer, thus removing *two* Pd atoms from the catalysis:



Such palladium dimers have been detected by Dekker,²¹ and one example has been structurally characterized.³⁹ Each of these three reactions (formation of Pd⁽⁰⁾, precipitation of Pd metal, formation of Pd₂²⁺ dimers) reduces the rate at which palladium hydrides can reenter the catalytic cycle. Presumably, oxidants function by oxidizing some or all of these "dead ends" to Pd²⁺, which can then immediately reenter the cycle, as in eq 21.

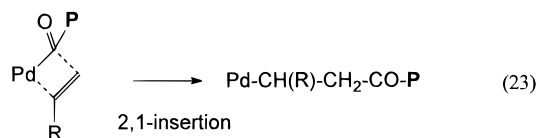
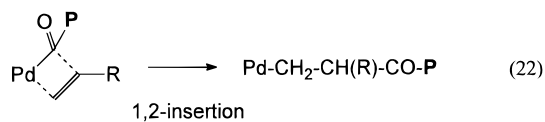


III. Copolymerization of Carbon Monoxide and Higher α -Olefins

A. Regio- and Stereochemical Control

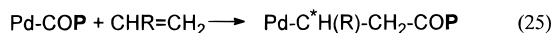
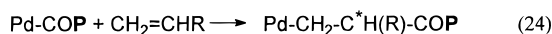
In the previous sections, we have described the use of cationic palladium catalysts to produce perfectly alternating CO/ethene copolymers. One of the unique features of these catalysts is their ability to also catalyze the alternating copolymerization of higher α -olefins (H₂C=CHR) with carbon monoxide. This allows the study of two additional aspects of CO/olefin copolymerization, namely regioselectivity and stereoselectivity of olefin insertion in palladium-acyl intermediates during chain propagation.

Because of the presence of a substituent, higher olefins can react with metal-acyl species by either 1,2- or 2,1-insertion.

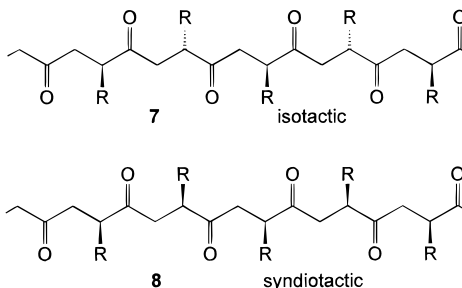


In principle, one can thus discriminate between two types of copolymers, i.e. regioirregular and regioregular copolymers. Regioregular polymers can be obtained via either 1,2- or 2,1-insertion; it can be difficult to distinguish between these possibilities.

Insertion of an α -olefin in a metal-acyl intermediate creates a center of chirality for both regioinsertion modes:



Assuming either a 1,2- or a 2,1-regioregular propagation, one could thus envisage formation of atactic (stereoirregular), isotactic (**7**), and syndiotactic (**8**) structures.⁴⁰ In contrast to olefin homopolymers, CO/olefin copolymers retain a chiral center per monomer unit because *regioregularity* induces a direction in the chain. In fact, isotactic CO/olefin copolymers appear to be one of the few man-made optically active polymers with main-chain chirality, synthesized directly from achiral monomers.



A large variety of α -olefins can be effectively copolymerized with carbon monoxide:

- (i) propene and higher homologues;^{18,41-44}
- (ii) functionalized olefins in which the functionality (e.g. -CH₂OH, -CH₂CN, -CH₂Cl, -COOH, -COOR) is separated by at least one methylene group from the olefinic bond;^{45,46}
- (iii) styrene and its (functionalized) analogues.^{38,54-59}

In addition, *internal* olefins can be reacted (albeit at much reduced rates) to give low molecular weight oligomers by a sequence of insertion and isomerization steps.⁴⁷ In this section we will discuss the factors which govern the regio- and stereochemical control of α -olefin insertion in palladium(II)-acyl intermediates. We will illustrate important aspects using propene and styrene as the representative examples of olefins belonging to class i and iii above.

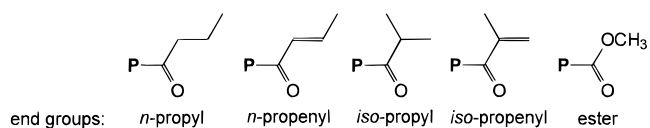
Direct, detailed analysis of regio- and stereochemistry of a polymerization reaction is often very difficult, and the present case is no exception. Fortunately, some of the polyketone catalysts have been found also to effect hydroformylation and/or hydroacylation, which involve some of the same elementary reaction steps. Although from a study of these reactions, no conclusions can be drawn with respect to rates and molecular weights achievable in polymerization, product analysis, which is much easier in this case, can assist in understanding factors controlling regioselectivity (and potentially also stereose-

lectivity) of the polymerization reaction. Therefore, we will discuss regiocontrol in these simpler model reactions.

B. Copolymerization of Propene and Carbon Monoxide

The alternating copolymerization of propene and carbon monoxide, first reported by us in the patent literature,^{41a} proceeds efficiently with catalysts of the general constitution L_2PdX_2 in which L_2 represents a bidentate phosphine and X stands for a weakly or noncoordinating anion. With a proper choice of diphosphine and anion, catalyst productivities can reach 100–1000 mol of converted propene (mol Pd)⁻¹ h⁻¹, while the molecular weight of the resulting copolymers can be varied over a wide range (up to $M_n \approx 30\,000$) by an appropriate choice of reaction conditions. These catalysts have thus provided access to a potentially interesting class of new materials. Since the original discovery, several groups^{1c,18,41–43} have investigated the copolymerization of propene with carbon monoxide. In particular, the challenge to accomplish complete regio- and stereochemical control of propene insertion has been the subject of recent studies.

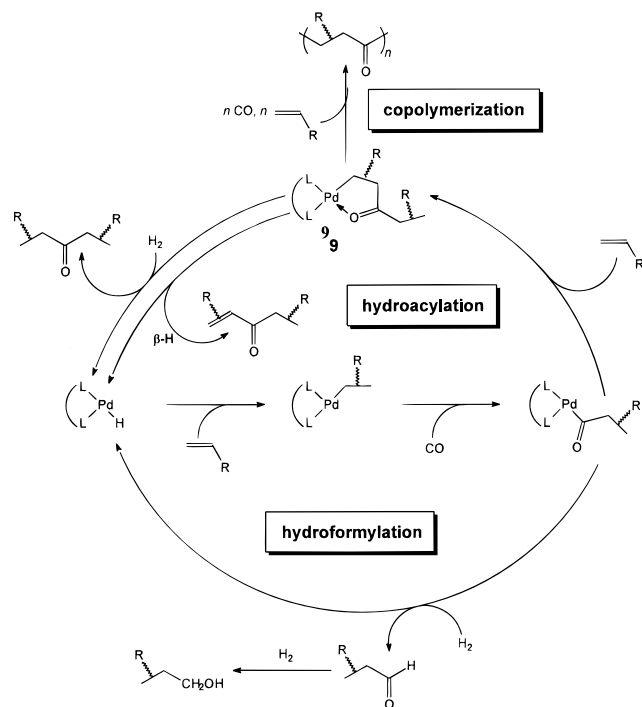
The gross structure of copolymers produced with different catalysts, as derived from ¹³C NMR spectra, does indeed reveal their perfect CO/C₃ alternation.⁴⁸ End group analysis by NMR of low molecular weight polymers shows the presence of mainly isopropyl/propenyl ketone and *n*-propyl/propenyl ketone chain ends. Even if the polymerization is carried out in methanol, only small amounts of ester end groups are observed. In contrast to the CO/ethene copolymers, in which unsaturated ketonic end groups are only obtained under special conditions,³⁰ β-H elimination now appears to be a major termination process. The resulting polymers are thus predominantly produced via Pd–hydride initiation⁴⁹ and termination.



