CO–ethene copolymerisation catalysed by [PdCl$_2$(PPh$_3$)$_2$]/PPh$_3$/HCl in MeOH

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Abstract

The system [PdCl$_2$(PPh$_3$)$_2$]/PPh$_3$/HCl catalyses the carbonylation of ethene in MeOH as a solvent to give methyl propanoate (MP) or a polyketone (PK).

The influence of temperature, Pd/P, CO/ethene and Pd/HCl ratios, and concentration of H$_2$O on the catalytic activity has been studied.

The catalytic system is active only in the presence of HCl and is stable when P/Pd is ≥6/1 up to 110 °C.

At 100 °C, with Pd/P/HCl = 1/6/1600 (HCl initially added), under 6.0 MPa total pressure, the main product is MP at 1.0 MPa of ethene, whereas is PK when the pressure of the olefin is higher than 4.0 MPa.

Water, which forms in the solvent, because of the reaction of MeOH with HCl, has a minor effect.

The PK product presents a 2.5–4/1 ratio between the keto and ester end groups. The proposed catalytic cycle takes into account the results.
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1. Introduction

In early 1980s two different research groups discovered that cationic Pd(II)–phosphine complexes catalyse, under relatively mild conditions, the copolymerisation of carbon monoxide with an α-olefin to give alternating PK [1,2]. Since then, considerable research efforts have been continuously devoted, because of the possibility of producing, from low cost and largely available monomers, these new thermoplastics which can find wide application. The subject has been extensively reviewed up to recently [3–20].

Since the earlier results of the CO–ethene copolymerisation, it was proposed that catalysts based on *cis*-chelating-diphosphine (typically dppp, 1,3-bis(diphenylphosphino)propane) are far superior, as far as both productivity and molecular weight, to the monophosphine-based ones because *cis*-coordination ensures that the other two coordination sites of the d^8-square planar palladium centre are also always *cis* to each other, which is ideal in favouring the chain growth, whereas monophosphine-based catalysts, undergoing *cis–trans* isomerisation, are less suitable to promote the formation of PK, but give preferentially oligomers or even, using MeOH as a solvent, MP. Moreover, for several years it was accepted that efficient copolymerisation required 1,3-propanedyl-bridged bidentate *cis*-chelating ligands and that monodentate ligands favoured the hydromethoxycarbonylation [21].

Using the C$_3$-bridged ligands RR′P(CH$_2$)$_3$PRR′ (R,R′ = *n*-Bu,*n*-Bu or *n*-Bu,cyclohexyl or cyclohexyl,cyclohexyl), of bite angle close to that of dppp and in which the alkyl substituents differ only slightly in electron-donating properties, but differ significantly for the steric bulk: R,R′ = *n*-Bu,*n*-Bu < *n*-Bu,cyclohexyl < cyclohexyl,cyclohexyl < *t*-Bu,*t*-Bu), it was later found that productivity and molecular weight decrease when steric bulkiness increases to the point that with the last ligand the main product was MP, which can be considered the lowest molecular weight product of the polymerisation process (98% selectivity, TOF 15,000 at 80 °C, 10 bar, CO/ethene = 1/1) [22]. Even higher performance to MP was obtained by using the C$_4$-bridged ligand dtbpx

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(99.98% selectivity, TOF = 50,000 h^{-1} under the same conditions; dtbpx = 1,2-bis[(di-t-butyl)phosphinomethyl]benzene) [23]. The sharp change in selectivity from PK to MP was explained on the basis of steric bulk considerations. Using the dtbpx-based catalyst it has been proved that a Pd–H species initiates the catalysis, by inserting ethene and CO, giving a Pd–acyl intermediate. Insertion of another molecule of CO does not occur for thermodynamic reasons, further ethene becomes less favoured as steric bulkiness increases, whereas termination by MeOH becomes faster [24]. The larger bite angle in the C$_4$-bridged dtbpx-based catalyst magnifies the steric bulk of the t-Bu group, this may account for the exceptionally high selectivity to MP obtained when this ligand is used.

