

# Carbon monoxide–ethylene copolymerisation catalysed by [PdCl<sub>2</sub>(dppp)] in methanol–water or in acetic acid–water as solvents (dppp = 1,3-bis(diphenylphosphine)propane)

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Received 17 November 2003; accepted 19 January 2004

## Abstract

The complex [PdCl<sub>2</sub>(dppp)] catalyses the copolymerisation of CO–ethylene when employed in a mixture of methanol and water as solvent. In the absence of H<sub>2</sub>O, it is inactive and at the end of the experiment, formation of metallic palladium has been noted. A sharp increase in the activity occurs at a water concentration above 5%, to reach a maximum of 4100 g copolymer/(g Pd h) by increasing the content of H<sub>2</sub>O up to 20% (mol/mol).

In AcOH as solvent the catalytic activity of [PdCl<sub>2</sub>(dppp)] is also strongly dependent on the content of H<sub>2</sub>O. In the absence of H<sub>2</sub>O it is inactive, though it does not decompose to palladium metal. Upon addition of H<sub>2</sub>O, it turns into a highly active system and the catalytic activity passes through a maximum of ca. 28 000 h<sup>-1</sup> when the molar ratio H<sub>2</sub>O/AcOH = 55%.

The <sup>13</sup>C NMR spectra show that the polymer chain is perfectly alternated. Polyketones obtained in MeOH–H<sub>2</sub>O (molecular weight ca. 6.5 × 10<sup>3</sup> g/mol) are of three types, differing for the nature of end-groups H(CH<sub>2</sub>CH<sub>2</sub>CO)<sub>n</sub>OMe, MeOCO(CH<sub>2</sub>CH<sub>2</sub>CO)<sub>n</sub>OMe and H(CH<sub>2</sub>CH<sub>2</sub>CO)<sub>n</sub>CH<sub>2</sub>CH<sub>3</sub>. In AcOH–H<sub>2</sub>O, only one type of polyketone forms having ketonic end-groups (average molecular weight ca. 2.7 × 10<sup>4</sup> g/mol).

On the basis of these experimental evidences, a mechanism for their formation is proposed. It is also proposed that the main role of H<sub>2</sub>O is that of forming an active Pd–H species which would start the catalysis upon interaction with CO through a reaction closely related to the water gas shift reaction (WGS) (during the catalysis there is formation of CO<sub>2</sub> in significant amounts). It is also proposed that the main role of acid is that of stabilizing Pd–H active species preventing their deprotonation to inactive species.

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**Keywords:** Palladium catalyst; dppp; Water; Acetic acid; Carbon monoxide; Ethylene; Copolymerisation; Polyketones

## 1. Introduction

Polyketones obtained by alternated carbon monoxide–olefin copolymerisation offer a unique set of properties of wide important application [1]. The discovery of a very efficient palladium-based catalyst for the terpolymerisation of CO, ethene and propene opened the possibility to their industrial production [2–4].

The basic principles that rule the catalysis, outlined since the first articles [5,6], have been investigated more thoroughly in subsequent papers, that focus the factors that account for the perfectly alternating structure [7] and with

chain termination model reactions [8]. Excellent reviews have also appeared [9–11].

In the case of CO–C<sub>2</sub>H<sub>4</sub> copolymerisation, Pd(II) complexes with a diphosphine ligand, having the phosphorous atoms bonded to aryl groups and linked by a hydrocarbon backbone of three methylene groups, are among the most efficient when the cationic charge is balanced by a weakly- or a non-coordinating anion, conjugated base of a strong acid (such as TsOH, CF<sub>3</sub>COOH, CF<sub>3</sub>SO<sub>3</sub>H and HBF<sub>4</sub>) that to allow easy access of the monomers to coordination to the metal thus assuring high catalytic activity. For example, the three catalysts systems PdX<sub>2</sub>/dppp = 1/1 (X: TsO, Cl or CH<sub>3</sub>COO) exhibit a significant different activity. In fact, in MeOH as solvent, at 90 °C and 4.5 MPa of CO and C<sub>2</sub>H<sub>4</sub> (CO/C<sub>2</sub>H<sub>4</sub> = 1/1), their pro-

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ductivity is 6200, 30 and 0 g polymer/(g Pd h), respectively [5].

In general, even better results are obtained in the presence of small, but significant amounts of H<sub>2</sub>O, that promotes the formation of active Pd–H species, through a reaction closely related to the water gas shift reaction (WGSR), and of an excess of strong acid of a weakly-coordinating conjugated base, which prevents deprotonation of the active hydride species [12].

Other catalytic precursors, with phosphines different from those employed by Drent et al., have been found efficient. In any case, it should be pointed out that starting from a chloride or acetate precursors, they become active only by replacing these anions with weakly-coordinating ones [13–16]. The same is true when employing water-soluble Pd(II) catalysts with hydrophile bidentate phosphines [17–22], and also when palladium is coordinated by bidentate nitrogen ligands of the type bipy, phen, or their alkyl-substituted derivatives [23–25], or by ligands containing both phosphorous- and nitrogen-coordinating atoms, or by other heteroditopic N–O, P–O and P–S ligands [11].

Recently, we reported that formic acid, when in relatively large concentration, can be used in place of a strong acid of a weakly-coordinating conjugated base. Thus, the precursor Pd(AcO)<sub>2</sub>/dppp in combination with HCOOH (HCOOH/Pd = 3000/1), in MeOH as solvent, gives ca. 7500 g polymer/(g Pd h) under 4.5 MPa of CO/C<sub>2</sub>H<sub>4</sub> (1/1) at 90 °C. Formic acid can act as a Pd–H source as well as water generated by the esterification of the acid with the solvent [26].

More recently, we found that the system Pd(AcO)<sub>2</sub>/dppp = 1/1, which is inactive in MeOH, turns into a highly active system when used in the presence of an excess of AcOH (7500 g polymer/(g Pd h) at 90 °C and 4.5 MPa when AcOH/Pd > 1.5 × 10<sup>4</sup>) and that even a much higher productivity is achieved by using AcOH–H<sub>2</sub>O as solvent in place of MeOH (27 500 g polymer/(g Pd h), at 90 °C and 4.5 MPa, H<sub>2</sub>O 37% (mol/mol)) [27]. Also in this case it has been suggested that H<sub>2</sub>O plays a key role in promoting the formation of a Pd–H species and that the acid prevents deprotonation of active hydride [27].

In this paper, we present the results obtained using [PdCl<sub>2</sub>(dppp)] in MeOH or AcOH as solvent in the presence of significant amount of H<sub>2</sub>O.