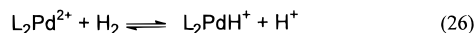
1. Hydrocarbonylation of Propene and Higher α-Olefins

When selected copolymerization catalysts are exposed to propene (or higher aliphatic olefins) in the presence of carbon monoxide and hydrogen at elevated temperature and in aprotic solvents aldehydes and/or monoketones can be generated with good rates and selectivities.^{50,51} Typical propene conversion rates are 100–1000 mol (mol Pd)⁻¹ h⁻¹ at 100–125 °C and $P_{CO} = P_{H_2} = 30$ atm in diglyme as reaction solvent. Scheme 4 summarizes the aldehyde and ketone formation, respectively hydroformylation and hydroacylation reactions and shows their relation with olefin/CO copolymerization. Aldehydes are produced by hydrogenolysis of Pd–acyl species, while saturated and unsaturated monoketones are formed by olefin insertion in the same Pd–acyl intermedi-

Scheme 4. Relation between Pd-Catalyzed Hydrocarbonylation of Olefins (Hydroformylation/Hydroacylation) and Olefin/CO Copolymerization (Wavy Lines Denote Arbitrary Regiochemistry)



ates, followed by either hydrogenolysis or β-elimination. The initial palladium hydride species is thought to be generated by heterolytic splitting of hydrogen at the electrophilic palladium center (eq 26).



In principle, the olefin can insert in a 1,2- or 2,1-fashion in both the Pd–H and the Pd–acyl bond. This leads to two possible aldehydes (linear and branched), three saturated ketones, and four unsaturated ketones. From the relative amounts of these products, we can deduce the regioselectivities of the insertion of the olefin at palladium; the results are summarized in Table 1. Inspection of the table shows that both ligands and counterions have a profound influence on the selectivities.

The *n*/iso ratios of both aldehyde and ketone products increase with increasing bulk of the ligand. However, the proportion of ketones derived from *n*-acyl intermediates is consistently higher than the proportion of *n*-aldehydes derived from the same intermediates. Anion variation can shift the balance from aldehyde production to ketone formation, but the regioselectivities of the products that are formed remain constant (Table 1, *n*-Bu ligand example). In our opinion, this must mean that both the olefin insertion in the Pd–H bond and the CO insertion in the Pd–alkyl bond are reversible.^{25,52} The acyl intermediate is then “trapped” either by hydrogenolysis to aldehyde or by olefin insertion to eventually give a ketone. Apparently, the olefin insertion reaction is more sensitive to the steric difference between *n*- and isoacyl intermediates, and therefore has a higher preference for trapping the *n*-acyl intermediate. This preference becomes even higher with bulky ligands or larger olefins.

Table 1. Hydrocarbonylation of α -Olefins^a

ligand R ^b	anion	olefin	aldehydes		ketones				
			% Ald ^c	% linear ^d	h to t ^e	h to h ^e	t to t ^e	1,2-sel ^f	<i>n</i> -acyl sel ^g
Ph	TFA ⁻	propene	75	72	55	14	31	65	82
<i>n</i> -Bu	OTs ⁻		40	60	83	11	6	93	88
	OTf ⁻		trace		82	11	7	92	88
<i>i</i> -Pr	TFA ⁻		~100	82					
	OTf ⁻		trace		92	6	2	98	94
<i>s</i> -Bu	TFA ⁻		~100	84					
	OTf ⁻		trace		93	5	2	98	95
<i>n</i> -Bu	TFA ⁻	1-octene	~100	70					
	OTf ⁻		trace		98	2	<1	≥99	≥98

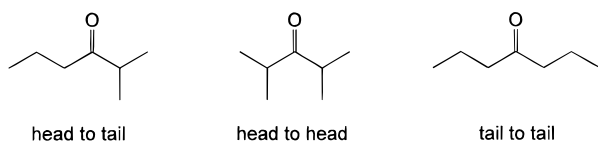
^a For experimental conditions, see text.^{50,51} ^b Ligands are diphosphines R₂P(CH₂)₃PR₂. ^c Including alcohols formed by reduction of aldehydes. ^d As a percent of total aldehyde. ^e Saturated + unsaturated, as a percent of total ketone formed. ^f Calculated as (**h** to **t**) + (**h** to **h**) - 0.01 × (**t** to **t**) × (**h** to **h**); see ref 68. ^g Calculated as (**h** to **t**) + (**t** to **t**) - 0.01 × (**h** to **h**) × (**t** to **t**); see ref 68.

Inspection of the table shows that olefin insertion in the Pd-acyl bond is preferentially 1,2. Larger ligands increase this preference, as expected. Surprisingly, the *aryl*phosphine ligand dppp has a very low regioselectivity, even though it is larger than the smallest *alkyl*phosphine ligands used in the examples. This suggests that electronic factors also contribute.

The degree of unsaturation of the product ketones reflects the relative rates of termination by β -elimination and hydrogenolysis. We have observed that the highest degree of unsaturation is found in the head-to-head coupled ketone. This may be related to the strength of the internal coordination of the carbonyl group. In the previous section, we have argued that internal coordination stabilizes alkyl species (e.g., **9** in Scheme 4) and suppresses β -elimination, resulting in long-chain polymers. Large substituents in both olefin units of intermediate **9** could destabilize the chelate structure and so promote β -elimination. This effect should be largest for the head-to-head coupled ketone, where both substituents are closest to the carbonyl group. Apparently, hydrogenolysis to give the saturated ketone is not hindered as much by chelate-ring formation; possibly, this reaction can take place without having to disrupt the Pd-O coordination completely.