Also the solvent influences the activity. This is well illustrated by comparing the catalytic activity of PPh$_3$-based cationic Pd(II) complexes. The system [Pd(CH$_3$CN)$_{4-n}$(PPh$_3$)$_n$](BF$_4$)$_2$ (n = 1–3) catalyses the CO–ethene copolymerisation at 25 °C and 20 bar in non-coordinating solvents such as CHCl$_3$ or CH$_2$Cl$_2$, whereas in MeOH significant activity is observed only at 70 °C and low molecular weight cooligomers are produced together with lower products, including the lightest one, MP [25]. The formation of lower products is favoured also by the fact that MeOH can terminate the chain growing process. Using the closely related catalyst [Pd(TsO)$_2$(PPh$_3$)$_2$], in the presence of an excess of free PPh$_3$, at 80–100 °C, the main product is MP [26,27].

The solvent has a dramatic effect also on the diphosphine-based catalysts. In MeOH, the catalyst [PdX$_2$(dppp)] (X = TfO, TsO, TFA, AcO, Cl) is active when X is weakly coordinating (ca. 6000–7000 g PK/(g Pd h) at 90 °C, 45 bar, CO/ethene = 1/1), whereas when X = AcO or Cl the catalyst is ineffective [21], but turn into very active one when used in H$_2$O-AcOH (27,000 g PK/(g Pd h) under the conditions just reported and with the solvent with 40–50% mol fraction of H$_2$O) [28,29].

In any case, a prerequisite common to both the monophosphine- and diphosphine-based catalysts, when used in MeOH, is that the cationic charge of the metal centre has to be balanced by a non- or a weakly coordinating anion, conjugated base of a strong acid (like TsOH, HBF$_4$, CF$_3$COOH, CF$_3$SO$_3$H) so that the metal centre presents "free" coordination sites easily accessible to the reacting molecules. When the anion has coordinating capacity, like Cl$^-$, the process of the monomers incorporation terminates after the insertion of just one molecule of each monomer with formation of MP and higher reaction temperatures are required [21].

Here, we present the results on the carbonylation of ethene (E) using the neutral complex [PdCl$_2$(PPh$_3$)$_2$] in combination of HCl and in the presence of PPh$_3$, in MeOH as a solvent.

2. Experimental

2.1. Reagents

Methanol was purchased from Baker; PdCl$_2$ was obtained from Engelhard; PPh$_3$, 1,1,1,3,3,3-hexafluoroisopropanol (99%) and CDCl$_3$ were Aldrich products. The complexes

[PdCl$_2$(PPh$_3$)$_2$] and [PdCl$_2$(PPh$_3$)]$_2$ were prepared as reported in literature [30,31]. Carbon monoxide and ethene were supplied by SIAD Company ('research grade', purity > 99.9%).

In order to prepare a reaction medium of the desired HCl concentration, a solution of higher concentration was first prepared by slowly bubbling the acid into MeOH at room temperature. The concentration of the acid was determined by titration with NaOH. The MeOH–HCl solution was then diluted with MeOH to the desired concentration. The content of H$_2$O was determined before and after running the catalytic reaction by the Karl–Fischer method.

2.2. Equipment

Gas-chromatographic analysis of the liquid phase was performed on a Hewlett-Packard Model 6890 chromatograph fitted with a HP5, 30 m × 0.32 μm × 0.25 μm column (detector: FID; carrier gas: N$_2$, 0.7 mL/min; oven: 40 °C (3.5 min) to 250 °C at 15 °C/min). Gas-chromatographic analysis of the gas phase was performed on a Hewlett-Packard Model 5890, Series II chromatograph fitted with a 18 ft × 1/8 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).

All the NMR spectra were recorded on a Bruker Avance 300 spectrometer. The ^{1}H NMR and ^{13}C NMR spectra of the polyketone were recorded in 1,1,1,3,3,3-hexafluoroisopropanol/CDCl$_3$ (10/1) using the inverse ^{1}H-gated decoupling technique.