## 2. Experimental

### 2.1. Reagents

Methanol (purity > 99.5%, 0.01% of water) and acetic acid (100%, glacial) were purchased from Baker. Palladium(II) acetate, and 1,3-bis(diphenylphosphine)propane, 1,1,1,3,3,3-hexafluoroisopropanol (99%) and CDCl<sub>3</sub> were Aldrich products. The complexes [PdX<sub>2</sub>(dppp)] (X: Cl,

AcO and TsO) were prepared as reported in literature [28,29]. Carbon monoxide and ethylene were supplied by SIAD Company ('research grade', purity > 99.9%).

### 2.2. Equipment

The catalyst components were weighed on a Sartorius Micro balance (precision 0.001 mg). Gas chromatographic analysis of the gas phase was performed on a Hewlett-Packard Model 5890, Series II chromatograph fitted with a 5.5 m × 3.18 mm SS Silica Gel, 60/80 packed column (detector: TCD; carrier gas: helium, 30 ml/min; oven: 40 °C (2 min) to 100 °C at 15 °C/min).

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 300 spectrometer in 1,1,1,3,3,3-hexafluoroisopropanol/CDCl<sub>3</sub> (10/1) using the inverse <sup>1</sup>H-gated decoupling technique.

### 2.3. Carbon monoxide–ethylene copolymerisation

The copolymerisation reactions were carried out by using a Hastelloy C autoclave of ca. 250 ml provided with a four-blade self-aspirating turbine. Solvent and catalyst were added in a ca. 150 ml Pyrex bottle, placed inside the autoclave, in order to prevent contamination by metallic species because of corrosion of the internal surface of the autoclave.

In a typical experiment, 0.500 mg of [PdCl<sub>2</sub>(dppp)] (8.47 × 10<sup>-4</sup> mmol) was added to 80 ml of solvent (AcOH–H<sub>2</sub>O, H<sub>2</sub>O = 55% (mol/mol) or MeOH–H<sub>2</sub>O, H<sub>2</sub>O = 20% (mol/mol)) contained in the bottle placed in the autoclave. The autoclave was washed by pressurising with a 1/1 mixture of CO/C<sub>2</sub>H<sub>4</sub> (ca. 0.5 MPa) and then depressurising to atmospheric pressure (this cycle was repeated five times, at room temperature with stirring). The autoclave was then pressurised with 0.5 MPa of the gas mixture and then heated to 90 °C during ca. 10 min without stirring. The pressure was then adjusted to the desired value (typically 4.5 MPa total pressure) and, while stirring, maintained constant throughout the experiment (1 h, rate stirring 700 rpm) by continuously supplying the gasses from the reservoir. At the end of the experiment, the autoclave was quickly cooled and carefully depressurised. The slurry product was filtered, washed with water and acetone and dried under vacuum at 80 °C. The reproducibility was within ca. 5%.

In order to check whether there was formation of CO<sub>2</sub> during the course of the copolymerisation a larger amount of catalyst was used, typically 5.00 mg. The autoclave was washed with the mixture of the two gases and pressurised with ca. 0.5 MPa at room temperature and before running the reaction, the gas mixture was analysed by GC. No CO<sub>2</sub> was detectable. After heating the autoclave at 90 °C, the reaction was carried out following the same procedure just described. Gas samples were withdrawn at regular intervals of time (15 min). CO<sub>2</sub> was unambiguously detected just after 30 min and its concentration regularly increased with time.

## 2.4. Solubility measurements

The solubility of the monomers in the solvent of reaction was measured by an absorption technique. In a typical experiment a known volume of solvent ( $V_s = 80$  ml) was charged into the autoclave used for the copolymerisation reaction and heated to a desired temperature ( $90^\circ\text{C}$ ). After the thermal equilibrium was attained, the void space above the liquid was carefully washed (without stirring the solvent) with a monomer and pressurised to a desired value ( $P_A$ ) by supplying the monomer from a tank reservoir of 88.0 ml volume ( $V_r$ ) maintained at constant temperature ( $T$ ). The initial pressure in the reservoir ( $P_i$ ) was adjusted at  $P_i > P_A$ . The liquid in the autoclave was then vigorously stirred till the pressure of the reservoir dropped to a constant final value,  $P_f$ . The moles of A absorbed are  $n_{A,\text{abs}} = V_r(P_i - P_f)(zRT)^{-1}$  and the molar fraction of A in the solvent is  $X_A = n_{A,\text{abs}}(n_{A,\text{abs}} + n_{\text{solvent}})^{-1}$ .

The Henry's law constant  $H$  (MPa) has been calculated as  $H = P_A X^{-1}$  for  $P_A \rightarrow 0$ .

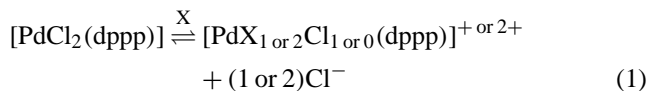
## 3. Results and discussion

### 3.1. Effect of water on the catalyst activity in MeOH

The complex  $[\text{PdCl}_2(\text{dppp})]$  catalyses the copolymerisation of CO–ethylene when employed in a mixture of methanol and water as solvent. Fig. 1 shows that the productivity is significantly influenced by the presence of water. In its absence the productivity is negligible; at the end of the experiment formation of metallic palladium has been noted. A sharp increase of the productivity occurs at a water

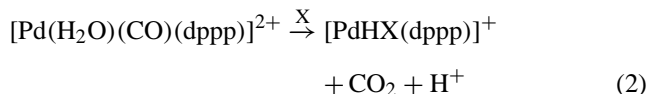
concentration above 5%, to reach a maximum of  $4100\text{ h}^{-1}$  by increasing the content of water up to 20% (mol/mol).

Since it is well known that water is capable of coordinating Pd(II) with the formation of aquo-complexes and also that the monomers are capable to coordinate Pd(II) [15,29], it is plausible to suppose that  $[\text{PdCl}_2(\text{dppp})]$  undergoes equilibrium (1).



where X:  $\text{H}_2\text{O}$ , MeOH and monomers.

Upon increasing the concentration of  $\text{H}_2\text{O}$ , the formation of a cationic aquo-complex is favoured also by the increasing of the dielectric constant of the reaction medium, which favours the separation of the charges. A Pd(II)–aquo-species is not a polymerisation initiating species, but upon reacting with CO it can be transformed into an active Pd–H species (see on the formation of the polyketones), through a reaction closely related to the WGSR [30–32] (reaction 2). As a matter of fact, we found that  $\text{CO}_2$  forms during the copolymerisation.



where X:  $\text{H}_2\text{O}$ , MeOH and monomers.