2. Regioselectivity of CO/Propene Copolymerization

On close inspection of the gross structure by ¹³C NMR, the spectra of samples produced with different catalysts display significant differences, which can be traced back to differences in regio- and/or stereoregularity of the polymers. Catalysts derived from *aryl*phosphines (e.g. dppp) have been shown to produce copolymers which are characterized by only a modest regioselectivity. The carbonyl region of the ¹³C NMR spectrum shows a "triplet" of fairly broad resonances, which are assigned to the three possible combinations of two olefinic units around the carbonyl group:^{41,42a}



From the intensity ratio of the resonances one can conclude that the two possible propene insertion modes (1,2 and 2,1) in Pd-acyl intermediates proceed with a relative frequency of about 3:1. The relatively low regioregularity of chain propagation of 75% agrees with the selectivity of 65% found in the monoketone formation discussed above. The observation of a low backbone regularity is in line with the absence of a sharp melting point for this material.

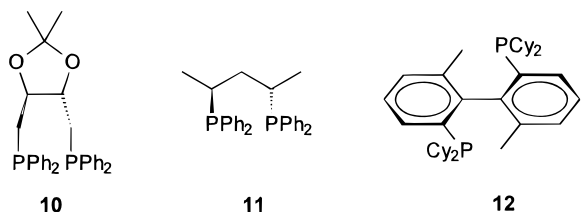
Much higher regioregularity (up to at least 99%) has been obtained using *alkyl*phosphine ligands, particularly in combination with noncoordinating anions. Again, these results are in line with the selectivities observed in monoketone formation. The resulting materials have well-defined melting points, e.g. 165 °C for a ~94% regular material obtained with dbpp,^{41c-e} and 260 °C for a >99% regular product prepared using dippp.^{42a} End group analysis of highly regular materials shows isopropenylketone groups but no *n*-propenylketone groups,^{42e} confirming that these polymers are formed by repeated 1,2-insertion. Apparently, the same factors that govern regiochemistry in hydrocarbonylation also determine regularity in polymer formation. Thus, we suggest that chain propagation in the CO/olefin copolymerization involves alternating *reversible* carbon monoxide insertion in Pd-alkyl species and *irreversible* olefin insertion in the resulting Pd-acyl intermediates.²⁸ The overall exothermicity of the polymerization is caused predominantly by the olefin insertion step, and regioselectivity is also determined in this step.

3. Stereochemistry of CO/Propene Copolymerization

The small line widths of the ¹³C NMR resonances and the high melting points observed for polymers produced using the *achiral* dippp ligand suggest the presence of some degree of *stereoregularity*.^{42e} It is, indeed, conceivable that a correlation might exist between the regioregularity of the growing chain and enantioface selection in olefin insertion into Pd-acyl intermediates: a regioregular chain end, which contains a center of chirality, as indicated above, could impose an enantioface-dependent steric limitation on the incoming olefin.

A similar correlation between stereochemical control and induced regioregularity is suggested by the

analysis of CO/propene copolymers produced using *chiral arylphosphine ligands* like **10** and **11**.^{41d,42}



A considerably increased head-to-tail C₃ enchainment of more than 90% is observed for these polymers, compared with the 75% observed with polymers produced with the achiral dppp ligand. Consiglio *et al* observed virtually complete head-to-tail C₃ enchainment for polymers produced using *chiral alkylphosphines* like **12**.^{42b} Their analysis of ¹³C NMR spectra in the methyl group region established that these polymers have a high degree of stereoregularity. The spectra could be interpreted on the basis of an enantiomorphic site control, similar to modern homogeneous isotactic olefin polymerization catalysis.

Sen, also recently reported “essentially perfect” head-to-tail coupling and isotacticity using the chiral DUPHOS ligand.⁴⁷ He also reported that mixtures of stereoregular copolymers of opposite chirality exhibited a curious melting behavior.⁵³

The circular dichroism spectra of these materials show an intense band in the n-π* region, which is similar in magnitude to that of optically active polyvinyl ketones. This implies high optical activity, which, in turn, can only be associated with an isotactic stereochemistry of the polymer chain.

C. Copolymerization of Styrene and Carbon Monoxide

The alternating copolymerization of styrene and carbon monoxide proceeds efficiently with palladium

complexes of bidentate nitrogen ligands (e.g., 2,2'-bipyridine or 1,10-phenanthroline) and weakly or noncoordinating anions in methanol as a solvent.^{38,54–57} An oxidizing cocatalyst (e.g., quinone) is also needed. The copolymer produced is insoluble in common organic solvents and has a melting point of ~280 °C. The ¹³C NMR spectrum of a solution of the copolymer is shown in Figure 2. The resonances at 43.2, 54.0, and 209.7 ppm are assigned to backbone methylene, methyne, and carbonyl carbons, respectively, of the repeating molecular unit –CH₂CHPhCO–. The aromatic carbon resonances are located at 127.7, 128.0, 129.5, and 136.1 ppm. In copolymers of sufficiently low molecular weight the end groups are also visible; ester (–CHPhCH₂COOCH₃) and ketone (–CHPhCOCH=CHPh) groups are usually observed in ratios close to 1. Thus, the NMR analysis confirms chemoselectivity to a perfectly alternating copolymer of carbon monoxide and styrene. In addition, it demonstrates 100% regioselectivity to head-to-tail enchainment of the styrene units to a polymer of the following overall structure:



The polymer chains are seen to be generated by a net oxidative carbonylation, with quinone as the oxidant, which is stoichiometrically converted to hydroquinone based on end groups of the polymer chains. In the absence of oxidants polymer formation is strongly reduced. Also, hydrogen has been found to be a powerful polymerization inhibitor.

The styrene/CO copolymerization system, catalyzed by palladium–bipyridine type complexes, is the only “real” polyketone system studied so far for which intermediates could be observed in low-temperature NMR studies.⁵⁹