2.3. Carbon monoxide–ethene copolymerisation

The copolymerisation reactions were carried out by using a stainless steel autoclave of ca. 250 mL provided with a four-blade self-aspirating turbine. In order to avoid contamination by metallic species because of corrosion of the internal surface of the autoclave, solvent and catalyst were contained in a ca. 150 mL Pyrex bottle placed inside the autoclave.

The monomers were supplied to the autoclave in the ratio 1/1 from a gas reservoir connected to the autoclave through a constant pressure regulator.

In a typical experiment, [PdCl$_2$(PPh$_3$)$_2$] and PPh$_3$ (35.00 and 52.50 mg, 0.05 and 0.20 mmol, respectively) were added in 80 mL of MeOH–HCl contained in the bottle placed in the autoclave. The autoclave was washed by pressurising with a 1/1 mixture of CO/C$_2$H$_4$ (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 100 °C in ca. 10 min without stirring. The pressure was then adjusted to the desired value (typically 6.0 MPa) and, while stirring, maintained constant throughout the experiment (1 h, rate stirring 700 rpm) by continuously supplying the monomers from the reservoir. At the end of the experiment the autoclave was quickly cooled and CO$_2$ was checked in the gas phase by GC analysis. The autoclave was then carefully depressurised and then opened. The liquid phase was analysed by GC. The HCl concentration was measured by NaOH titration. The slurry was filtered, washed with MeOH, the PK was dried under vacuum at 70 °C and weighted.

The recovered PK appeared greyish coloured, indicating that some catalyst decomposition to palladium metal occurred, even under the most favourable conditions for the stability of the Pd(II) precursor.

3. Results and discussion

3.1. General aspects

The carbonylation of ethene catalysed by $[PdCl_2(PPh_3)_2]$–HCl in the presence PPh_3, using MeOH as a solvent, yields MP and/or an insoluble PK of moderate molecular weight, depending on the reaction conditions. These main products form together with minor amounts of methyl 4-oxohexanoate and other higher soluble oligomers. No dimethyl succinate or higher diesters form.

Preliminary experiments have shown that: (i) the catalytic system is stable when the P/Pd is >4–6/1, (ii) the formation of the PK is favoured at relatively high E/CO ratio and (iii) the catalytic activity becomes significant at relatively high HCl/Pd ratio (>1000). Therefore we studied the influences of these variables, together with the influence of the temperature and of the concentration of water, which forms because of the reaction of the solvent with the acid (reaction (1)) and because water may be involved in the chain-transfer process.

$$MeOH + HCl \rightarrow MeCl + H_2O \qquad (1)$$
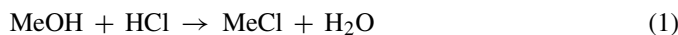
Most of the experiments have been carried out under conditions that favour the formation of PK, since this product was unexpected because in a previous study it was found that a closely related catalytic system based on $Pd(AcO)_2/PPh_3/HCl$ in the ratio 1/30/20 under 4.5 MPa, CO/E = 1/1 gives MP with selectivity 98%, though at relatively high temperature, 115 °C [21]. PK was unexpected also because catalysis occurs in the presence of excess PPh_3 and of relatively large amounts of HCl, *i.e.* under conditions that are not favourable to the creation of "free" coordination site.

Under the conditions relevant to Figs. 1, 2 and 5, in which in particular the monomers are used in the ratio CO/E = 1/5, MP forms in undetectable/negligible amounts.

3.2. On the stability of the catalytic system

3.2.1. Influence of the P/Pd ratio

Under the conditions of Fig. 1, $PdCl_2$ is ineffective because it decomposes to inactive Pd metal. $[PdCl_2(PPh_3)]_2$ partially decomposes, freeing some of the PPh_3 ligand which stabilises the still undecomposed complex. $[PdCl_2(PPh_3)_2]$ is more stable, decomposition occurs to a minor extent. MP does not form in appreciable amounts, whereas the productivity of PK is maximum. Excess of ligand inhibits the catalysis to some extent, even though the activity remains appreciable even when P/Pd = 10/1.

