

Selective alternating copolymerisation of carbon monoxide and ethene catalysed by $[\text{PdCl}_2(\text{dppf})]$ in acetic acid–water as a solvent [dppf = 1,1'-bis(diphenylphosphino)ferrocene]

Andrea Vavasori^a, Alessia Bellieni^a, Lucio Ronchin^a, Federico Dall'Acqua^a,
Luigi Toniolo^{a,*}, Gianni Cavinato^b

^a Department of Chemistry, University Ca' Foscari of Venice, Dorsoduro 2137, 30123 Venice, Italy

^b Department Chemistry Sciences, University of Padua, via Marzolo 1, 35100 Padua, Italy

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Abstract

The title complex is highly active and selective for the alternating copolymerisation of carbon monoxide and ethene in $\text{CH}_3\text{COOH}-\text{H}_2\text{O}$ as a solvent. Under typical reaction conditions, 90 °C, 4.5 MPa, CO/ethene = 1/1, the productivity passes through a maximum of 15,500 gPK (gPd h)⁻¹ when the concentration of the acid is 40% (mol mol⁻¹), whereas the limiting viscosity number (LVN) increases upon increasing the acid concentration. Under the above conditions, but in the presence of sodium acetate, a polyketone (PK) of higher molecular weight is obtained, though at the expense of the productivity. Under higher pressure of ethene both productivity and LVN increase; under higher pressure of CO the productivity slightly decreases, whereas the LVN increases. These results are discussed taking into account the factors relevant to the chain growing and the termination processes.

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1. Introduction

Cis-coordinated diphosphine cationic complexes of Pd(II) have been found active catalysts in the carbonylation of ethene to a wide spectrum of important products ranging from high molecular weight perfectly alternating polyketones or cooligomers or lower carbonylated derivatives down to monocarbonylated products such as diethyl ketone (DEK) or propanoic acid and its esters [1–12].

Normally, MeOH is used as a solvent. Catalysis initiates from species having Pd–H or Pd–OCH₃ bonds and proceeds through the insertion of the monomers till the termination step gives the product and the species that starts a new catalytic process. *Cis*-coordination is ideal for favouring both the insertion reactions and the termination step [13,14].

The selectivity of the reaction mainly depends on the nature of the ligand. C₃-bridged diarylphosphines are highly

active in the copolymerisation process [15], whereas bulkier diphosphines such as *t*-BuP(CH₂)₃PBu-*t* [16] or 1,2-bis[(di-*t*-butyl)phosphinomethyl]benzene [6–9] are very active and selective in promoting the methoxycarbonylation to methyl propanoate (MP). That steric bulk plays a role of paramount importance in controlling the selectivity is well evidenced also by the results obtained using cationic Pd(II) complexes of 1,1'-bis(diorganophosphino)ferrocene ligands. When the organo-substituent is a phenyl group the products is a PK of moderately high molecular weight, cooligomers and other molecules of even lower molecular weight, such as dimethyl 4-oxoheptanoate, dimethyl succinate, methyl 4-oxohexanoate and methyl propanoate [17]; when it is a methyl group only PK forms; when the substituent is an ethyl group PK of lower molecular weight is obtained, whereas with an *i*-Pr substituent the products are MP and DEK [18].

In order to easy the coordination of the reacting molecules, a prerequisite is that the cationic charge of the metal centre has to be balanced by a non- or weakly-coordinating anion, conjugated base of a strong acid, for example TsOH

* Corresponding author. Tel.: +39 041 2348553; fax: +39 041 2348517.
E-mail address: toniolo@unive.it (L. Toniolo).

(*p*-toluenesulfonic acid), HBF₄, HPF₆, CF₃COOH, CF₃SO₃H [13].

With catalysts which promote the formation of low molecular weight products the selectivity may depend significantly also from the nature of the anion. For instance, in the case of ethane-bridged bis(phosphabicyclononane)-based catalyst the selectivity changes from a low molecular weight polymer to MP when the counter-anion is CH₃SO₃⁻ or propanoate, respectively [19].