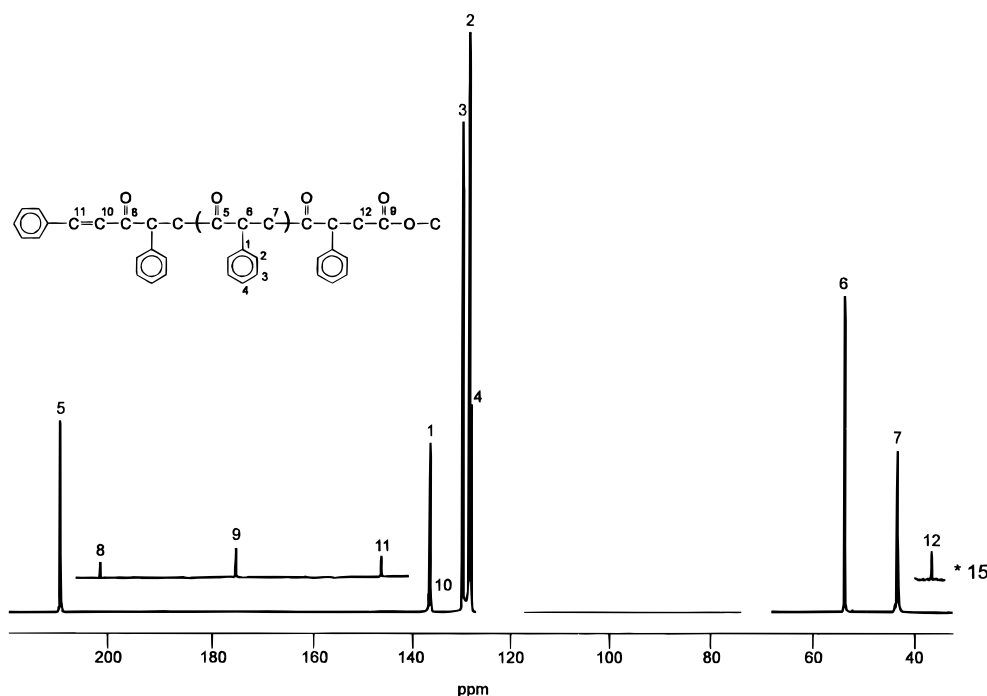


Figure 2. ¹³C NMR (250 MHz) spectrum of CO/styrene copolymer [dissolved in HFIPA/CDCl₃ (70/30)] produced with palladium 2,2'-bipyridyl catalyst.³⁸

1. Hydrocarbonylation of Styrene

As observed for propene, reaction of styrene with CO and H₂ in the presence of a polyketone catalyst results in formation of aldehydes and/or ketones with good rates (styrene conversion rates 200–500 mol (mol Pd)⁻¹ h⁻¹ at 115–125 °C, $P_{\text{CO}} = P_{\text{H}_2} = 30$ atm, e.g. anisole as solvent).^{51,58} The results of the product analysis, obtained with a selection of polyketone catalysts, are collected in Table 2. Where *aldehydes* are obtained, we see a preference for the linear isomer, i.e. the product derived from 1,2-insertion in the Pd–H bond. As with propene, this preference is larger with bulkier ligands. When *ketones* are formed we find a high preference for the *t*-to-*t* isomer. This isomer can only be formed by 1,2 insertion in Pd–H and a consecutive 2,1-insertion in Pd–acyl. As the *unsaturated h*-to-*t* ketone isomer, 1,4-diphenylpent-1-ene-3-one, is formed exclusively, we may conclude that styrene insertion in Pd–acyl takes place exclusively in the 2,1-fashion.

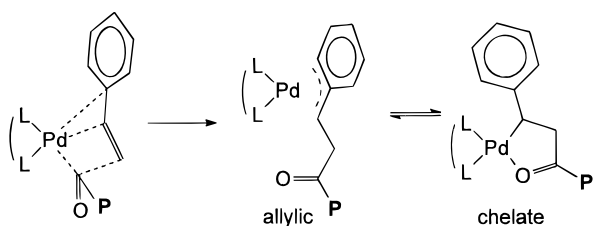
Table 2. Hydrocarbonylation of Styrene^a

ligand R ^b	anion	aldehydes		ketones	
		%Ald	%linear ^c	<i>h</i> to <i>t</i> ^d	<i>t</i> to <i>t</i> ^d
Ph	TFA ⁻	~100	85		
	OTs ⁻	50	84	2	98
Et	TFA ⁻	~100	72		
	OTf ⁻	trace		16	84
phenanthroline ^e	BF ₄ ⁻	7	67	1	99

^a For experimental conditions, see text.⁵¹ ^b Ligands are diphosphines R₂P(CH₂)₃PR₂, except for the last entry. ^c As a percent of total aldehyde. ^d Saturated+unsaturated, as a percent of total ketone formed. ^e From ref 58.

The percentage of ketone products derived from 1,2 Pd–H insertion, is consistently higher than the percentage of *n*-aldehydes also formed via the same 1,2-insertion mode in Pd–H. The aldehyde product distribution clearly shows that insertion in the Pd–H bond can occur in both ways and that both insertion products can insert CO, so we conclude that styrene insertion preferentially traps the *n*-acyl intermediate, presumably for steric reasons. This is in line with the results obtained for propene described above.

The most surprising aspect here is that styrene, in contrast to propene, inserts into the Pd–acyl bond *exclusively* in a 2,1-fashion. Possibly, steric hindrance between the acyl group and the phenyl group in the 1,2-insertion transition state blocks the 1,2-regiochemistry. It could also be that interaction between the palladium atom and the phenyl ring *during the insertion* provides a lower energy insertion pathway. Brookhart⁵⁹ has shown that *after* insertion, the product exists as a rapidly exchanging mixture of allylic and chelate structures ($K \approx 1/3$ at –80 °C), demonstrating that the allylic coordination is quite strong (see also ref 21).

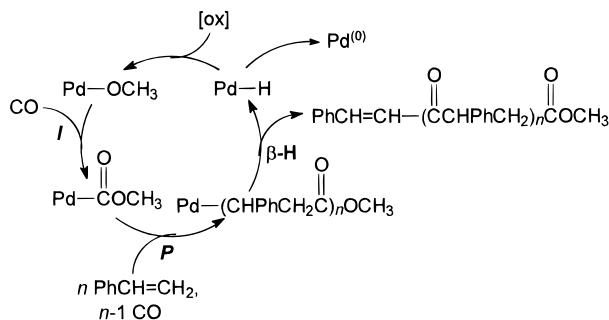


The peculiar regiochemistry—an apparent reversal of regioselectivity between insertion into Pd–hydride and Pd–acyl species—has also been observed with other functionalized olefins, such as acrylic olefins.⁵¹ As with styrene, it is suggested that both steric effects and the interaction of the electron-rich functionality with the electrophilic palladium center contribute to the observed high selectivity to α,ω -functionalized products.

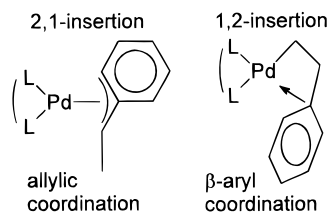
2. Regioselectivity of CO/Styrene Copolymerization

Initiation of CO/styrene copolymerization is by 2,1-insertion of styrene in a palladium–carbomethoxy species, and propagation occurs by 2,1-insertion in Pd acyls, in perfect agreement with the results for styrene hydrocarbonylation. The main *termination* mechanism is β -elimination, which produces a transient palladium hydride. The function of the oxidant is to reoxidize this back to a palladium methoxide before it can decompose to Pd metal (Scheme 5). In

Scheme 5. CO/Styrene Copolymerization in the Presence of an Oxidant



the absence of oxidants or in the presence of hydrogen, the copolymerization (at 25–75 °C) is completely suppressed. This implies that, for some reason, palladium hydride species are unable to start the polymerization cycle at this low temperature. The problem cannot be with the insertion of styrene in the palladium–hydride bond, since the same system is an efficient catalyst for the *hydrogenation* of styrene even at room temperature. Once an acyl has been formed, polymerization can continue even at –80 °C, as shown by Brookhart et al.⁵⁹ Therefore, the difficult step must be the *formation of the first acyl species*, i.e. the insertion of CO into the Pd–styryl bond. Possibly, both Pd–styryl isomers are so strongly stabilized that CO insertion is too endothermic to occur. The 2,1-insertion isomer could be stabilized by allylic coordination, and the 1,2-isomer by β -aryl coordination.⁶⁰ Since CO insertion is prevented, the palladium hydride or styryl eventually decomposes to palladium metal, unless it is oxidized to a methoxide first. At higher temperatures, CO insertion in the Pd–styryl bond *does* occur, but then β -hydrogen elimination is so rapid that only monoketone products are obtained, as discussed in the previous section.