3.2.2. Influence of the temperature

Under the conditions reported in Fig. 2, the catalytic system is stable up to 110 °C; at 120 °C the rate of E transformed into PK
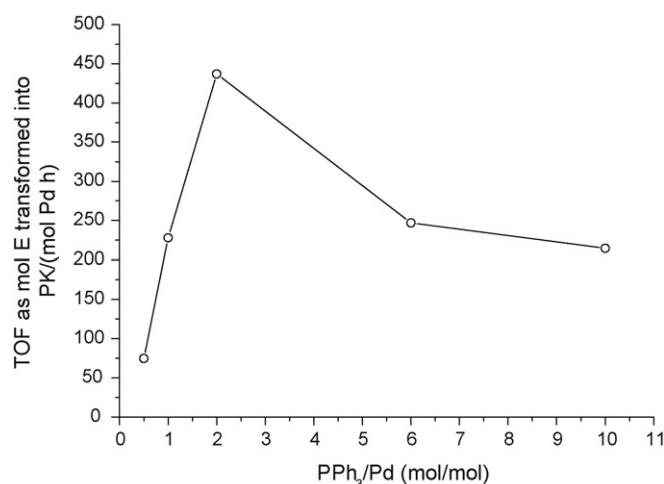

Fig. 1. Influence of PPh_3 on the rate of absorption of E. Run conditions: Pd(II) 0.05 mmol, solvent (MeOH + HCl) 80 mL, HCl (initially added 80 mmol, after reaction 8.7 mmol), $H_2O_{initial}$ 0.12%, H_2O_{final} 2.60%, 100 °C, 6.0 MPa (CO/E = 1/5), 1 h, 700 rpm.

is maximum, though the formation of some Pd metal is observed after catalysis; at higher temperatures the rate of E absorption rapidly falls. Only minor amounts of MP are detectable at all the experienced temperatures.

3.3. Influence of the pressure of the monomers under constant total pressure

The influence of the pressure of the monomers has been studied under a total pressure of 6.0 MPa. Under the conditions reported in Fig. 3, at relatively high pressure of CO partial decomposition to Pd metal occurs even when a relatively high excess of ligand is used. Therefore a catalytic system with a ratio P/Pd = 6/1 has been used, even though the results presented in Fig. 1 indicate that excess ligand inhibits the catalysis.