The coordinating capacity depends not only on the nature of the anion, but also on the solvent. Polar solvents help the dissociation of the anion from the cationic active catalyst, thus favouring the polymerisation process. This is well illustrated by comparing the activity of the catalysts [PdX₂(dppp)] (X = TfO, TsO, TFA, AcO, Cl). In MeOH the activity is comparable when X is weakly coordinating like TfO, TsO, TFA (*ca.* 7000–6000 gPK (gPd h)⁻¹ at 90 °C, 4.5 MPa, CO/ethene = 1/1). When X = CH₃COO or Cl the catalyst is ineffective [13], but it turns into a very active one when used in CH₃COOH–H₂O (*ca.* 27,000 gPK (gPd h)⁻¹, under the conditions just reported and with CH₃COOH in the molar concentration of *ca.* 60–40%) [20,21].

This article deals with the CO-ethene copolymerisation catalysed by the title complex in CH₃COOH–H₂O as solvent.

2. Experimental

2.1. Reagents

Acetic acid (100%, glacial) was purchased from Baker; Palladium(II) chloride was purchased from Engelhard Italiana SRL; 1,1'-bis(diphenylphosphino)ferrocene (dppf), 1,1,1,3,3,3-hexafluoroisopropanol (99%), CD₃COOD and CDCl₃ were Aldrich products. The complexes [PdCl₂(PhCN)₂] and [PdCl₂(dppf)] was prepared as reported in literature [22,23]. Carbon monoxide and ethene were supplied by SIAD Company ('research grade', purity > 99.9%).

2.2. Equipment

The catalyst precursor was weighed on a Sartorius Micro balance (precision 0.001 mg). Gas-chromatographic analysis of the liquid phase was performed on a Hewlett-Packard Model 5890, Series II chromatograph fitted with a HP1, 30 m × 0.35 μm × 0.53 μm column (detector: FID; carrier gas: N₂, 0.2 ml min⁻¹; oven: 50 °C (2 min) to 200 °C at 15 °C min⁻¹). 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⁻¹; oven: 40 °C (2 min) to 100 °C at 15 °C min⁻¹).

All the NMR spectra were recorded on a Bruker Avance 300 spectrometer. The ¹H NMR and ¹³C NMR spectra of the polyketone were recorded in 1,1,1,3,3,3-hexafluoroisopropanol/CDCl₃ (10/1) using the Inverse ¹H-Gated Decoupling Technique. The ³¹P NMR spectra of the complex [PdCl₂(dppf)] were recorded in CD₃COOD–H₂O and CDCl₃.

2.3. Carbon monoxide–ethene 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. 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, 0.650 mg of [PdCl₂(dppf)] (8.88 × 10⁻⁴ mmol) was added to 80 ml of solvent (CH₃COOH–H₂O, CH₃COOH = 40% mol mol⁻¹) contained in the bottle placed in the autoclave. The autoclave was washed by pressurising with a 1/1 mixture of CO/C₂H₄ (*ca.* 0.5 MPa) and then depressurising to atmospheric pressure (this cycle was repeated 5 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 in *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 monomers 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 70 °C.

The dried polymer was weighted and the productivity was calculated as gPK (gPd h)⁻¹; the reproducibility was within *ca.* 5%.

In the liquid phase, analysed by CG, no propanoic acid or other low molecular weight products were found.

The CO₂ evolution during the reaction was monitored by sampling with a micro-syringe the gas phase of the reactor which was then analysed by a gas-chromatograph, following the same procedure already reported [20].

2.4. Limiting viscosity number (LVN) measurement and average viscosity molecular weight calculation

The LVN of a dilute polyketone solution was determined by using the Huggins relationship between the viscosity number and the polymer concentration by extrapolation to zero concentration [24]. The polyketone solution was prepared in *m*-cresol as a solvent and the viscosity was measured by using a Cannon–Fenske type capillary viscosimeter, thermostated at 25 °C.