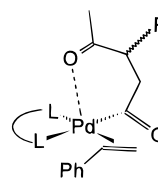
We can conclude that styrene is special in that *initiation* is the difficult step here. For other olefins, polymerization can start with either a hydride or a carbomethoxy species, and termination can occur by either β -elimination or protolysis to regenerate an active species. For styrene, *termination* always produces a *hydride*, but *initiation* requires a *methoxide*, so an oxidant is needed to close the catalytic cycle. It is interesting to note that Brookhart et al. have circumvented the use of an oxidant by (1) taking a palladium–acyl initiator complex and (2) carrying out the polymerization at sufficiently low temperatures, such that chain termination does not occur (“living polymerization”).

Thus far, copolymerization of carbon monoxide and styrene has not been observed with catalysts containing phosphine ligands. This might seem surprising in the light of the results observed in monoketone synthesis (Table 2). Certainly, all ketones produced in styrene hydrocarbonylation must have been formed by 2,1-insertion of styrene in Pd–acyls for both nitrogen and phosphorus ligands. So, why do we require nitrogen (or sulfur, see below) ligands to get further propagation to polymers? One explanation could be that the CO/styrene copolymer has a higher tendency to terminate by β -elimination than the other copolymers we have considered. β -Elimination is opposed by internal coordination of carbonyl groups, and this coordination will be strongest if the metal is very electrophilic. So, polymers having a higher tendency to undergo β -elimination need “harder” ligands (nitrogen, sulfur ligands) to prevent that reaction.

3. Stereochemistry of CO/Styrene Copolymerization

The narrow line width of the ^{13}C NMR resonances, the high melting point, and insolubility in common organic solvents observed for CO/styrene copolymers all indicate a high degree of stereochemical regularity in these materials. Indeed, Pino et al.⁵⁵ have established that the polymers produced using 2,2'-bipyridyl ligands are largely syndiotactic, with a racemic diad contents of about 90%. A high enantioface discrimination during styrene insertion in Pd–acyl intermediates must, thus, take place during chain propagation. Consiglio et al.^{54a,61} have shown that by applying large amounts of benzoquinone as the oxidant, the selectivity of the reaction can be shifted toward low molecular weight products. This work has, similarly, suggested a preferential *u*-topicity of the enantiofaces of two consecutive styrene units, giving a syndiotactic enchainment. Since the palladium center itself does not possess elements of chirality, the chirality of the polymer chain end must be responsible for enantioface selection. Such a very effective chain end-controlled enantioface selection may, at first sight, seem surprising since the distance

between the existing and newly formed chiral centers is rather large. However, we suggest that during the insertion the γ -carbonyl group of the acyl chain end stays close to the palladium center. This would cause a close proximity between the chain end chiral center and the palladium site, thus imposing chirality on the styrene coordination site prior to insertion (structure **13**).



13

A remarkably different microstructure is observed in CO/styrene copolymers produced using bis(thioethers) (e.g., 1,2-bis(thioethyl)ethane) as ligands.⁶² Both the alternation and the regioselectivity of the styrene insertions remain intact, but the stereochemical control is completely lost, leading to atactic material. This is nicely illustrated by the absence of a melting point (glass temperature $\sim 100^\circ\text{C}$), the high solubility in organic solvents like chloroform, and the broad ^{13}C NMR resonances of the chain carbon atoms. As an illustration, Figure 3 shows the ^{13}C NMR resonances of the methyne and methylene carbons of materials produced using 2,2'-bipyridine (**3a**) and 1,2-bis(ethylthio)ethane (**3b**). We suggest that the reasons for the loss of stereochemical control must be sought in the flexible structure of the bis-(alkylthio)ether ligands relative to the rigid structure of bis-pyridyl type ligands. Apparently, the former ligands can easily adapt their conformation to accommodate the various stereochemical styrene insertion modes. These results clearly illustrate that

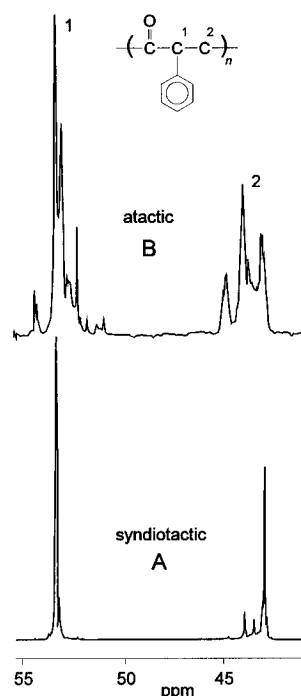


Figure 3. Methyne and methylene ^{13}C NMR resonances [250 MHz, dissolved in HFIPA/ CDCl_3 (70/30)] of syndiotactic (A) and atactic (B) CO/styrene copolymers.^{38,62}

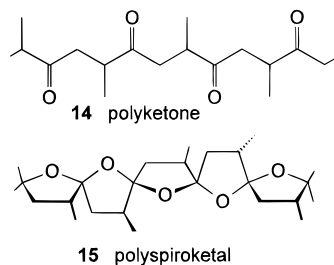
chain end stereocontrol requires a cooperation between the palladium center and the polymer chain end.

It can now also be made plausible why stereochemical control during the copolymerization with *achiral* ligands is more difficult with aliphatic olefins than with styrenes. As we have shown in section III.B, alkyl olefins generally insert in a 1,2-fashion in Pd acyls. Therefore, the chain-end center of chirality is even further removed from the palladium center, which makes it less probable that this center of asymmetry can impose its chirality on the catalyst center. Therefore, any "weak" chain end control mechanism can generally easily be overruled by enantiomorphic site control through the use of *chiral* ligands as shown above. Usually, this will lead to isotactic copolymers.

Recently, some interesting examples have been published, which demonstrate that the chain end controlling syndiotactic stereochemistry in 4-*tert*-butylstyrene/CO copolymers can also be overruled by an enantiomorphic site control mechanism with certain chiral bis-oxazoline ligands.⁶³ With the use of enantiomerically pure ligands, it is thus possible to prepare highly isotactic, optically active CO/styrenic copolymers.

IV. The Formation of Polyspiroketal Structures

Surprisingly, the alternating copolymerization of both propene (or higher olefins) and cyclic olefins with carbon monoxide often produces spiroketal repeat units (**15**) instead of the expected ketone repeat units (**14**). In the following sections, we will discuss the characterization of these structures and their implications for the copolymerization mechanism.