Decomposition is significantly avoided when the ratio E/CO is >2/4. This fact suggests that at relatively low pressure of E
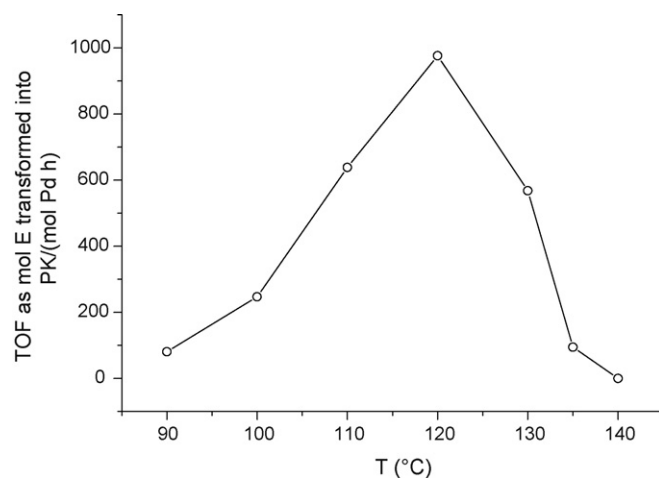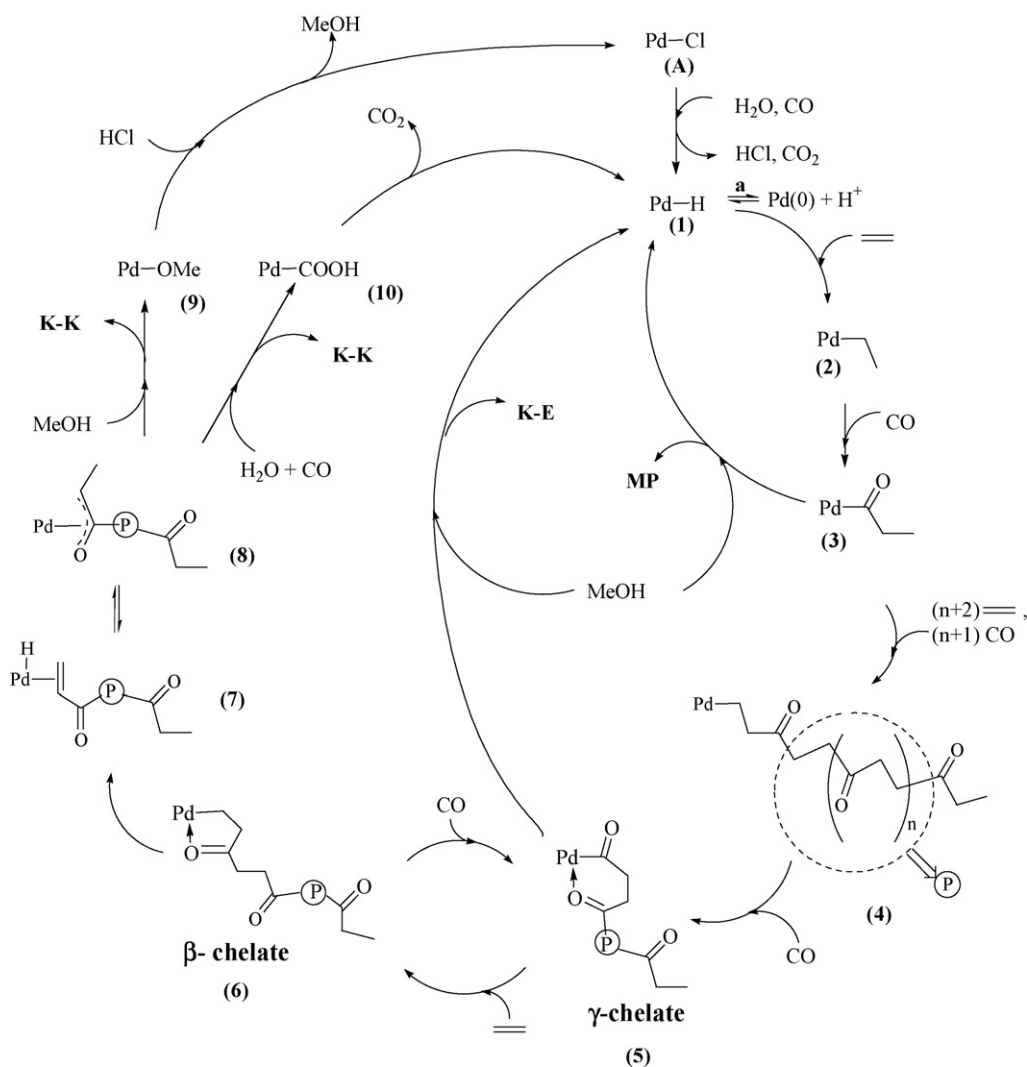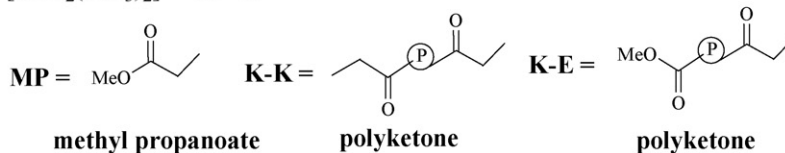

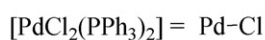
Fig. 2. Effect of temperature on the rate of absorption of E. Run conditions: $PdCl_2(PPh_3)_2$ 0.05 mmol, PPh_3 0.20 mmol, solvent (MeOH + HCl) 80 mL, HCl (initially added 80 mmol, after reaction 10 mmol), $H_2O_{initial}$ 0.12%, H_2O_{final} 2.60%, 100 °C, 6.0 MPa (CO/E = 1/5), 1 h, 700 rpm.