Pd–hydride complexes of this type, under neutral conditions, usually are unstable and deprotonate to inactive or less active Pd(0) or Pd(I) species [11]. This is one of the routes responsible of the loss of catalytic activity. The fact that the catalyst becomes active in the presence of  $\text{H}_2\text{O}$  suggests that, once the hydride is formed, the insertion of  $\text{C}_2\text{H}_4$  in

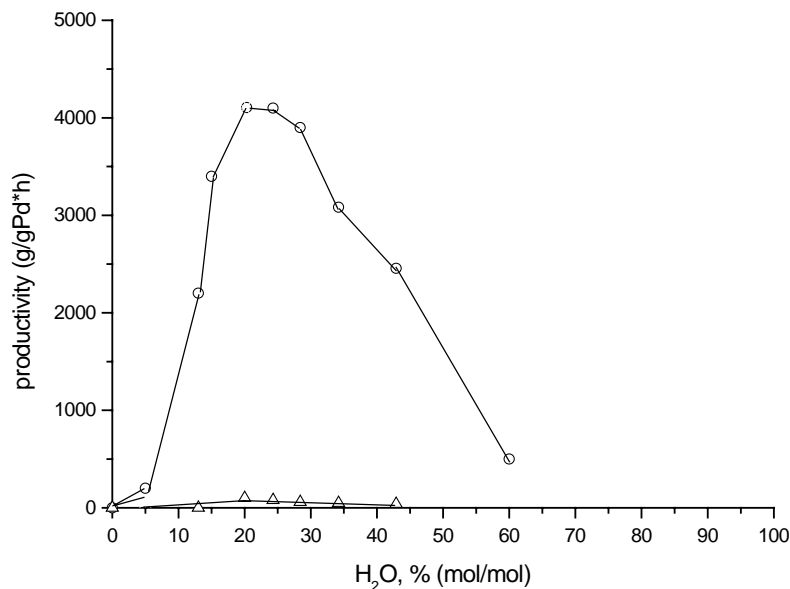


Fig. 1. Effect of water on the productivity with MeOH as solvent. Conditions:  $[\text{PdCl}_2(\text{dppp})] = 8.5 \times 10^{-3}$  mmol (○);  $[\text{Pd}(\text{AcO})_2(\text{dppp})] = 8.5 \times 10^{-3}$  mmol (Δ); volume = 80 ml;  $T = 90^\circ\text{C}$ ;  $P = 4.5$  MPa ( $\text{CO}/\text{C}_2\text{H}_4 = 1/1$ ); reaction time = 1 h and stirrer = 700 rpm.

Table 1  
Henry constants for CO and ethylene at 90 °C

Solvent	$H_{\text{CO}}$ (MPa)	$H_{\text{C}_2\text{H}_4}$ (MPa)
MeOH	$2.7 \times 10^2$	51.3
H <sub>2</sub> O	$8.3 \times 10^3$	$1.25 \times 10^3$
AcOH	$4.5 \times 10^2$	55.7
H <sub>2</sub> O/MeOH = 20% (mol/mol)	$5.2 \times 10^2$	71.0
H <sub>2</sub> O/AcOH = 20% (mol/mol)	$7.8 \times 10^2$	91.5
H <sub>2</sub> O/AcOH = 37% (mol/mol)	$1.1 \times 10^3$	$1.5 \times 10^2$
H <sub>2</sub> O/AcOH = 55% (mol/mol)	$1.9 \times 10^3$	$2.8 \times 10^2$
H <sub>2</sub> O/CH <sub>3</sub> SO <sub>3</sub> H = 98% (mol/mol)	$7.9 \times 10^3$	$1.1 \times 10^3$

the Pd–H bond (see below on the formation of the polymer) is faster than the deprotonation of the Pd–H species.

Fig. 1 also shows that above 20% concentration, water depresses the catalyst activity which suggests that it may compete with the monomers for the coordination to the metal. The catalytic activity may lower also because the monomers are less soluble in water than in methanol. Table 1 shows that the Henry's constants ( $H$ ) for carbon monoxide and ethylene are strongly influenced by the solvent composition. A kinetic study on the copolymerisation catalysed by [Pd(TsO)<sub>2</sub>(dppp)] in MeOH showed that the overall reaction rate is 0.63 and 0.72 order with respect to dissolved CO and ethylene, respectively [33,34].

In Fig. 1 the catalytic activity of [Pd(AcO)<sub>2</sub>(dppp)] is also reported. At difference of the chloride analogue, the acetate shows a poor activity at any H<sub>2</sub>O concentration and decomposes to Pd metal.

In Table 2 the results obtained using different catalytic systems are compared. It is interesting to note that the two precursors [PdX<sub>2</sub>(dppp)] (X: Cl and TsO) show a similar catalytic activity in a MeOH–H<sub>2</sub>O mixture (entries 1 and 2), while in pure MeOH only the tosylate complex is active ( $6200 \text{ h}^{-1}$ , the chloride complex is inactive and decomposes, entries 3 and 4).

The [PdCl<sub>2</sub>(dppb)] precursor is also active in H<sub>2</sub>O–MeOH (20%), more than the TsO analogue in pure MeOH (entries 5 and 6). The chloride precursor in the absence of water is inactive and decomposes (entry 7). Analogously, the

[PdCl<sub>2</sub>(dppe)] precursor is active in H<sub>2</sub>O–MeOH (entry 8) though less than the TsO analogue in pure MeOH (entry 9); in this solvent, [PdCl<sub>2</sub>(dppe)] is inactive and decomposes (entry 10).

### 3.2. Effect of an acid on the catalyst activity in MeOH–H<sub>2</sub>O

The effect of HCl, AcOH, TsOH and HBF<sub>4</sub> has been tested. Fig. 2 shows that the presence of HCl drastically depresses the productivity. The catalyst becomes inactive at a molar ratio HCl/Pd higher than 50/1, probably because it may shift the proposed equilibrium (1) back to inactive [PdCl<sub>2</sub>(dppp)].

Quite interestingly, TsOH also, at low concentration, inhibits the copolymerisation, though not to the same extent as HCl. This is in line with the results reported in Table 2 (entries 1 and 2). However, at acid/Pd ratio > 20, while HCl inhibits the catalysis, TsOH has a beneficial effect and at a acid/Pd ratio > 200/1 the productivity,  $4500 \text{ h}^{-1}$ , is even slightly higher than that obtained when using the precursor [Pd(TsO)<sub>2</sub>(dppp)] in the absence of added TsOH (Table 2, entry 2).

A similar trend is observed when [PdCl<sub>2</sub>(dppp)] is used in combination of AcOH. The productivity is lowered to a minimum of ca.  $200 \text{ h}^{-1}$  at a AcOH/Pd ratio = 20, while at higher concentration also AcOH has a beneficial effect, though not as high as that of TsOH.

These results suggest that the acid has a dual capacity, on one hand its anion coordinates the metal thus lowering the catalytic activity and on the other hand, the acid inhibits the deprotonation of the active Pd(II)–H species:



When we use HCl the first prevails, the proposed equilibrium (1) is shifted to [PdCl<sub>2</sub>(dppp)] which is inactive or else Cl<sup>−</sup> competes for coordination with the monomers (reaction (2)). This is not the case when we use the other two acids. Note that HBF<sub>4</sub> does not depress the catalytic activity, according to the fact that BF<sub>4</sub><sup>−</sup> is the least-coordinating anion.