A. CO/Propene Copolymers

Copolymers containing ketal repeat units were first reported by Van Doorn et al.^{41c} Subsequently, the synthesis of these polymers has been discussed by Consiglio et al.⁶⁴ and Wong et al.⁶⁵ The copolymerization proceeds efficiently at low temperatures with catalysts based on *dbpp* under nonacidic conditions. Under these neutral conditions, the catalysts are susceptible to reduction to Pd⁰, resulting in low reaction rates and a gray color of the resulting polymers. Good rates and high molecular weights, however, are obtained when either an oxidant or a water scavenger is present,^{41c} suggesting that water plays a role in the deactivation process.

The ¹³C NMR spectrum of a sample of the polymer dissolved in HFIPA (Figure 4a) is consistent with an alternating polyketone structure. The narrow car-

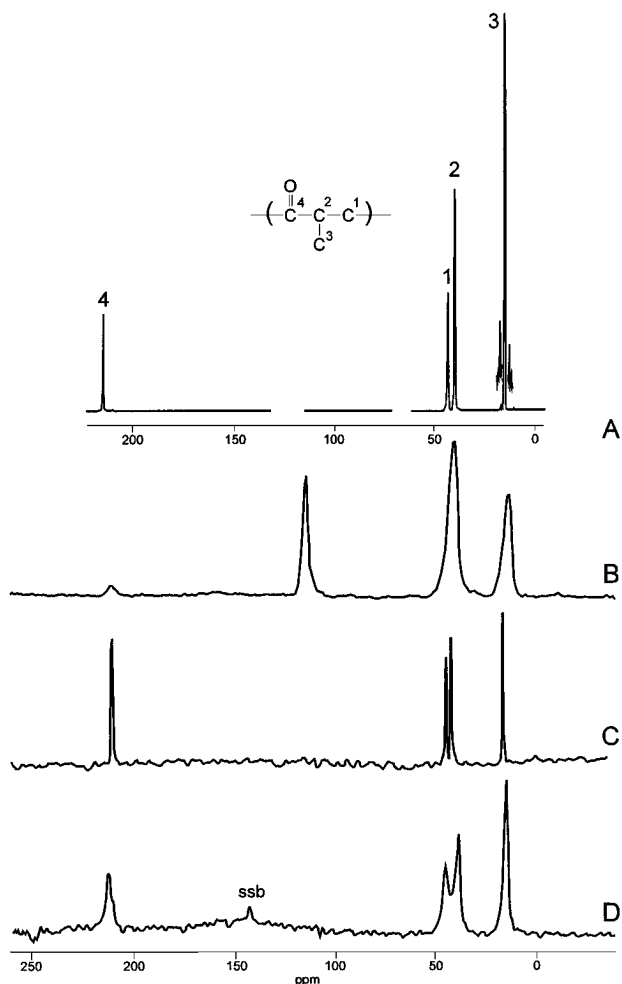


Figure 4. ¹³C NMR spectra of CO/propene copolymers (A) dissolved in HFIPA, and MAS solid-state ¹³C NMR spectra (B) before work-up, (C) at 210 °C, and (D) at room temperature, after heating to 210 °C.

bonyl resonance at 217 ppm suggests highly regioselective (but not stereoselective) incorporation of propene. The small peaks at 12.3, 17.0, and 17.4 ppm can be attributed to *n*-propyl and isopropyl end groups. Ester end groups, which would be expected in the vicinity of 176–178 ppm, are not observed.

Room temperature solid-state ¹³C MAS NMR of the same polymer *before workup* shows a surprisingly low intensity of the carbonyl resonance (now at 210.7 ppm). Instead, a new resonance centered at 114.3 ppm is observed, which we can assign to the spiroketal carbon atom (Figure 4b). The fraction of repeat units present in the spiroketal form appears to vary between 70–90% (by NMR), depending on the polymerization conditions. A MAS spectrum recorded at high temperature (210 °C, Figure 4c) shows a "normal" polyketone structure, which does *not* revert to the spiroketal structure on cooling (Figure 4d). Differential thermal calorimetry (DSC) measurements have shown an endothermic conversion process with an onset temperature at around 70 °C and an enthalpy change of about 2.5 kcal/mol. Thus, both heating and dissolution in HFIPA cause an irreversible opening of the spiroketal structure to the ketone structure. This suggests that the spiroketal structure is formed *during* the catalytic chain growth, as discussed below.

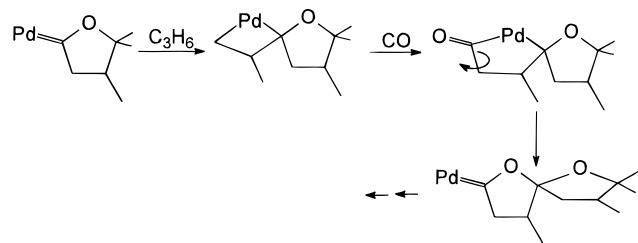
In principle, any aldehyde or ketone can form an acetal or ketal oligomer or polymer. The *enthalpy* of polyketal formation depends on the degree of substitution of the carbonyl compound. Increased substitution opposes ketal formation since the polymerization brings two such substituted carbon atoms close together. For monomeric carbonyl compounds, polyketal formation is unfavorable because of its associated *entropy* loss. The balance between enthalpy and entropy factors is such that formaldehyde polymers and oligomers are fairly stable, whereas ketones have a very low ceiling temperature of polymerization.⁶⁶

For the *polyketones* considered in this review, the entropy loss associated with polyspiroketal formation is small, since the total number of molecules does not change. Substituents in the monomer units might *promote* spiroketal formation here because of the Thorpe–Ingold effect, especially if the polymer is regioregular. The effect of these factors is that spiroketal isomers of polyketones might have an enhanced stability compared to ketal polymers of monoketones. Nevertheless, we find that polyspiroketal isomers of CO/propene copolymers rearrange easily to the open structures; Sen has claimed the isomerization, in particular with (isotactic) higher olefin/CO copolymers, to be reversible in the absence of catalyst, with the equilibrium position depending on temperature and solvent.⁴⁷ Spiroketal units have never been observed in CO/ethene copolymers: either they are never formed during the polymerization, or they open up so rapidly afterward that they are converted before the polymers can be isolated and characterized.