The average molecular weight of the polyketone was derived from the LVN using the following Mark–Houwink equation [25]:

$$[\eta]_{m\text{-cresol}, 25^\circ\text{C}} = 1.01 \times 10^{-4} \bar{M}_w^{0.85}$$

3. Results and discussion

In H₂O or CH₃COOH the title complex does not catalyse the carbonylation of ethene to an appreciable extent, whereas

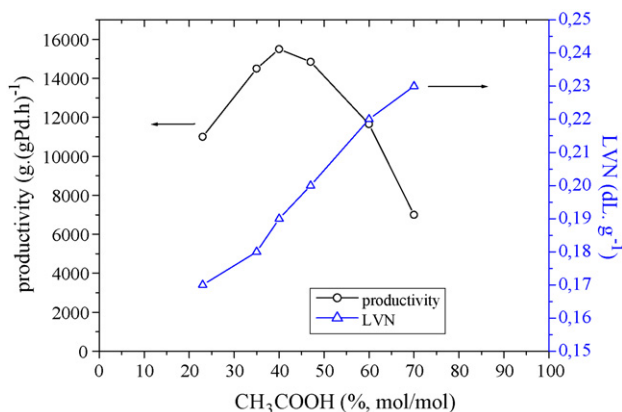


Fig. 1. Effect of concentration of CH₃COOH on the productivity and on the LVN. Run conditions—[PdCl₂(dppf)]: 8.88 × 10⁻⁴ mmol; solvent: CH₃COOH–H₂O, 80 ml; T: 90 °C; P: 4.5 MPa; time: 1 h; stirrer: 700 rpm.

Table 1
Effect of concentration of CH₃COOH on the productivity and on the LVN

CH ₃ COOH (% mol mol ⁻¹)	Productivity (g(gPd h) ⁻¹)	LVN (dl g ⁻¹)	M _v ^a (g mol ⁻¹)
23	11000	0.17	6317
35	14500	0.18	6757
40	15500	0.19	7200
47	14850	0.20	7650
60	11653	0.22	8555
70	7000	0.23	9015

Run conditions—[PdCl₂(dppf)]: 8.88 × 10⁻⁴ mmol; solvent: CH₃COOH–H₂O, 80 ml; T: 90 °C; P: 4.5 MPa; time: 1 h; stirrer: 700 rpm.

^a M_v: Calculated average viscosity molecular weight.

when used in a CH₃COOH–H₂O mixture it turns into a highly active and selective catalyst yielding of a perfectly alternating PK of moderate molecular weight. The catalytic activity strongly depends on the solvent composition, passes through a maximum of 15,500 gPK (gPd h)⁻¹ when the ratio CH₃COOH/H₂O is 40/60 (mol mol⁻¹), as shown in Fig. 1 and Table 1.

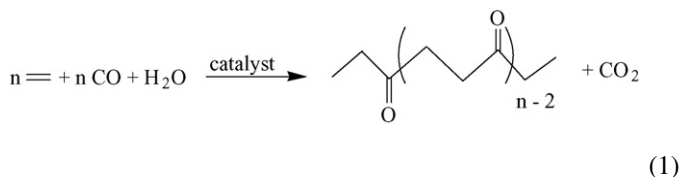
The ¹³C NMR spectrum of the PK shows the presence of keto-end groups (CH₃CH₂CO)-, only. Moreover, catalysis occurs with concomitant formation of CO₂. Based on these evidences and on previous knowledge, the proposed catalytic cycle is shown in Scheme 1.¹

The ³¹P NMR signal of the title complex in H₂O–CD₃COOD shifts from 37.5 ppm when H₂O is 20% to 39.1 ppm when H₂O is 60%, in between that in CDCl₃ (35.1 ppm) and that of the cationic complex [Pd(H₂O)₂(dppf)]X₂ (44.9 and 48.1 ppm for X = TsO or TfO, respectively, in CDCl₃[26]), indicating that H₂O interacts with the chloride complex.

Under the actual catalysis conditions, CO and H₂O can interact with the palladium centre yielding a Pd-hydride species, through a reaction closely related to the water–gas shift reaction [20,21,27–29]. The hydride initiates the catalytic cycle,

which proceeds through sequential incorporation of ethene and CO, with formation of β- and γ-chelate intermediates, which rules the alternating insertions [17,30]; termination occurs *via* protonolysis, which is known to involve a pre-equilibrium of a β-chelate intermediate with its enolate isomer by a β-H elimination/hydride migration and protonation of the more nucleophilic oxygen atom to give an enol, which rearranges to the terminating ketone [31,32]. Interaction with CO or with CO and H₂O when X = OH or CH₃COO, respectively, gives the hydride back to the catalytic cycle (Scheme 1).