Table 2  
Effect of ligand on the productivity in MeOH as solvent

Entry no.	Complex	Additives	Additives/Pd (mol/mol)	H <sub>2</sub> O (% (mol/mol))	Productivity (h <sup>−1</sup> )	Notes
1	[PdCl <sub>2</sub> (dppp)]	–	–	20	4100	–
2	[Pd(TsO) <sub>2</sub> (dppp)]	–	–	20	4200	–
3	[PdCl <sub>2</sub> (dppp)]	–	–	–	30	Pd metal
4	Pd(OAc) <sub>2</sub>	TsOH, dppp	2/1/1	0.05	6200	[5,12]
5	[PdCl <sub>2</sub> (dppb)]	–	–	20	3350	–
6	[Pd(TsO) <sub>2</sub> (MeCN) <sub>2</sub> ]	dppb	1/1	–	2300	[5]
7	[PdCl <sub>2</sub> (dppb)]	–	–	–	–	Pd metal
8	[PdCl <sub>2</sub> (dppe)]	–	–	20	500	–
9	[Pd(TsO) <sub>2</sub> (MeCN) <sub>2</sub> ]	dppe	1/1	–	1000	[5]
10	[PdCl <sub>2</sub> (dppe)]	–	–	–	–	Pd metal

Run conditions: [PdX<sub>2</sub>(dppp)] =  $8.5 \times 10^{-3}$  mmol;  $T = 90^\circ\text{C}$ ;  $P_{\text{tot}} = 4.5 \text{ MPa}$  (CO/C<sub>2</sub>H<sub>4</sub> = 1/1, at 90 °C); volume = 80 ml; solvent = MeOH; reaction time = 1 h and stirrer = 700 rpm.

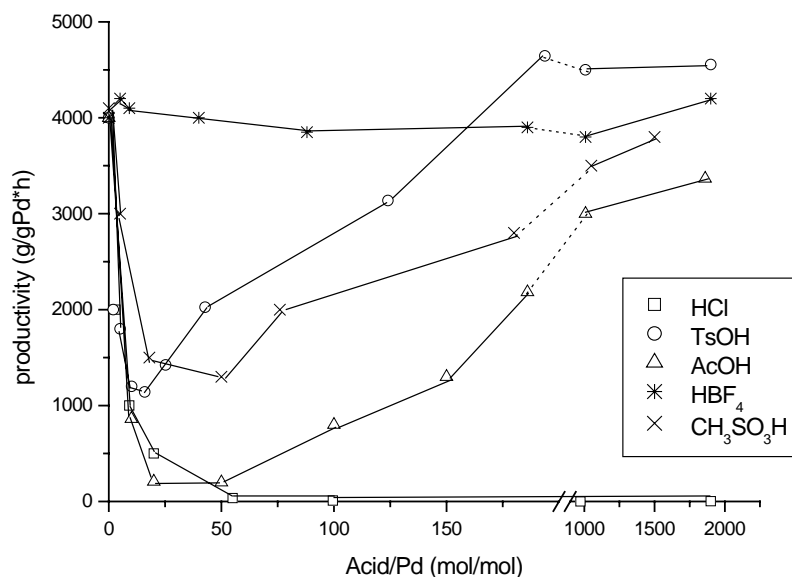
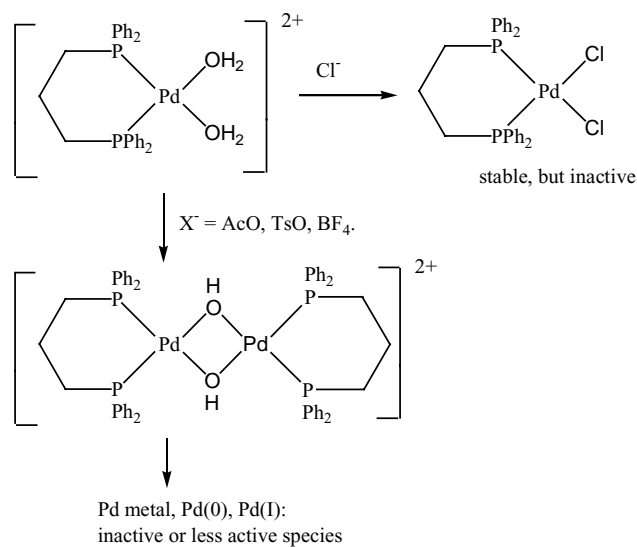


Fig. 2. Effect of different acid promoter on the productivity in MeOH as solvent. Conditions:  $[\text{PdCl}_2(\text{dppp})] = 8.5 \times 10^{-3}$  mmol;  $T = 90^\circ\text{C}$ ;  $P = 4.5$  MPa ( $\text{CO}/\text{C}_2\text{H}_4 = 1/1$ ); volume = 80 ml ( $\text{H}_2\text{O} = 20\%$ , (mol/mol) in MeOH); reaction time = 1 h and stirrer = 700 rpm.

### 3.3. Effect of a salt on the catalyst activity in MeOH–H<sub>2</sub>O

The results of the effect of LiCl, NaTsO, NaAcO and NaBF<sub>4</sub> are reported in Table 3. All of them inhibit the catalysis, even at low concentration.

The effect of LiCl salt may be associated to the coordination capacity of the anion. The effect of NaAcO may be due also to the coordination capacity of the anion as well its capacity to act as a base that abstracts a proton from an active Pd(II)–H species. It has been found that, in the presence of water, bis aquo-species form and that, under neutral conditions, there is formation of less active  $\mu$ -OH species from monomeric Pd–OH species, and also decomposition to palladium metal [11,35] (Scheme 1). The formation of dimeric species may be favored also by non-coordinating groups. This may explain why in the presence of NaTsO and NaBF<sub>4</sub>, that gives rise to neutral solutions, the catalytic



Scheme 1. Formation of inactive or less active Pd species.