1. Mechanistic Considerations

Consiglio et al. suggested⁶⁴ that spiroketal formation is inconsistent with a chain growth mechanism involving stepwise alternating insertions of olefin in Pd–acyl intermediates and CO insertion in Pd–alkyls. Therefore, they have proposed a mechanism in which propagation involves a carbene intermediate (Scheme 6). However, there is no mechanistic information to support this hypothesis. Since the isomeric polyspiroketal and polyketone structures are so close in energy for α -olefin/CO copolymers, conditions (solvent, temperature) can shift the equilibrium from one to the other. Isomerization is catalyzed by both acids and bases, but could be slow in the absence of any catalyst. Therefore, it is dangerous to draw conclusions about the mechanism of polyspiroketal formation from characterization of the polymers obtained. *If* the polyspiroketal structure is formed *during* polymerization, as suggested by Consiglio, we can propose a mechanism that closely parallels the

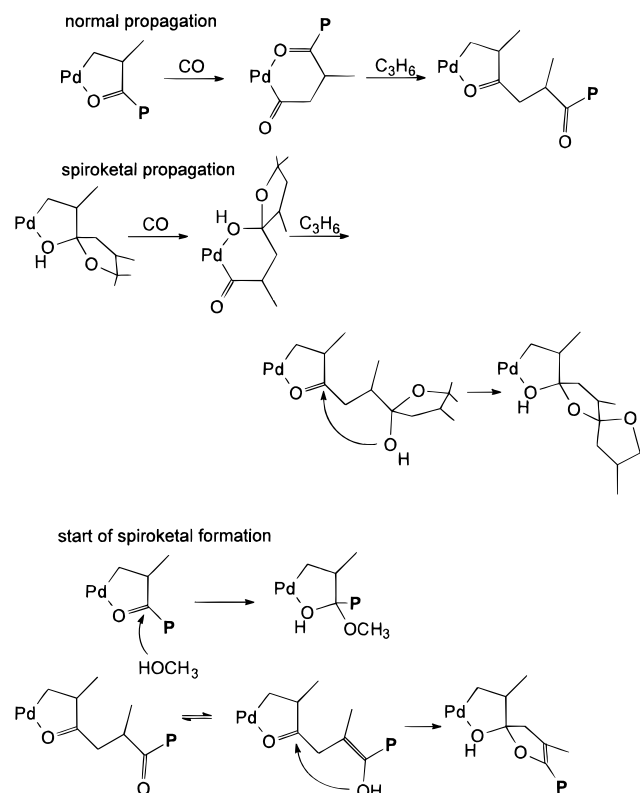
Scheme 6. Carbene Mechanism for Polyspiroketal Formation⁶⁴



normal polyketone propagation (see below). However, the observation of *reversible* polyspiroketal formation by Sen suggests that it is also possible to interpret most observations on the basis of exclusively “normal” polyketone propagation and a completely separate isomerization reaction.

In our alternative to the Consiglio carbene mechanism, chain propagation still proceeds via “classic” organometallic chemistry (Scheme 7). Internal coordination of the β -carbonyl group to Pd at the Pd–alkyl stage activates it toward nucleophilic attack by a hemiketal OH group in the neighboring unit. Thus, spiroketal formation could proceed “in tandem” with the chain growth. It would also slightly weaken the internal coordination at the alkyl stage, because an alcohol group is a poorer donor than a carbonyl group; thus it could facilitate the next CO insertion step. Factors governing regio- and stereoselectivity should be rather similar for the ketone and ketal structures. Polyspiroketal formation could *start* either by enolization or by attack of external methanol. Since in our scheme polyketone *propagation* still occurs by the original mechanism, *termination* could also occur by the same route as that for the normal polyketone. For example, β -elimination and protolysis could occur both before and after the alkyl group has isomerized to the spiroketal structure.

Scheme 7. “Tandem” Mechanism for Polyspiroketal Formation



B. CO/Dicyclopentadiene Copolymers

The alternating copolymerization of CO and dicyclopentadiene (DCPD) has been reported by us in patent literature.³⁸ The polymerization proceeds efficiently at room temperature with cationic palladium complexes of 2,2'-bipyridine in methanol in the presence of an oxidant (benzoquinone). The

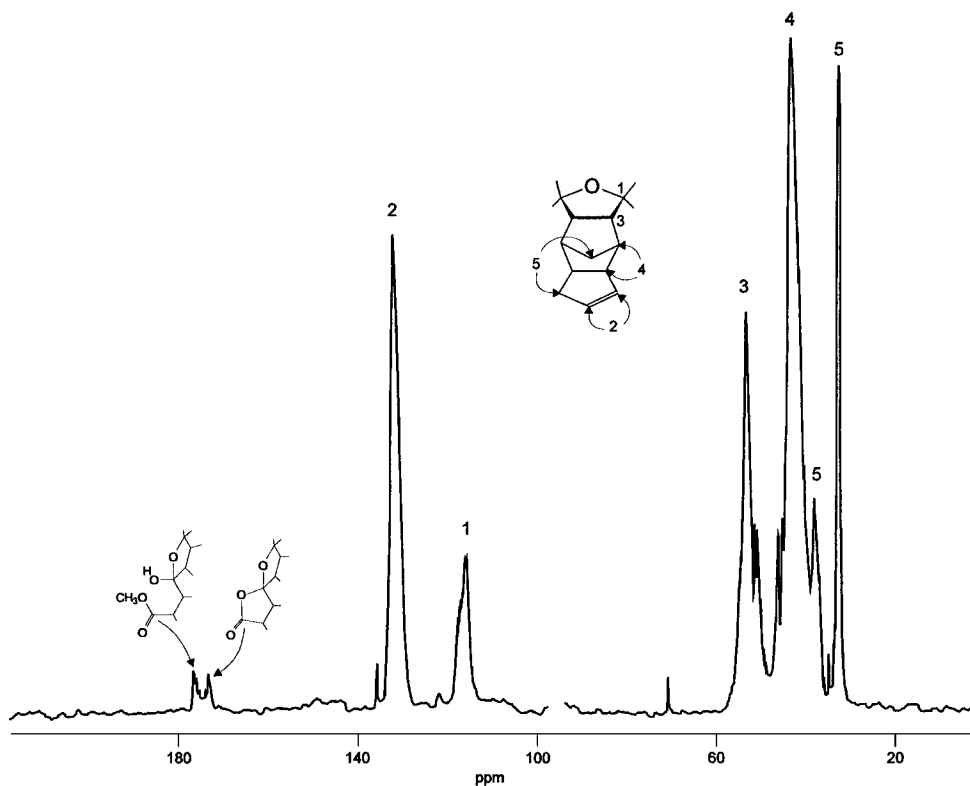
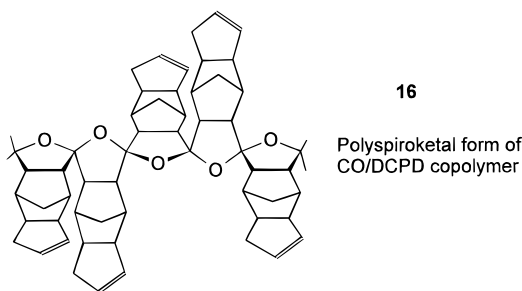


Figure 5. ^{13}C NMR (250 MHz) spectrum of CO/DCPD copolymer (dissolved in CCl_4).

resulting polymers are soluble in some organic solvents, such as tetrachloromethane; they have a relatively low molecular weight. Figure 5 shows the ^{13}C NMR spectrum of such a polymer together with a tentative assignment of the carbon atoms. The most remarkable characteristic of the spectrum is the complete absence of carbonyl resonance expected at 217–220 ppm. Instead, a new resonance at 117 ppm is observed, which we assign to a ketal carbon. The spectrum is consistent with the polyspiroketal backbone structure **16**. We suggest that the low-intensity resonances at 177 and 178 ppm are due to lactone and ester end groups of the polymer chains.

