



Influence of the operating conditions on the catalytic activity of [PdCl₂(dapp)] in the CO–ethene copolymerization in the H₂O–CH₃COOH as a solvent (dapp = 1,3-bis(di(2-methoxyphenyl)phosphino)propane)

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ABSTRACT

The influence on the productivity of [PdCl₂(dapp)] in H₂O–CH₃COOH in the CO–ethene copolymerization and on the LVN of the copolymer of the following reaction parameters has been studied: (i) composition of the H₂O–CH₃COOH reaction medium; (ii) temperature; (iii) CO/ethene ratio at a given total pressure; (iv) total pressure at fixed ratio CO/ethene = 1/1; (v) CO or ethene partial pressure at a given pressure of one monomer; (vi) reaction time. High molecular weight PKs are obtained under high pressure with the monomers in the ratio 1/1 at relatively low temperature and with a H₂O/CH₃COOH 40–50% with productivity ranging from 4 to 20 kg PK(g Pd h)⁻¹.

The relation between productivity and LVN has been discussed in the light of the key steps of the catalytic cycle.

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1. Introduction

Cationic palladium–phosphine complexes catalyze the copolymerization of carbon monoxide with ethene (E) to yield a wide spectrum of important products ranging from perfectly alternating polyketones (PKs) to derivatives of low molecular weight products such as diethyl ketone or propanoic acid and its esters [1–8].

In general, compared to monophosphine complexes, which may present trans- and cis-coordination, diphosphine complexes that maintain cis-coordination throughout the catalytic cycle, are far superior because cis-coordination favours all the elementary steps of the catalytic cycle [1,5], including the product-forming one [9].

The selectivity mainly depends on the nature of the ligand. C₃-bridged diarylphosphines, such as dppp or dapp (dppp = 1,3-bis(diphenylphosphino)propane; dapp = 1,3-bis(di(2-methoxyphenyl)phosphino)propane), are highly active in the copolymerization process [8]. Upon increasing steric bulk, the chain-growing process becomes more and more inhibited, whereas the chain-transfer termination step is favoured [9]. This is well illustrated by substitution of the aryl groups with butyl groups, in which case both the productivity and molecular weight decrease to the point that with *t*-Bu₂(CH₂)₃Bu₂-*t*

the main product is methyl propanoate (MP), which can be considered the lightest product of the copolymerization process (97.4% selectivity, TOF 25,000 h⁻¹ at 120 °C, 40 bar, CO/ethene = 2/1, MeOH as a solvent) [10]. A even higher selectivity is achieved using a dtbpx-based catalyst (dtbpx = 1,2-bis(di-*t*-butyl)phosphinomethyl]benzene; 99.98%, TOF = 50,000 h⁻¹, 80 °C, 10 bar, CO/ethene = 1/1 [11]. In this case, the wider bite angle of dtbpx magnifies the steric bulk of the *t*-Bu groups, which may account for the exceptionally high selectivity to MP.

Other factors that influence the activity and selectivity are: the nature of the counter anion, the solvent, the operating conditions and added promoting agents, protic acids, organic oxidant and water [12–14].

The nature of the solvent may exert a dramatic influence on the performance of the catalyst. It was reported, first by us, that the neutral precursors [PdX₂(dppp)] (X = AcO, Cl), inactive in MeOH, the solvent of most common use, turn into highly active systems when used in H₂O/AcOH as a solvent [13,15]. In spite of the lower solubility of the monomers in H₂O–CH₃COOH, with respect to those in MeOH, the productivity of the [PdX₂(dppp)]/(H₂O–CH₃COOH) system is much higher than that of the corresponding cationic complex (X = TsO) in MeOH (27 kg PK(g Pd h)⁻¹ versus 6 kg PK(g Pd h)⁻¹. These studies have been extended to the use of [PdCl₂(dppf)] (dppf = 1,1'-bis(diphenylphosphino)ferrocene), which is also inactive in MeOH. It has been found that in H₂O/AcOH it is highly active to give PKs of moderately high molecular weight [16]. Instead, the

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analogous cationic precursors having TsO^- as counter anion used in MeOH yields co-oligomers and other molecules of even lower molecular weight, such as dimethyl 4-oxoheptanoate, methyl 4-oxohexanoate, dimethyl succinate and MP [17].