Apart the initial formation of CO₂ by the reaction that activates the catalytic precursor to a Pd-H species, CO₂ evolution occurs at any catalytic cycle. Thus the neat reaction is:



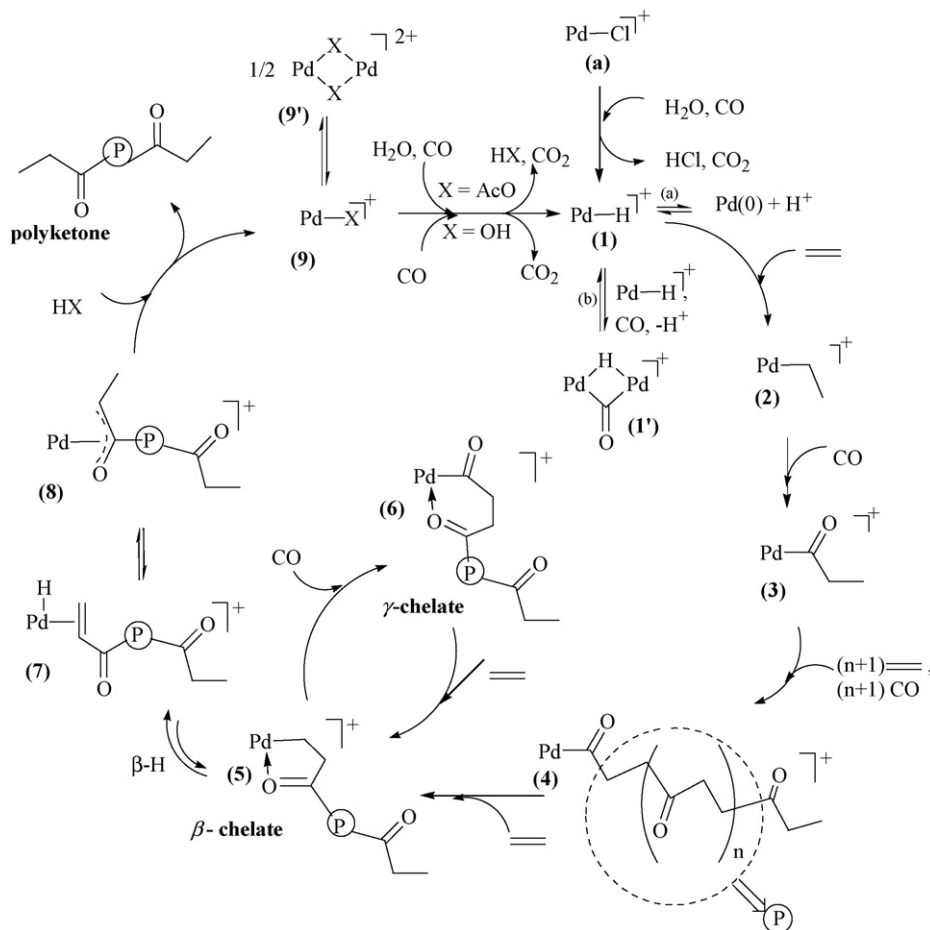
On the basis of experimental evidences obtained using the cationic catalyst precursor [Pd(H₂O)₂(dppf)](TsO)₂ in MeOH in both autoclave and high-pressure NMR tube, it was concluded that catalysis occurs *via* both the “hydride” and the “methoxy” cycles [17]. MP, which can be considered the lowest member of the polymerisation process, can form *via* both cycles (Scheme 2).

When MP forms *via* the “hydride” mechanism it involves an acyl intermediate **3** as in the case when the title complex is used in CH₃COOH–H₂O. However, in this case there is not formation of monocarbonylated products and of low cooligomers, but catalysis proceeds further through fast alternating insertion of the monomers till the product forming termination step yields the PK. Thus the acid favours the insertion of a second molecule of ethene into the Pd-acyl intermediate **3** as well as the subsequent copolymerisation process, probably by making easier the opening of the five- or six-membered rings of β- and γ-chelate intermediates **5** and **6**, which have been found to be relatively stable [30].