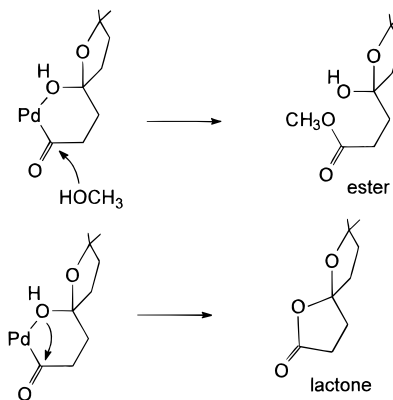


The DCPD spiroketal isomer is considerably more stable than the propene spiroketal structure: even prolonged heating in an acidic environment does not lead to conversion to the polyketone isomer.

1. Mechanistic Considerations

Polyspiroketal formation during the CO/DCPD copolymerization should be very similar to that discussed for CO/propene copolymers. The observation of both ester and lactone end groups is in accordance with an oxidative carbonylation mechanism, stoichiometrically based on the end groups of

the polymer. Such oxidative carbonylation was also observed in ethene and styrene copolymerization with carbon monoxide utilizing the same catalyst and oxidant. The lactone end groups can be considered as the *intramolecular* variant of the methanolysis termination step that normally produces ester end groups:

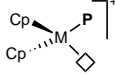
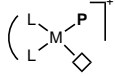


It could be that “locking” of the polyspiroketal chain end by a lactone moiety is partly responsible for the good stability against heat and acids of the DCPD polyspiroketal structure relative to the corresponding polyketone isomer. However, the constraints imposed by the monomer unit skeleton (“double” Thorpe–Ingold effect) could also stabilize the spiroketal structure to such an extent that opening to a polyketone structure becomes thermodynamically unfavorable in this case.

V. Conclusions

Attaining high chemo-, regio-, and stereoselectivity in catalytic reactions like hydroformylation and hy-

Table 3. Comparison of Pd-Catalyzed CO/Olefin Copolymerization and Early Transition Metal Catalyzed Olefin Polymerization^a

	polyolefins	polyketones
metal ion	Ti ^{IV} , Zr ^{IV} , Hf ^{IV}	Pd ^{II}
ligands	2Cp ⁻ , 2X ⁻	2L, 2X ⁻
anions	"noncoordinating"	"weakly or noncoordinating"
coordination geometry	tetrahedral	square planar
active center		

^a Cp = cyclopentadienyl.

droalkoxycarbonylation has long been recognized as one of the great challenges to the homogeneous catalysis community. The synthesis of the alternating CO/olefins copolymers, discussed in this paper, presents a new chapter in the history of polymerization. Moreover, it constitutes one of the scarce examples of transition metal-catalyzed carbonylations with potentially almost perfect control over selectivity. Both chemo- and regioselectivity can be achieved in nearly all cases. For propene, highly isotactic materials can be prepared using chiral ligands. For styrene, chain end control results in syndiotactic structures for a suitable choice of ligands. This chain end control can, however, be overruled by the application of certain chiral ligands to give isotactic structures.

We have made it plausible that the interaction of the polar polymer chain end with the electrophilic palladium center is crucial to the success of control over selectivity in achieving not only the alternating mode of chain propagation (chemoselectivity), but also in obtaining a high regio- and stereoselectivity for higher olefin insertion in intermediate palladium-acyls. The resulting polymer architecture therefore, is a product of the intimate cooperation between the palladium center and the polymer chain end. In a certain sense, the polymer, thus, organizes its own formation, whereas the catalyst assists in providing efficient pathways for the necessary bond-breaking and bond-making processes.

It is interesting to draw a parallel between the palladium-catalyzed homogeneous CO/olefin copolymerization and the modern homogeneous olefin polymerization catalyzed by early transition metal complexes⁶⁷ (Table 3). The following can be noted from this table:

(i) The metal cations are rendered electrophilic, in both instances, by the use of weakly coordinating anions. Thus, the monomer activation will proceed via electrophilic attack by the metal center.

(ii) Both cations have a ligand coordination number of four. Early transition metal cations, generally being four-valent, require four anionic ligands, two strongly coordinating (e.g. cyclopentadienyl) anions and two weakly coordinating anions. Palladium, being two-valent, requires two neutral and two (weakly coordinating) anionic ligands.

(iii) At both active centers, the growing polymer chain and the vacant site for binding a monomer require *cis* positions. In d⁰ metallocene complexes, the *cis* arrangement is automatically arranged by the

pseudotetrahedral coordination environment of the metal. In the square-planar d⁸ palladium complexes, *cis* coordination is enforced by the use of neutral bidentate ligands.

However, there is also a major difference between the two types of catalysts. The olefin polymerization metallocene catalysts are much more electrophilic than the palladium(II) complexes discussed in this paper. For polyketone formation, electrophilicity needs to be balanced such that the olefin can still compete with carbon monoxide for coordination to the metal atom. If the metal is too electrophilic, CO coordination will be too strong, and CO will act as a poison rather than participate in the polymerization. The moderate electrophilicity of Pd^{II} catalysts also makes them more tolerant to a variety of heteroatom functionalities in the olefin substrate, allowing us to prepare functionalized polymers. In this respect, polyketone catalysis can have a wider applicability than early transition metal polyolefin catalysis, which is generally highly intolerant of functional groups.

One further difference between the two types of catalysis is the measure to which they have been studied. Whereas 40 years of studies of Ziegler-Natta catalysis have led to impressive improvements in catalyst activity and selectivity, fundamental studies of polyketone catalysis could only recently be started by the discovery of the efficient, well-defined catalysts described in this review. We have presented some initial examples of studies of chemo-, regio-, and stereoselectivity, and we have rationalized some of the observed phenomena. However, further studies, both of polymerization characteristics and of elementary steps underlying the catalysis, will be needed to fully exploit the potential of these selective polymerizations.

VI. Abbreviations Used in This Text

dppp	1,3-bis(diphenylphosphino)propane
d(s)bpp	1,3-bis(di- <i>n</i> (<i>s</i>)-butylphosphino)propane
dipp	1,3-bis(di-isopropylphosphino)propane
OTf	trifluoromethanesulfonate (triflate)
OTs	<i>p</i> -toluenesulfonate (tosylate)
TFA	trifluoroacetate
HFIPA	1,1,1,3,3,3-hexafluoroisopropyl alcohol

VII. Acknowledgments

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