Scheme 1. The proposed reaction mechanism.

its insertion into the Pd–H bond of the species that initiates the catalysis (*cf.* equilibrium **a** in Scheme 1 of the proposed catalytic cycles) is not fast enough compared to deprotonation to Pd(0) species even in the presence of a relatively high acid concentration.

In any case, even at relatively low E partial pressure the concentration of the undecomposed Pd–H species is enough to allow the formation of MP in significant amounts, whereas the formation of PK is negligible. These facts suggests that, after the insertion of just one molecule of ethene and of CO into the Pd–H species, CO inhibits the process of chain growing and/or that methanolysis of the resulting Pd–acyl intermediate is faster than

the insertion of a second molecule of olefin which would initiate the copolymerisation process. Copolymerisation becomes evident when the monomers are in the ratio 1/1, in which case MP and PK form at a comparable rate. Above 4.0 MPa of E the process of chain growing largely prevails and MP forms in negligible amounts. The number-average molecular weight of PK obtained under 50 MPa of ethene is 2400 g/mol.

3.4. Influence of the HCl/Pd ratio

Upon varying the amount of HCl added, the concentration of water varies too, because of reaction (1). In order to point out
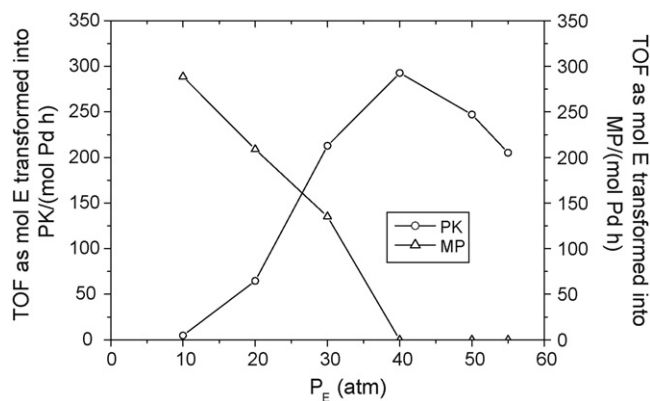
Fig. 3. Influence of E partial pressure on the rate of absorption of E. Run conditions: PdCl$_2$(PPh$_3$)$_2$ 0.05 mmol, PPh$_3$ 0.20 mmol solvent 80 mL (MeOH + HCl), HCl (initially added 80 mmol, after reaction 10.7 mmol), H$_2$O$_{initial}$ 0.12%, H$_2$O$_{final}$ 2.60%, 100 °C, 6.0 MPa (CO + E), 1 h, 700 rpm.

a possible effect of added HCl, the reactions have been carried out at constant water concentration, *ca.* 12%. Under the conditions reported in Fig. 4, in the absence of added HCl, PK does not form and extensive decomposition to Pd metal occurs. Upon adding HCl, the rate of E transformed into PK increases significantly up to a maximum of *ca.* 300 mol E/(mol Pd h) when HCl/Pd = 1600/1, then it slightly decreases.

It is reasonable to suppose that the promoting effect of the acid is due to the possibility that it stabilises the hydride that initiates the catalysis, thus providing a higher concentration of the hydride upon increasing the acid concentration, (*cf.* equilibrium **a** on Scheme 1).