In addition, the rate of carbonylation is significantly higher than that observed in MeOH using the cationic precursor [Pd(H₂O)₂(dppf)](TsO)₂ [17], in spite of the higher solubility of the monomers in MeOH than in CH₃COOH–H₂O [21]. The acid may prevent deprotonation of the active Pd-hydride (equilibria (a) and (b) in Scheme 1) thus providing a higher concentration of the species that initiates the catalysis. Moreover, the acid may have the same function of TsOH when using the cationic complex in MeOH [17]. In this case, in the chain-transfer termination–initiation step through hydrolysis by the water present in the solvent, there is formation of the μ-OH dimeric complex [Pd(μ-OH)(dppf)]₂(TsO)₂ [17,32], from species **9** (X = OH) of Scheme 1, which turns into an effective catalyst only in the presence of TsOH [17].

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 PPh₃ or with its monosulfonated derivative PPh₂PhSO₃H, in acetic acid and in the presence of TsOH (Pd/P/TsOH = 1/8/80–800, 90 °C,

¹ In this and other schemes and reactions the species Pd–Cl⁺, Pd–H⁺, etc. are coordinated also by the diphosphine and one monomer or Cl⁻, or AcO⁻, or H₂O or an oxygen atom of keto-group of a β- or of a γ-chelate of the growing chain (see below).



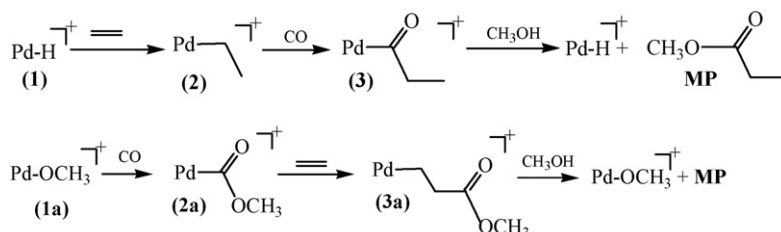
Scheme 1. Proposed catalytic cycle for the formation of PK catalysed by the precursor [PdCl₂(dppf)].

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 [33,34]. A similar acid effect has been found with the dtbpe-based catalyst in MeOH for the production of DEK, as the selectivity lowers from 99% DEK to *ca.* 33%, *ca.* 60% being cooligomers [11].

In addition to the promoting effect of CH₃COOH, water may have also a beneficial effect. Labile coordination of H₂O may stabilise three-coordinated species which may form during the catalysis, against their tendency to dimerise to achieve the usual four-coordination of Pd(II). In general dimeric species are less active [3].

Fig. 1 shows that there is not a simple relation between the concentration of the acid and the productivity, as this decreases when the acid concentration is higher than *ca.* 40% and even though the solubility of the monomers increases. Since upon varying the acid concentration, the acetate anion concentration varies too, some experiments have been carried out in the presence of NaAcO at constant acid concentration, 40%. The results reported in Fig. 2 and in Table 2 show that the salt effectively depresses the productivity. Quite interestingly, in the presence of this salt, the LVN is significantly effected (see below).

Fig. 1 shows also the influence of the acid concentration on the LVN, which (slightly) increases upon increasing the concentration of the acid. From the LVN the average viscosity molecular weight can be calculated (Table 1). Not only the trend of the LVN



Scheme 2. "Hydride" and "methoxyde" mechanisms for the hydromethoxycarbonylation of ethene.