Subsequently, the catalytic activity of other $[\text{PdCl}_2(\text{P-P})]$ complexes ($\text{P-P} = 1,2\text{-bis}(\text{di}(2\text{-methoxyphenyl})\text{phosphino})\text{ethane}$, dapp and dapp with substituents in the C_3 -bridging chain in $\text{H}_2\text{O}/\text{AcOH}$ has been briefly reported [18,19].

The cationic dapp-based system in MeOH has been developed by Schell for industrial application for producing PKs. It gives a satisfactory balance between productivity and molecular weight, better than the analogous dppp-based system (with $\text{Pd}(\text{AcO})_2/(\text{P-P})/(\text{TFAH}) = 1/0.5/2$ (TFAH = trifluoroacetic acid; productivity $12,700 \text{ g PK}(\text{g Pd h})^{-1}$ versus $7100 \text{ g PK}(\text{g Pd h})^{-1}$, LVN 1.58 dL/g versus 1.05 dL/g under 50 atm ($\text{CO}/\text{E} = 1/1$), at 90°C for 1 h [8]).

Recently, several industries have shown a renewed keen interest in high molecular weight PKs for applications in the field of fibers [20,21]. This prompted us to take into consideration the use of $[\text{PdCl}_2(\text{dapp})]$ in $\text{H}_2\text{O}/\text{AcOH}$ with the aim of obtaining high molecular weight PKs with high productivity. Here, we present an extensive study on the influence of the operating conditions on the catalytic activity on the CO–ethene copolymerization catalyzed by this system.

2. Experimental

2.1. Reagents

Acetic acid (100%, glacial), solvents, triethylamine, *m*-cresol, CDCl_3 , were purchased from Aldrich; palladium(II) chloride was purchased from Chimet S.p.A.; 1,1,1,1,3,3,3-hexafluoro-2-propanol (99%) was purchased from Riedel De Haen. The complex $[\text{PdCl}_2(\text{PhCN})_2]$ was prepared as reported in literature [22]. The complex $[\text{PdCl}_2(\text{dapp})]$ was prepared from $[\text{PdCl}_2(\text{PhCN})_2]$ and dapp (1/1) in $\text{CH}_2\text{Cl}_2/\text{EtOH}$ ($^{31}\text{P}\{^1\text{H}\}$ NMR 16.30 ppm at r.t. in CD_2Cl_2). Dapp was provided by Hyosung Corporation. Carbon monoxide and ethene were supplied by SIAD Company ('research grade', purity > 99.9%).

2.2. Equipment

The catalyst precursor was weighted 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, $30 \text{ m} \times 0.35 \mu\text{m} \times 0.53 \mu\text{m}$ column (detector: FID; carrier gas: N_2 , 0.2 mL/min; oven: 50°C (2 min) to 200°C at $15^\circ\text{C}/\text{min}$). Gas-chromatographic analysis of the gas phase was performed on a Hewlett Packard Model 5890, Series II chromatograph fitted with a $18 \text{ ft} \times 1/8 \text{ SS Silica Gel, } 60/80$ packed column (detector: TCD; carrier gas: helium, 30 mL/min; oven: 40°C (2 min) to 100°C at $15^\circ\text{C}/\text{min}$).

All the NMR spectra were recorded on a Bruker Avance 300 spectrometer. The ^1H NMR and ^{13}C NMR spectra of the polyketone were recorded in 1,1,1,1,3,3,3-hexafluoroisopropanol/ CDCl_3 (10/1) using the Inverse ^1H -Gated Decoupling Technique. The ^{31}P NMR spectra of the complex $[\text{PdCl}_2(\text{dapp})]$ were recorded in CD_2Cl_2 , external $85\% \text{ H}_3\text{PO}_4$.

2.3. Carbon monoxide–ethene copolymerization

The copolymerization 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 due to 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, 0.60 mg of $[\text{PdCl}_2(\text{dapp})]$ ($8.88 \times 10^{-4} \text{ mmol}$) was added to 80 mL of solvent ($\text{CH}_3\text{COOH}-\text{H}_2\text{O}$, $\text{H}_2\text{O} = 55\%$ (mol/mol) contained in the bottle placed in the autoclave. The autoclave was washed by pressurising with a 1/1 mixture of $\text{CO}/\text{C}_2\text{H}_4$ (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 and, while stirring (700 rpm), maintained constant throughout the experiment 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 $\text{g PK}(\text{g Pd h})^{-1}$; 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 CO_2 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 [13].