Table 3  
Effect of salts on the productivity in H<sub>2</sub>O–MeOH as solvent

Entry no.	Complex	Additives	Additives/Pd (mol/mol)	H <sub>2</sub> O (%)	Productivity (h <sup>-1</sup> )	Notes
1	Pd(OAc) <sub>2</sub>	TsOH/dppp	2/1/1	0.05	6200	[12]
2	Pd(OAc) <sub>2</sub>	TsOH/dppp	2/1/1	0.5	3800	[12]
3	[Pd(TsO) <sub>2</sub> (dppp)]	–	–	20	4200	–
4	[PdCl <sub>2</sub> (dppp)]	–	–	–	30	Pd metal
5	[PdCl <sub>2</sub> (dppp)]	–	–	20	4100	–
6	[PdCl <sub>2</sub> (dppp)]	NaOAc	4/1	20	250	Pd metal
7	[PdCl <sub>2</sub> (dppp)]	NaTsO	4/1	20	350	Pd metal
8	[PdCl <sub>2</sub> (dppp)]	NaBF <sub>4</sub>	4/1	20	300	Pd metal
9	[PdCl <sub>2</sub> (dppp)]	LiCl	4/1	20	150	–
10	[PdCl <sub>2</sub> (dppp)]	NaOH	4/1	20	–	Pd metal

Run conditions:  $[\text{PdX}_2(\text{dppp})] = 8.5 \times 10^{-3}$  mmol;  $T = 90^\circ\text{C}$ ;  $P = 4.5$  MPa ( $\text{CO}/\text{C}_2\text{H}_4 = 1/1$ , at  $90^\circ\text{C}$ ); volume = 80 ml; solvent = MeOH; reaction time = 1 h and stirrer = 700 rpm.

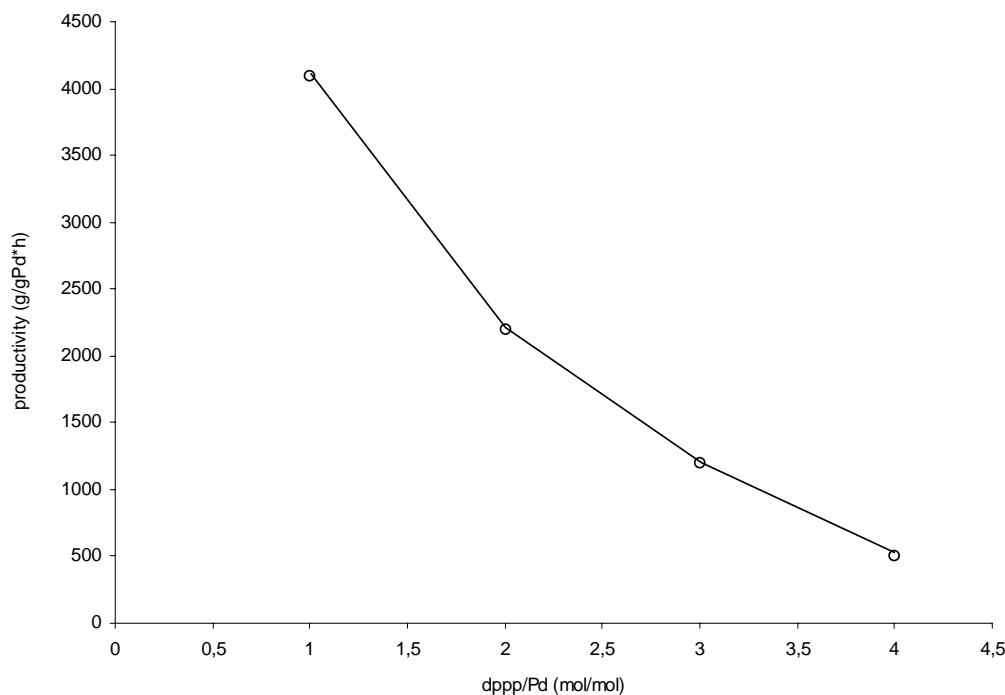


Fig. 3. Effect of dppp on the productivity in MeOH as solvent. Conditions:  $[\text{PdCl}_2(\text{dppp})] = 8.5 \times 10^{-3}$  mmol; reaction volume = 80 ml;  $\text{H}_2\text{O} = 20\%$  (mol/mol);  $T = 90^\circ\text{C}$ ;  $P = 4.5$  MPa ( $\text{CO}/\text{C}_2\text{H}_4 = 1/1$ ); reaction time = 1 h and stirrer = 700 rpm.

activity is also depressed, even though the anions are weakly or non-coordinating.

However, it should be underlined that the above comparison might be distorted because the formation of palladium metal might occur to a different extent using different salts. In addition, decomposition to the metal releases the ligand which has also a depressing effect on the catalyst that re-

main undecomposed. Fig. 3 shows the effect of the addition of dppp on the catalytic activity.

#### 3.4. Catalytic activity in AcOH–H<sub>2</sub>O

In AcOH as solvent, the catalytic activity of  $[\text{PdCl}_2(\text{dppp})]$  is strongly dependent on the content of H<sub>2</sub>O (Fig. 4). In

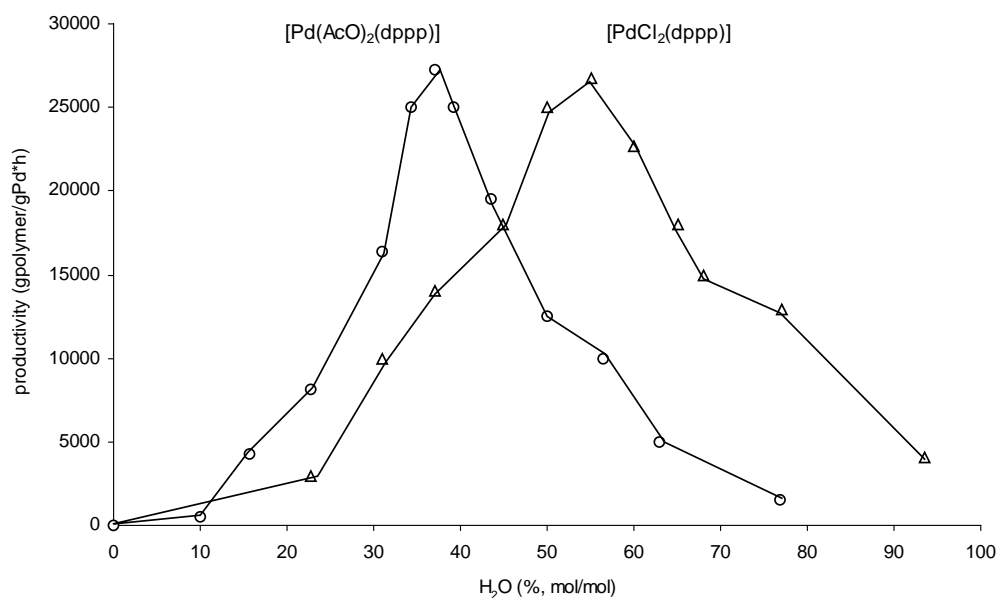


Fig. 4. Effect of percent of water on the productivity using different catalyst precursor in acetic acid as solvent. Conditions:  $[\text{Pd}(\text{AcO})_2(\text{dppp})]$ ,  $[\text{PdCl}_2(\text{dppp})] = 8.5 \times 10^{-4}$  mmol;  $P = 4.5$  MPa ( $\text{CO}/\text{C}_2\text{H}_4 = 1/1$ , at the working temperature);  $T = 90^\circ\text{C}$ ; volume: 80 ml; reaction time = 1 h and stirrer = 700 rpm.