In addition, the acid may destabilise the relatively stable β- and γ-chelate intermediates through which the chain growing process occurs [32–36], as it has been proposed for the production of diethyl ketone catalysed by the system formed *in situ* from Pd(AcO)$_2$/dtbpe/CH$_3$SO$_3$H (dtbpe = 1,2-bis(di-*t*-butylphosphino)ethane). When an excess of acid is used, the selectivity lowers from 99% DEK to *ca.* 33%, *ca.* 60% being cooligomers. It has been proposed that the acid may destabilise the β-chelate intermediate, through which DEK forms, *via* proton interaction with the β-carbonyl [22].
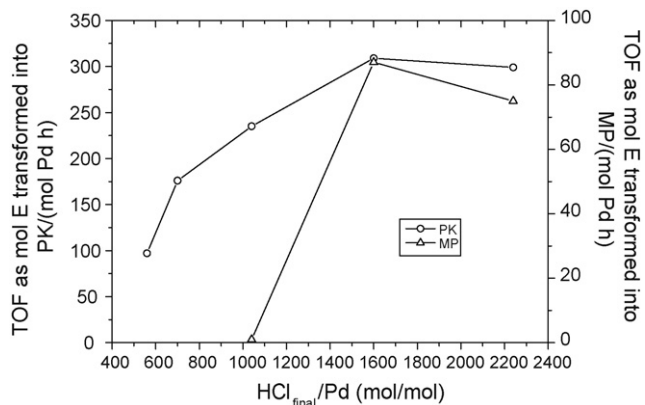
Such a destabilisation has been also proposed in order to explain the different selectivity shown by the cationic catalyst [Pd(H$_2$O)$_2$(dppf)](TsO)$_2$ in MeOH (dppf = 1,1′-bis(diphenylphosphino)ferrocene), which promotes the formation of low molecular weight cooligomers together with molecules of lower molecular weight, included MP, and the corresponding neutral catalyst [PdCl$_2$(dppf)] in H$_2$O-AcOH, in which case the process of chain growing proceeds further to yield only polyketones of moderate molecular weights [37].

A promoting effect of an acid on the process of copolymerisation has been observed also in the case of the carbonylation of ethene using Pd(AcO)$_2$ in combination with an excess of PPh$_3$ or with its monosulfonated derivative PPh$_2$PhSO$_3$H, in acetic acid and in the presence of TsOH (Pd/P/TsOH = 1/8/80–800, 90 °C, 0.10–0.50 MPa). The reaction switches from monocarbonylation with formation of propanoic acid to oligocarbonylation products and to polyketones as the pressure and concentration of TsOH increase; the yield in polyketones also increases upon increasing the acidity [38,39].

It is noteworthy that, in the present case, at high concentration of the acid, MP forms, too. These results suggest that at high concentration of acid, in addition to the Pd species involved in the process of chain growing, a different Pd species operates, in which methanolysis occurs after the insertion of just one molecule of E and of one molecule of CO, leading to the formation of MP and of the Pd–H species that initiates another catalytic cycle.

3.5. Influence of the water concentration

As already pointed out water forms because of the reaction of the solvent with HCl. Fig. 5 shows that the rate of E transformed into PK decreases upon increasing the water concentration. The limiting viscosity number of a dilute PK solution in *m*-cresol, measured at 25 °C as reported in [37], shows a similar trend as LVN decreases from 0.16 to 0.10 dL/g.
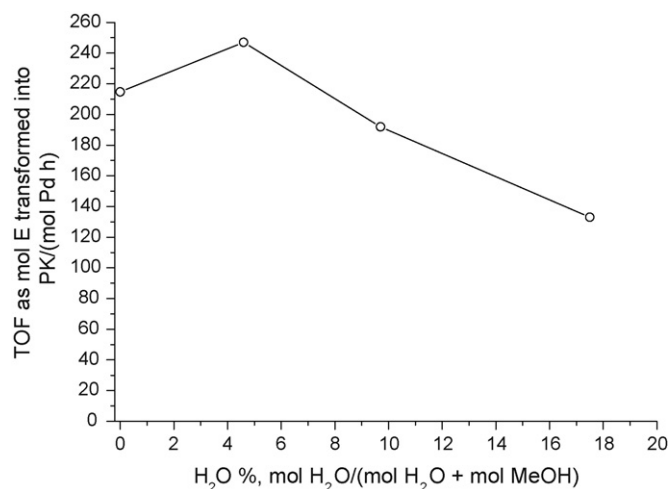
Fig. 5. Influence of H$_2$O (molar fraction) on the rate of absorption of E and on LVN. Run conditions: PdCl$_2$(PPh$_3$)$_2$ 0.05 mmol, PPh$_3$ 0.20 mmol, solvent (MeOH + HCl) 80 mL, HCl (initially added) 80 mmol, 100 °C, 6.0 MPa (CO/E = 1/5), 1 h, 700 rpm.