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 [23]. 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 can be calculated from the LVN using the following Mark–Houwink equation [24]:

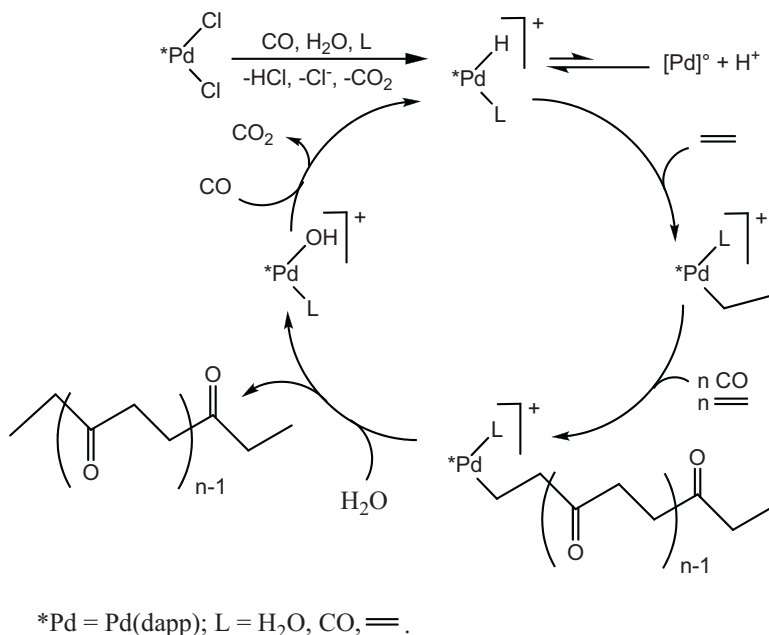
$$[\eta]_{m\text{-cresol}, 25^\circ\text{C}} = 1.01 \times 10^{-4} \overline{M}_w^{0.85}$$

3. Results and discussion

The influence on the productivity of the catalyst and on the LVN of the copolymer of the following reaction parameters has been studied: (i) composition of the $\text{H}_2\text{O}-\text{CH}_3\text{COOH}$ reaction medium; (ii) temperature; (iii) CO/ethene ratio at a given total pressure; (iv) total pressure at fixed ratio CO/ethene = 1/1; (v) CO and ethene partial pressures at a given pressure of one monomer; (vi) reaction time.

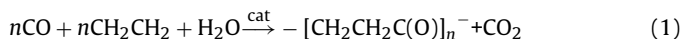
^1H and ^{13}C NMR analyses show that the monomers are perfectly alternating in the PK chains even when one monomer is used in large excess with respect to the other. Moreover, the chains end exclusively with keto groups [12]. In addition, during catalysis there is CO_2 evolution. This is consistent with the mechanism in which the catalysis is initiated by a $\text{Pd}-\text{H}^+$ species and is terminated by a protonolysis step with H_2O [13,15], which gives the PK and a $\text{Pd}-\text{OH}^+$ species, which regenerates the $\text{Pd}-\text{H}^+$ after insertion of CO and evolution of CO_2 . The mechanism of the catalytic copolymerization has been extensively studied [1,3]. Scheme 1 shows a simplified catalytic cycle.

Apart the CO_2 that is formed for the activation of the starting precursor to give the $\text{Pd}-\text{H}^+$ species, the overall copolymerization



Scheme 1. Catalytic cycle for the CO–E copolymerization.

reaction is:



It is well known that H₂O, CO and E are capable of interacting with Pd(II). This interaction may cause the displacement of a Cl[−] ligand, which may be favoured also by the solvation with H₂O and the high dielectric constant of the reaction medium. In this way the precursor becomes more available toward coordination. The initial Pd–H⁺ species may form through the interaction of H₂O and CO with the cationic centre, by a reaction closely related to the WGS [7,25]. The high pressure of the monomers and the high concentration of H₂O may favour also the dissociation of the other Pd–Cl bond, giving rise to a cationic coordinatively-unsaturated Pd–H⁺ species having easily available coordination sites similar to the one generated from a cationic precursor with weakly coordinating anions which is active in MeOH. This may explain why the [PdCl₂(dapp)], having strongly coordinating Cl[−] anions, inactive in MeOH, turns into a highly active catalyst when used in H₂O/CH₃COOH as a solvent [13,15,16].