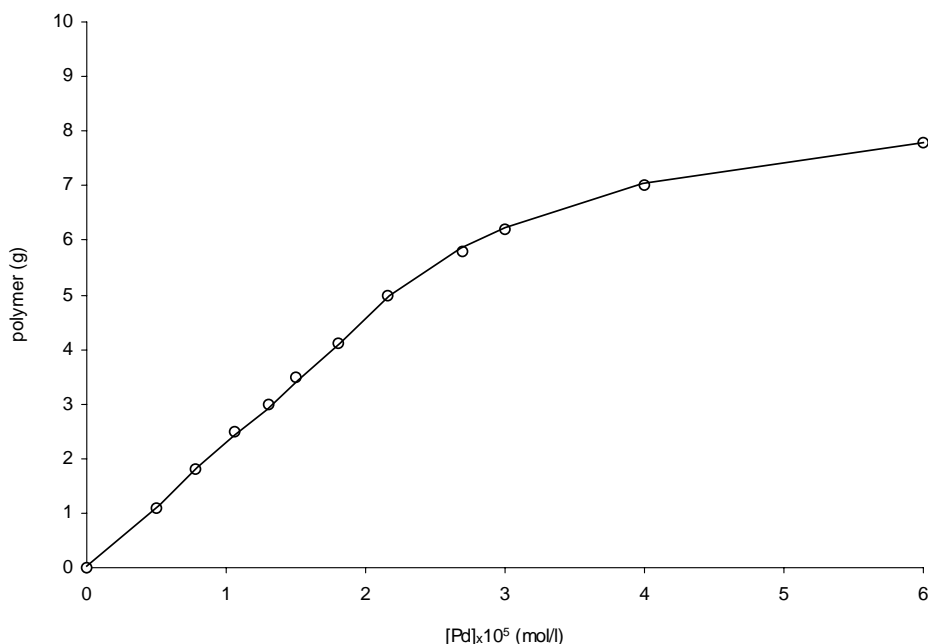


Fig. 5. Effect of catalyst concentration on the productivity in acetic acid as solvent. Conditions:  $[\text{PdCl}_2(\text{dppp})] = 8.5 \times 10^{-4}$  mmol;  $P = 4.5$  MPa ( $\text{CO}/\text{C}_2\text{H}_4 = 1/1$ , at the working temperature);  $T = 90^\circ\text{C}$ ; volume = 80 ml;  $\text{H}_2\text{O} = 55\%$  (mol/mol); reaction time = 1 h and stirrer = 700 rpm.

the absence of  $\text{H}_2\text{O}$  it is inactive, though it does not decompose to palladium metal. Upon addition of  $\text{H}_2\text{O}$  it turns into a highly active system. When the molar ratio  $\text{H}_2\text{O}/\text{AcOH} = 55\%$  the catalytic activity passes through a maximum of ca.  $28\,000\text{ h}^{-1}$ , ca. 4.5 times higher than that obtained using the precursor  $\text{Pd}(\text{AcO})_2/2\text{TsOH}/\text{dppp}$  in  $\text{MeOH}$  [5], even though the solubility of the two monomers in  $\text{AcOH}-\text{H}_2\text{O}$  is much lower than that in pure  $\text{MeOH}$  (see Table 1). In Fig. 4 it is also shown that the catalytic activity of  $[\text{Pd}(\text{AcO})_2(\text{dppp})]$ , which reaches a maximum of ca.  $28\,000\text{ h}^{-1}$ , but at a lower concentration of water, 37% [27]. Thus, considering that the solubility of the monomers lowers upon increasing the water concentration, the chloride precursor is particularly active. The fact that the two precursors give practically the same productivity is not due to g/l mass transfer limitation, because the amount of polymer produced per hour increases linearly with increasing of the catalyst concentration up to  $2 \times 10^{-5}$  mol/l, well-above the standard concentration employed in this work,  $1 \times 10^{-5}$  mol/l (see Fig. 5), analogously to what proved for the acetate precursor [27]. Thus, the chloride anion, even at a very low concentration, and in the presence of an excess of acetate anions, due to the reaction medium, has a significant effect on the catalytic activity, as shown by the results reported in Table 4. In the presence of four equivalents of  $\text{LiCl}$  the productivity using  $[\text{PdCl}_2(\text{dppp})]$  is lowered to  $12\,500\text{ h}^{-1}$  (entry 2). By adding two equivalents of  $\text{LiCl}$  to  $[\text{Pd}(\text{AcO})_2(\text{dppp})]$ , the productivity is  $27\,500\text{ h}^{-1}$  (entry 4), practically the same as that obtained using  $[\text{PdCl}_2(\text{dppp})]$  (entry 1), whereas in the presence of six equivalents of chloride anion the productivity is lowered to  $13\,500\text{ h}^{-1}$  (entry 5), practically the same as that in entry 2.

As when  $\text{MeOH}-\text{H}_2\text{O}$  is used as solvent, also in this case we suggest that the main function of  $\text{H}_2\text{O}$  is that of a  $\text{Pd}-\text{H}$  active source, and that the main function of the acid is to prevent deprotonation of these hydrides or of aquo-species that lead to deactivation of the catalyst (see also on the formation of the polyketone).

Table 5 shows the activity of  $[\text{PdCl}_2(\text{dppe})]$  and  $[\text{PdCl}_2(\text{dppb})]$  precursors in  $\text{H}_2\text{O}-\text{AcOH}$  (55%) as solvent. In this solvent,  $[\text{PdCl}_2(\text{dppe})]$  is inactive (entry 4) whereas  $[\text{PdCl}_2(\text{dppb})]$  reaches a productivity of  $16\,000\text{ h}^{-1}$  (entry 6) which is ca. seven times higher than the productivity obtained in pure methanol (entry 3).

### 3.5. Catalytic activity in $\text{CH}_3\text{SO}_3\text{H}-\text{H}_2\text{O}$

$[\text{PdCl}_2(\text{dppp})]$  is active in water also when metansulphonic acid ( $\text{CH}_3\text{SO}_3\text{H}$ ) is used in place of acetic acid. Fig. 6 shows that the catalytic activity passes through a maximum of ca.  $3500-4000\text{ h}^{-1}$  when  $\text{H}_2\text{O}/\text{CH}_3\text{SO}_3\text{H} = 98/2$  (molar

Table 4  
Effect of  $\text{LiCl}$  addition on the productivity in  $\text{H}_2\text{O}-\text{AcOH}$  as solvent

Entry no.	Precursor	Additives	Additives/Pd (molar ratio)	Productivity ( $\text{h}^{-1}$ )
1	$[\text{PdCl}_2(\text{dppp})]$	–	–	28 000
2	$[\text{PdCl}_2(\text{dppp})]$	$\text{LiCl}$	4/1	12 500
3	$[\text{Pd}(\text{AcO})_2(\text{dppp})]$	–	–	8000
4	$[\text{Pd}(\text{AcO})_2(\text{dppp})]$	$\text{LiCl}$	2/1	27 500
5	$[\text{Pd}(\text{AcO})_2(\text{dppp})]$	$\text{LiCl}$	6/1	13 500

Run conditions: precursor =  $8.5 \times 10^{-4}$  mmol;  $\text{H}_2\text{O} = 55\%$  molar ratio;  $T = 90^\circ\text{C}$ ;  $P = 4.5$  MPa (at  $90^\circ\text{C}$ ,  $\text{CO}/\text{C}_2\text{H}_4 = 1/1$ ); volume = 80 ml; reaction time = 1 h and stirrer = 700 rpm.