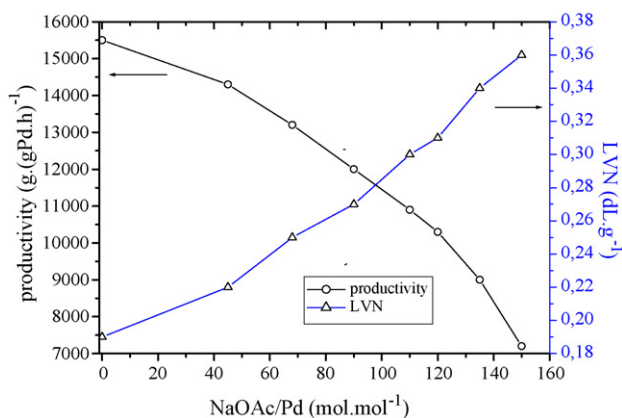


Fig. 2. Effect of NaOAc addition on the productivity and on the LVN. Run conditions— $[\text{PdCl}_2(\text{dppf})]$: 8.88×10^{-4} mmol; solvent: $\text{CH}_3\text{COOH}-\text{H}_2\text{O}$, 80 ml; CH_3COOH : 40% (mol mol $^{-1}$); T : 90 °C; P : 4.5 MPa (CO/C $_2\text{H}_4$ = 1/1); reaction time: 1 h; stirrer: 700 rpm.

seems in contrast with that of the productivity shown in Fig. 1, but also a lowering of the molecular weight upon increasing the acid concentration could be expected, since the termination step occurs through protonolysis. However, using several catalysts based on different ligands, it was found that in the termination process enolate formation is much slower than protonolysis (see Scheme 1, the steps involving intermediates 5, 7, and 8). It was concluded that enolate formation is the rate determining step [32].

Fig. 2 shows also the influence of the NaOAc/Pd ratio on the viscosity. Quite interestingly, upon increasing the concentration of the salt, the viscosity significantly increases, suggesting that enolate formation is inhibited and that the copolymerisation process proceeds further though at a lower rate (see also the effect of increasing CO pressure reported below).

Figs. 3 and 4 and Table 3 show the influence of the pressure of the monomers on the productivity and on the LVN at different CH_3COOH concentrations.

Taking as reference the results shown in Fig. 1, indicated with the symbol o, the productivity increases only slightly upon doubling the pressure of both monomers (results indicated with symbol x). Upon doubling only the pressure of CO the productivity is significantly depressed (results indicated with *),

Table 2
Effect of NaOAc addition on the productivity and on the LVN

NaOAc/Pd (mol mol $^{-1}$)	Productivity (g (gPd h) $^{-1}$)	LVN (MW) (dl g $^{-1}$ (g mol $^{-1}$))
0	15500	0.19 (7200)
45	14300	0.22 (8556)
68	13200	0.25 (9944)
90	12000	0.27 (10887)
110	10900	0.30 (12323)
120	10300	0.31 (12808)
135	9000	0.34 (14278)
150	7200	0.36 (15272)

Run conditions— $[\text{PdCl}_2(\text{dppf})]$: 8.88×10^{-4} mmol; solvent: $\text{CH}_3\text{COOH}-\text{H}_2\text{O}$, 80 ml; CH_3COOH : 40% (mol mol $^{-1}$); T : 90 °C; P : 4.5 MPa (CO/C $_2\text{H}_4$ = 1/1); reaction time: 1 h; stirrer: 700 rpm.

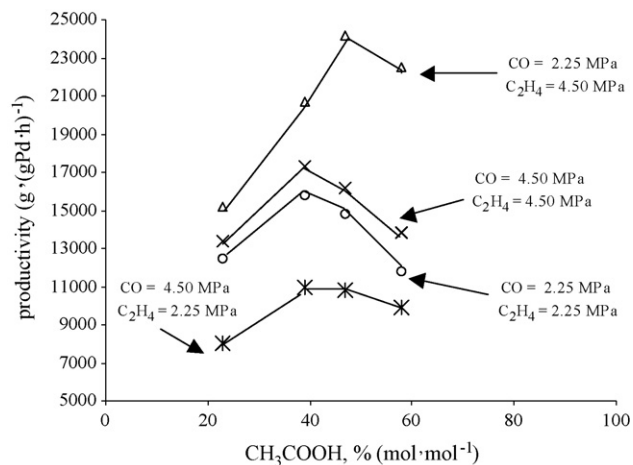


Fig. 3. Effect of the concentration of CH_3COOH and of the partial pressure of the monomers on the productivity. Run conditions— $[\text{PdCl}_2(\text{dppf})]$: 8.88×10^{-4} mmol; solvent: $\text{CH}_3\text{COOH}-\text{H}_2\text{O}$, 80 ml; T : 90 °C; time: 1 h; stirrer: 700 rpm.

whereas the viscosity slightly increases. In any case the productivity passes through a maximum when the $\text{CH}_3\text{COOH}/\text{H}_2\text{O}$ ratio is *ca.* 40/60 (mol mol $^{-1}$).