3.1. Influence of the composition of the reaction medium

Fig. 1 shows the influence of the composition of the solvent carrying out the copolymerization for 4 h at 60 °C under 45 atm of total pressure (CO/E = 1/1).

The productivity increases upon increasing the concentration of H₂O up to a maximum of 7000 g PK(g Pd h)^{−1} at 55% (mol/mol). The beneficial effect of H₂O has been outlined above. In addition labile coordination of H₂O may stabilize the coordinatively unsaturated Pd(II) species, for example of the type [(dapp)Pd(OH)]⁺ which is formed in the protonolysis chain-transfer termination step (*cf.* Scheme 1), against their tendency to dimerize to achieve the usual four-coordination of Pd(II). In general dimeric species are less active [1,3]. On the other hand, upon increasing the H₂O concentration the solubility of the two monomers decreases [13] and hence the copolymerization rate (see later). Concerning the acid, not only the solubility of the monomers increases with increasing its concentration, but also a higher concentration of active Pd–H⁺ species may be accomplished because the acid may prevent the deprotonation of the hydride with formation of hydride-deficient formally-Pd(I)

species of the type [(dapp)(μ-H)(μ-CO)Pd(dapp)]²⁺ or [(dapp)(μ-CO)₂Pd(dapp)]²⁺, which ultimately may lead to the formation of inactive Pd(0) [1,3]. In addition, the acid may destabilize the β- and γ-chelate rings through protonation at the oxygen atoms of the rings which have been proposed to be resting states in the incorporation of the monomers into the growing chain [26].

Protonation at the oxygen atm of the β-chelate intermediate in the synthesis of diethyl ketone (DEK) by carbonylation of ethene catalyzed by a Pd(AcO)₂/dtbpe/TfOH system (dtbpe = 1,2-bis(di-β-butylphosphino)ethane, TfOH = trifluoromethansulfonic acid) has been proposed to explain the significant increasing of oligomers/copolymers formation upon increasing the TfOH/Pd ratio [10]. A promoting effect of an acid on the copolymerization process 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 AcOH 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

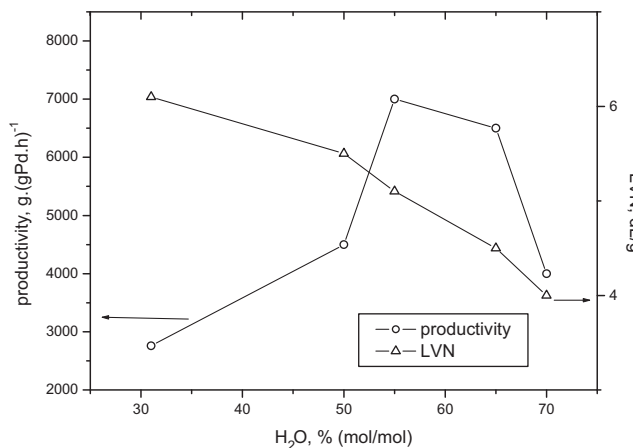


Fig. 1. Influence of H₂O on the productivity and on the LVN. Run conditions: [PdCl₂(dapp)]: 8.88 × 10^{−4} mmol; solvent: H₂O–CH₃COOH; V: 80 mL; 45 atm (CO/ethene = 1/1); 60 °C; 4 h; 700 rpm.

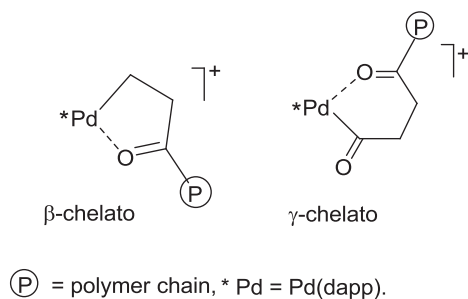


Fig. 2. β and γ chelate.

and to polyketones as the pressure and concentration of TsOH increase; the yield in polyketones also increases upon increasing the acidity [27,28].