Table 5  
Effect of chelating ligand on the productivity in H<sub>2</sub>O–AcOH as solvent

Entry no.	Precursor	Additives	Additives/Pd (molar ratio)	Solvent	Productivity (h <sup>-1</sup> )	Reference
1	[Pd(TsO) <sub>2</sub> (MeCN) <sub>2</sub> ]	dppe	1/1	MeOH	1000	[5]
2	[Pd(TsO) <sub>2</sub> (MeCN) <sub>2</sub> ]	dppp	1/1	MeOH	6000	[5]
3	[Pd(TsO) <sub>2</sub> (MeCN) <sub>2</sub> ]	dppb	1/1	MeOH	2300	[5]
4	[PdCl <sub>2</sub> (dppe)]	–	–	H <sub>2</sub> O–AcOH	–	
5	[PdCl <sub>2</sub> (dppp)]	–	–	H <sub>2</sub> O–AcOH	28 000	
6	[PdCl <sub>2</sub> (dppb)]	–	–	H <sub>2</sub> O–AcOH	16 000	

Run conditions: precursor =  $8.5 \times 10^{-4}$  mmol; H<sub>2</sub>O = 55% molar ratio;  $T = 90^\circ\text{C}$ ;  $P = 4.5$  MPa (at  $90^\circ\text{C}$ , CO/C<sub>2</sub>H<sub>4</sub> = 1/1); volume = 80 ml; reaction time = 1 h and stirrer = 700 rpm.

ratio), practically the same of that obtained in H<sub>2</sub>O/AcOH = 98/2. However, it should be noted that AcOH has a beneficial effect also at concentration higher than 2%.

### 3.6. On the formation of the polyketone

In MeOH, the formation of polyketones occurs in three steps: (i) initiation step, in which the initiating species are formed (Pd–H or of Pd–OCH<sub>3</sub>); (ii) propagation step, in which the alternate insertion of C<sub>2</sub>H<sub>4</sub> and CO gives the polyketone growing chain and (iii) termination step, in which alcoholysis, hydrolysis, protonolysis or  $\beta$ -hydride elimination of the Pd-growing chain lead to the polyketone and to the initiating species [5,9]. Scheme 2 shows that, in MeOH–H<sub>2</sub>O as solvent, polyketones having different end-groups (I–VII) can be obtained, together with the species which re-start the catalytic cycles, depending on the initiation and on the termination steps.

The <sup>13</sup>C NMR spectra of the polyketones obtained in MeOH–H<sub>2</sub>O, show multiplets at 216.8 (CH<sub>3</sub>CH<sub>2</sub>C=O), 176.2 (COOCH<sub>3</sub>), 52.0 (COOCH<sub>3</sub>), 27.7 (CH<sub>2</sub>–C(O)OCH<sub>3</sub>) and

6.8 (CH<sub>3</sub>CH<sub>2</sub>), which indicates the presence of copolymers of the type I–III. These copolymers, having an average molecular weight of ca.  $6.5 \times 10^3$  g/mol (determined by end-groups analysis), are obtained when catalysis starts from the Pd–H and Pd–OCH<sub>3</sub> species and termination occurs by reaction with CH<sub>3</sub>OH or H<sub>2</sub>O. Termination with CH<sub>3</sub>OH reproduces the [Pd–OCH<sub>3</sub>]<sup>+</sup> species (protonolysis) or the [Pd–H]<sup>+</sup> species (methanolysis). In the first case, polyketone I is produced if the initiating species is [Pd–OCH<sub>3</sub>]<sup>+</sup> or polyketone III is produced if the initiating species is [Pd–H]<sup>+</sup>. In the second case, polyketone II is produced if the initiating species is [Pd–OCH<sub>3</sub>]<sup>+</sup> or polyketone I is produced if the initiating species is [Pd–H]<sup>+</sup>. Analogously, termination with H<sub>2</sub>O reproduces the [Pd–OH]<sup>+</sup> species (protonolysis) or the [Pd–H]<sup>+</sup> species (hydrolysis). In the first case, polyketone I is produced if the initiating species is [Pd–OCH<sub>3</sub>]<sup>+</sup> or polyketone III if the initiating species is [Pd–H]<sup>+</sup>. In the second case, polyketone IV is produced if the initiating species is [Pd–OCH<sub>3</sub>]<sup>+</sup> or polyketone V if the initiating species is [Pd–H]<sup>+</sup>. Since the <sup>13</sup>C NMR spectra shows the absence of –COOH end-groups, it is plausi-