Upon doubling the pressure of ethene both productivity and viscosity significantly increase and the highest productivity is obtained at a slightly higher CH_3COOH concentration ($\text{CH}_3\text{COOH}/\text{H}_2\text{O}$ = 50/50). These results suggest that the monomers compete for coordination to the metal and are in agreement with the suggestion that ethene insertion is kinetically relevant in the process of chain growing and that this insertion may be CO assisted [13,30,35].

The fact that upon doubling the pressure of CO only, the viscosity increases even though the productivity decreases, deserves a further comment. It has been pointed out that the termination step occurs through an enolate intermediate, which involves two coordination sites, one of them in competition with coordination with any species capable of coordinating, including CO. Thus upon increasing the CO pressure, enolate formation

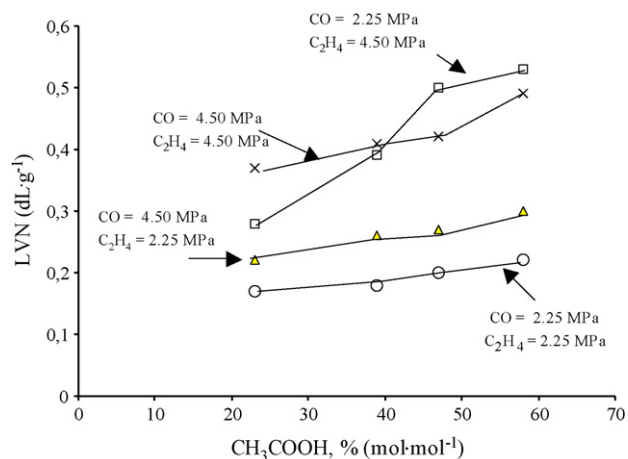


Fig. 4. Effect of the concentration of CH_3COOH and of the partial pressure of the monomers on the LVN. Run conditions— $[\text{PdCl}_2(\text{dppf})]$: 8.88×10^{-4} mmol; solvent: $\text{CH}_3\text{COOH}-\text{H}_2\text{O}$, 80 ml; T : 90 °C; time: 1 h; stirrer: 700 rpm.

Table 3

Effect of the concentration of CH₃COOH and of the partial pressure of the monomers on the productivity and on the LVN

CH ₃ COOH (% (mol mol ⁻¹))	<i>P</i> _{CO} / <i>P</i> _{C₂H₄} (MPa MPa ⁻¹)							
	2.25/2.25		4.50/2.25		2.25/4.50		4.50/4.50	
	Productivity (g (gPd h) ⁻¹)	LVN (dl g ⁻¹)	Productivity (g (gPd h) ⁻¹)	LVN (dl g ⁻¹)	Productivity (g (gPd h) ⁻¹)	LVN (dl g ⁻¹)	Productivity (g (gPd h) ⁻¹)	LVN (dl g ⁻¹)
23	11000	0.17	15200	0.28	8000	0.22	13400	0.37
35	14000	0.18	19300	0.34	10200	0.25	16250	0.40
40	15500	0.19	20700	0.39	11000	0.26	17300	0.13
47	14850	0.20	24140	0.50	10800	0.27	16200	0.42
60	11653	0.22	22500	0.53	9900	0.30	13800	0.49

Run conditions—[PdCl₂(dppf)]: 8.88 × 10⁻⁴ mmol; solvent: CH₃COOH–H₂O, 80 ml; *T*: 90 °C; time: 1 h; stirrer: 700 rpm.

is disfavoured and hence the process of chain growing to PKs of higher molecular weight goes on, even though the productivity lowers because CO competes also for the coordination of the other monomer. A similar explanation may hold for the effect of added NaAcO on the productivity and the LVN.

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