In the present case, Fig. 1 shows that as far as the productivity is concerned the best compromise between the favourable and unfavourable influences of H_2O and AcOH seems to be achieved when they are in the ratios 55–70/45–30. The trend shown in Fig. 1 has been observed also in the CO–E copolymerization catalyzed by $[\text{PdCl}_2(\text{dppf})]$ in H_2O – CH_3COOH [16].

Differently, LVN increases regularly with lowering the H_2O concentration. This fact suggests that the chain-transfer termination step occurs *via* protonolysis mainly by H_2O even in the presence of relatively large amounts of CH_3COOH . Concurrently, the increasing of acid concentration increases the solubility of the monomers and eases the destabilization of the β - and γ -chelates, which favour also the formation of higher molecular weight polymers. Therefore, particularly high LVNs are achievable at the expenses of the productivity. It is interesting to point out that the trend of LVN shown in Fig. 1 is the opposite of that found using $[\text{PdCl}_2(\text{dppf})]$ in H_2O – CH_3COOH , in which case LVN increases (slightly) upon decreasing H_2O concentration [16] (see Fig. 2).

3.2. Influence of the temperature

The influence of the temperature on productivity and LVN has been studied under the conditions of Fig. 3. On increasing the temperature the productivity increases but the LVN decreases. This result suggests that the chain growing process presents an activation energy lower than the one of the chain-transfer termination step. This is not surprisingly because only after a relatively large number of monomer insertion steps only one termination step occurs.

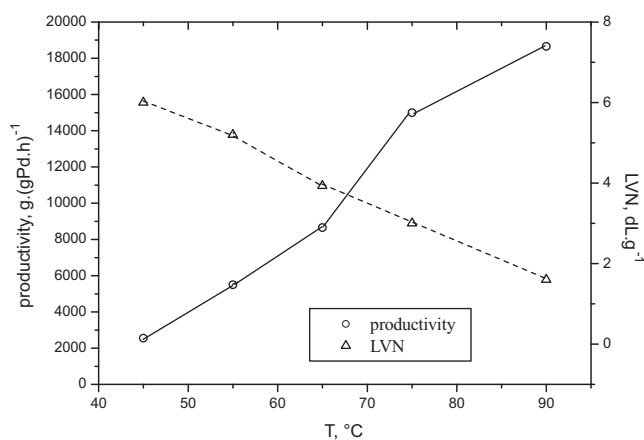


Fig. 3. Influence of temperature on the productivity and on the LVN. Run conditions: $[\text{PdCl}_2(\text{dapp})]$: 8.88×10^{-4} mmol; solvent: H_2O – CH_3COOH , H_2O : 55%; V: 80 mL; 45 atm (CO/ethene = 1/1); 1 h; 700 rpm.

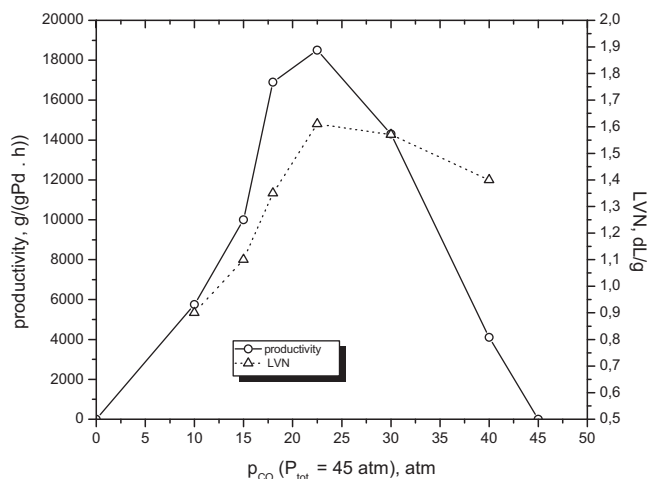


Fig. 4. Influence of CO partial pressure under constant CO–E total pressure on the productivity and on the LVN. Run conditions: $[\text{PdCl}_2(\text{dapp})]$: 8.88×10^{-4} mmol; solvent: H_2O – CH_3COOH , H_2O : 55%; V: 80 mL; 45 atm (CO + ethene); 90 °C; 1 h; 700 rpm.