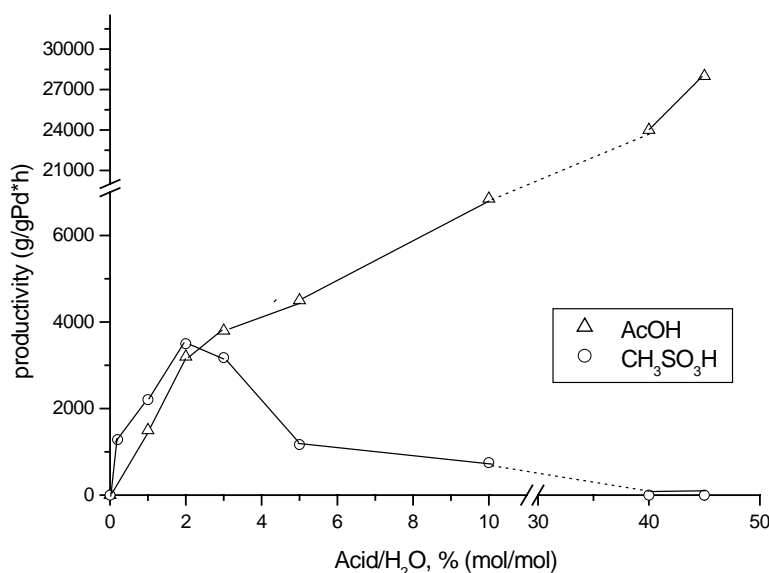
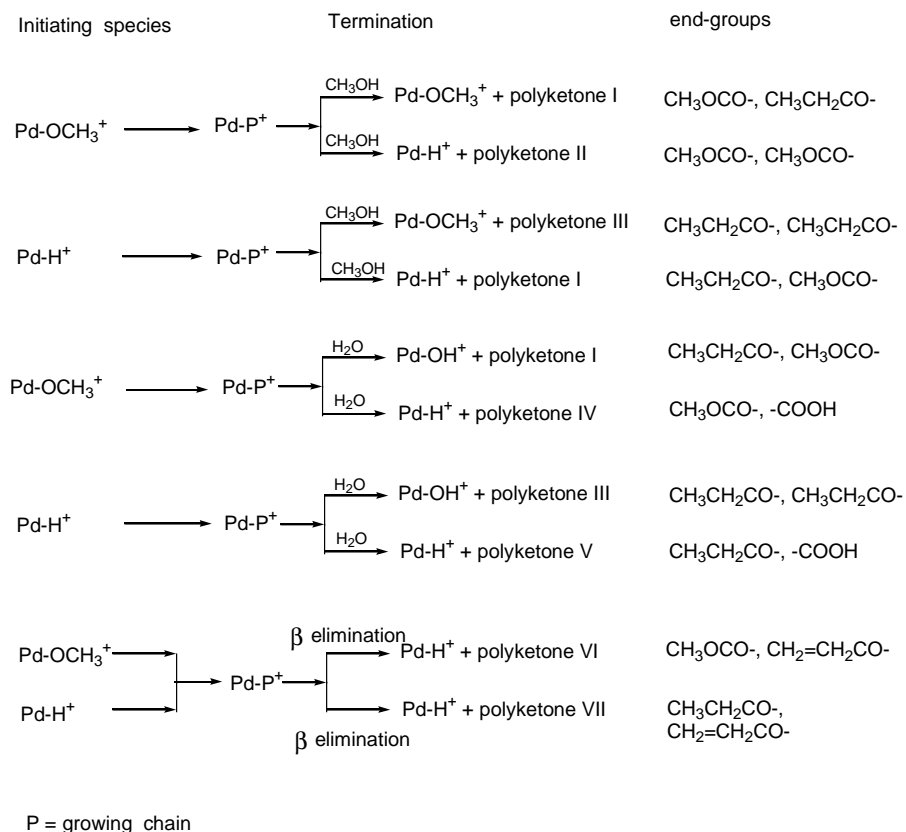


Fig. 6. Effect of metansulphonic acid and acetic acid on the productivity in water as solvents. Conditions: [PdCl<sub>2</sub>(dppp)] =  $8.5 \times 10^{-3}$  mmol;  $T = 90^\circ\text{C}$ ;  $P = 4.5$  MPa (CO/C<sub>2</sub>H<sub>4</sub> = 1/1); volume = 80 ml; reaction time = 1 h and stirrer = 700 rpm.



Scheme 2. Copolymerisation mechanism proposed in H<sub>2</sub>O–MeOH as solvent.

ble to consider that the termination with H<sub>2</sub>O occurs only by protonolysis. The [Pd–OH]<sup>+</sup> species, when formed, may insert carbon monoxide to give the Pd–COOH intermediate which does not initiate a new cycle, but decomposes with CO<sub>2</sub> evolution and formation of a [Pd–H]<sup>+</sup> species. CO<sub>2</sub> has been detected during the copolymerisation reaction.

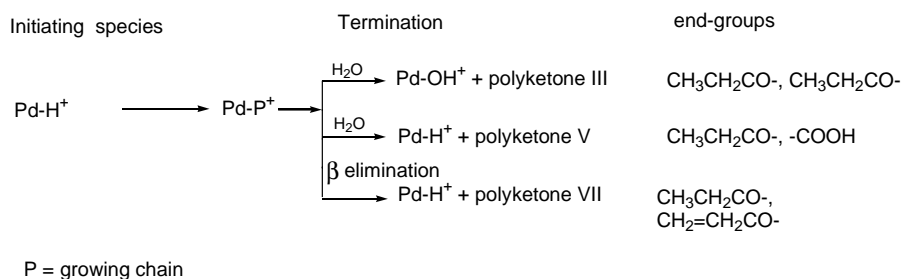
Furthermore, there is no evidence of CH<sub>2</sub>=CH–end-groups, which excludes that termination occurs via β-hydride elimination with formation of polymers **VI** and **VII**.

Since the integration of the <sup>13</sup>C NMR signals shows that in the polymer obtained in MeOH–H<sub>2</sub>O the abundance of the CH<sub>3</sub>CH<sub>2</sub>CO– end-groups is higher than that of the –COOCH<sub>3</sub> one (ca. 3/1), the initiation step involves mainly

a Pd–H species. On the light of this result, it is plausible to suppose that the promoting effect of water is due to the formation of an active initiating [Pd–H]<sup>+</sup> species, through for example reactions (1) and (2).

Note that the protonolysis of the Pd–(growing chain) bond may occur also by reaction with an acid (for instance AcOH) which leads to polyketones **I**, or **III** (depending on the initiation step) and the Pd–OAc species which is easily converted in the active [Pd–H]<sup>+</sup> or [Pd–OCH<sub>3</sub>]<sup>+</sup> species by reaction with H<sub>2</sub>O and CO or CH<sub>3</sub>OH.

When CH<sub>3</sub>COOH–H<sub>2</sub>O is used as a solvent, the <sup>13</sup>C NMR analysis shows a polyketone perfectly alternated and having an average molecular weight of ca. 2.7 × 10<sup>4</sup> g/mol and exclusively ketonic end-groups.

Scheme 3. Copolymerisation mechanism proposed in H<sub>2</sub>O–AcOH as solvent.

The overall mechanism in MeOH is basically similar to the one proposed by Drent [5] and in H<sub>2</sub>O–AcOH is basically similar to the one proposed by Sheldon et al. [11,27,32]. In the latter case only a [Pd–H]<sup>+</sup> species start the catalytic cycle by inserting a molecule of C<sub>2</sub>H<sub>4</sub> and the chain grow occurs via perfectly alternating insertion of CO into a Pd–alkyl bond and of C<sub>2</sub>H<sub>4</sub> into a Pd–acyl bond; termination occurs only by protonolysis (in Scheme 3 exemplified with H<sub>2</sub>O) of a Pd–alkyl bond with reformation of a [Pd–OH]<sup>+</sup> species. The [Pd–OH]<sup>+</sup> re-enters the catalytic cycle as just proposed. Also in this case there are no NMR evidences of CH<sub>2</sub>=CH– or –COOH end-groups that excludes that termination occurs via β-hydride elimination or hydrolysis.

On the basis of these experimental evidences, it is proposed that the main role of H<sub>2</sub>O is that of producing active Pd–H species through a reaction with CO closely related to the WGS and that the main function of the acid is that of preventing deprotonation of the active hydride or the formation of μ-OH species, thus preventing deactivation of the catalyst.

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