Fig. 4. Influence of HCl on the rate of absorption of E. Run conditions: PdCl$_2$(PPh$_3$)$_2$ 0.05 mmol, PPh$_3$ 0.20 mmol, solvent (MeOH + HCl) 80 mL, H$_2$O$_{final}$ 11.53%, 100 °C, 6.0 MPa (CO/E = 1/5), 1 h, 700 rpm.

Water is capable of coordinating Pd(II) centres [40], thus it may compete with the monomers for coordination to the metal centre thus slowing down the copolymerisation rate. Moreover, the ^{1}H NMR analysis of the end groups of the PK chains shows that there is an excess of keto groups with respect the ester groups (2.5/1–4.0/1). This can be explained by considering the catalytic cycle proposed here below.

3.6. Proposed catalytic cycles for the formation of MP and of PK

The proposed catalytic cycles for the formation of MP and PK are shown in Scheme 1, in which the species (**1**)–(**10**) are coordinated also by PPh$_3$, which is omitted clarity. They can be neutral or cationic. Cationic species may form by displacement of Cl$^-$ by neutral ligands such as the monomers, H$_2$O or the solvent [29].

In principle catalysis may initiates from a Pd–H or a Pd–OMe (or Pd–COOMe) species. Termination may occur *via* methanolysis of a Pd–acyl–polymer species or *via* protonolysis of a Pd–alkyl–polymer species, with formation of a polyketone having keto–ester, keto–keto or ester–ester end groups [21]. As already mentioned, the ^{1}H NMR analysis of the polymer shows that there is an excess of keto end groups. Moreover, the light products that have been detected by GC do not have ester–ester end groups. Therefore, it is unlikely that catalysis initiates from a Pd–OCH$_3$ species. In addition it has been found that complexes of the type *trans*-[PdCl(COOR)(PPh$_3$)$_2$] are unstable even at r.t. in the presence of HCl giving *trans*-[PdCl$_2$PPh$_3$)$_2$], CO and ROH [41]

Hydride (**1**) that initiates the catalysis can form from the precursor (**A**) by interaction of H$_2$O and CO with the metal centre, through a reaction closely related to the water gas shift reaction (WGSR) [42–47].

Catalysis is observed only in the presence of HCl, which stabilises hydride (**1**) against deprotonation to Pd(0), which ultimately lead to the formation of inactive Pd metal. Hydride (**1**) inserts E to give the ethyl intermediate (**2**), which inserts CO to give the acyl intermediate (**3**). Methanolysis of this species lead to MP and hydride (**1**) back to the catalytic cycle. Under relatively high pressure of E, this inserts into intermediate (**3**) before methanolysis to MP; multiple alternating insertion of the monomers lead to chain growing. Alternating insertions occur because of kinetic and thermodynamic reasons [9,48,49]. Chain growing occurs through the intermediary of γ- and β-chelates, which also contribute to the alternating insertions [34]. Methanolysis of intermediates (**4**) or (**5**) yields a PK with keto and ester end groups in the ratio 1/1. Since an excess of keto groups has been found by ^{1}H NMR analysis (*cf. 3.5*), termination occurs also *via* protonolysis by MeOH or H$_2$O, both leading to the formation of a keto end group [21,35,36,50].

Protonolysis involves a β-chelate (**6**) through a pre-equilibrium with its enolate isomer (**8**) by a β-H elimination/hydride migration and protonation to the more nucleophilic oxygen atom to give an enol, which rearranges to the keto end group [51,52].

Protonolysis with MeOH yields a Pd–OMe species, which is unstable in the presence of a large excess of HCl and gives the precursor (**A**), which re-enters in the catalytic cycle after interaction with CO and H$_2$O.

Protonolysis with H$_2$O yields a Pd–OH species, which reacts with HCl to give the precursor or with CO to give a Pd–COOH (**10**) species, that gives hydride (**1**) after CO$_2$ evolution [27,28,53]. CO$_2$ has been found to be present in the gas phase by GC analysis.

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