3.3. Influence of the pressure of the monomers

The results shown in Fig. 5 refer to experiments carried out at a constant total pressure (45 atm) and different CO/E ratios. The highest productivity and LVN are obtained when the monomers are approximately in the ratio 1/1. A similar trend has been also observed using the cationic precursor $[\text{Pd}(\text{TsO})(\text{H}_2\text{O})(\text{dppp})](\text{TsO})$ in MeOH as a solvent [14].

Fig. 5 shows the influence of the pressure of E keeping the pressure of CO constant. The productivity increases on increasing the pressure of E up to 50 atm, then it decreases whereas LVN increases also above 50 atm. Similar trends have been observed on increasing the pressure of CO keeping constant that of the other monomer (Fig. 6). The fact that the productivity passes through a maximum on increasing the pressure of one monomer and keeping the pressure of the other monomer constant at a relatively low value, suggests that the two monomers compete for the coordination to the metal centre, so that at a relatively high pressure of one monomer the coordination of the other is disfavoured. This picture is in agreement with the trend of productivity shown in Fig. 7, where the productivity regularly increases upon increasing the pressure of both monomers used in the ratio 1/1. The same trend was observed using the precursor $[\text{Pd}(\text{TsO})(\text{H}_2\text{O})(\text{dppp})](\text{TsO})$ in

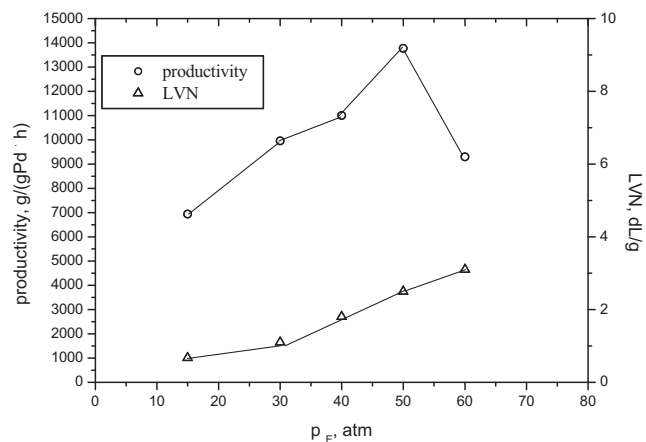


Fig. 5. Influence of E partial pressure on the productivity and on the LVN. Run conditions: $[\text{PdCl}_2(\text{dapp})]$: 8.88×10^{-4} mmol; solvent: CH_3COOH + H_2O , H_2O : 55%; V: 80 mL; p_{CO} : 15 atm, 90 °C, 1 h, 700 rpm.

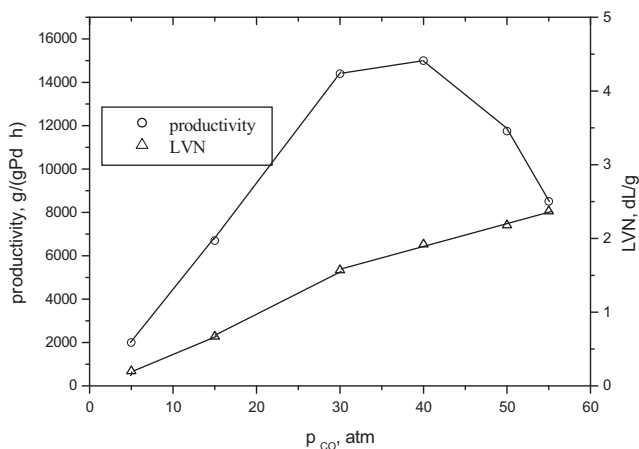


Fig. 6. Influence of CO partial pressure on the productivity and on the LVN. Run conditions: $[\text{PdCl}_2(\text{dapp})]$: 8.88×10^{-4} mmol; solvent: $\text{CH}_3\text{COOH} + \text{H}_2\text{O}$, H_2O : 55%; V : 80 mL; p_E : 15 atm, 90°C , 1 h, 700 rpm.

MeOH [14]. These results show that in order to reach both high productivity and LVN the monomers must be balanced.

Going back to Figs. 5 and 6, whereas the productivity decreases at a relatively high pressure of one monomer, LVN increases regularly. This fact suggests that, even though the reaction rate slows down the polymer chain growing process goes on, *i.e.* the termination chain transfer step is inhibited. This may be explained taking into account the mechanism of the termination step, which involves a pre-equilibrium of a β -chelate species with its enolate isomer by a β -H elimination/hydride migration and protonation to the more nucleophilic oxygen atom to give an enol [29,30], which rearranges to the ketone with concomitant formation of a $[\text{Pd}-\text{OH}]^+$ species (Scheme 2), which is converted to active $\text{Pd}-\text{H}^+$ via a partial water gas-shift reaction (*cfr.* Scheme 1). It was found that the enolate formation is much slower than protonolysis [29,30]. Since enolate formation requires the availability of another coordination it may be inhibited under a relatively high pressure of one monomer, so that the chain growing process can proceed further, even though at a lower rate because the two monomers are an unbalanced ratio (*cfr.* Fig. 4). Under the conditions of Fig. 7 both productivity and LVN increase regularly also at relatively high pressures because the two monomers are used in the ratio 1/1, so that the process of chain growing may go on without being accompanied by a declining of the reaction rate.

It is interesting to compare the trends of the productivity shown in Figs. 5 and 6 with those observed when using the cationic dapp-Pd(II)/TFAH catalytic system in MeOH. It was found that keeping constant the pressure of CO or that of E (25 atm in both cases) the productivity increases linearly upon increasing the pressure of E up to 25 atm, whereas in the other case the productivity passes through a maximum at $p_{\text{CO}} = \text{ca. } 15$ atm and declines at higher pressure. It was suggested that CO impedes coordination of E [31].

3.4. Influence of the temperature and of the total pressure with the monomers in the ratio 1/1

The previous experiments have shown that high LVN can be achieved under high total pressure and at low temperature, whereas in order to achieve a high productivity it is necessary to increase the temperature. Fig. 8 gives a picture of the influence of both temperature and pressure on productivity and LVN. At 90°C under 110 atm a productivity as high as $22,800 \text{ gPK}(\text{g Pd h})^{-1}$ is achieved with $\text{LVN} = 3.8 \text{ dL/g}$, whereas at 60°C a much higher LVN is achievable (11.2 dL/g), though at the expenses of the productiv-

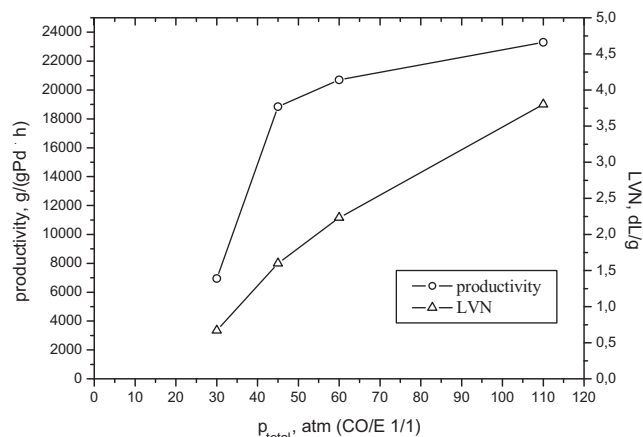


Fig. 7. Influence of total pressure ($\text{CO/E} = 1/1$) on the productivity and on the LVN. Run conditions: $[\text{PdCl}_2(\text{dapp})]$: 8.88×10^{-4} mmol; solvent: $\text{CH}_3\text{COOH} + \text{H}_2\text{O}$, H_2O : 55%; V : 80 mL; 90°C , 1 h, 700 rpm.

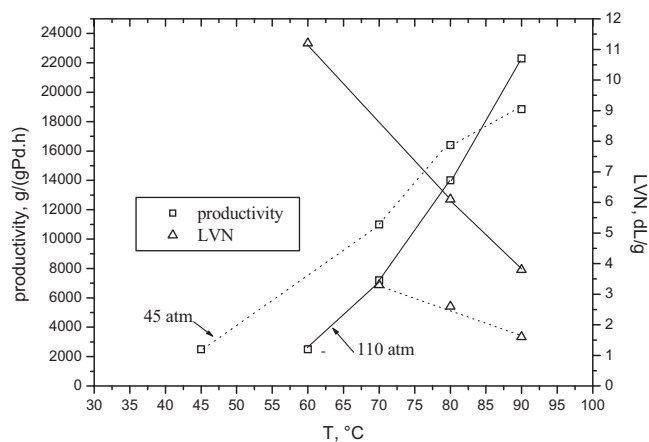


Fig. 8. Influence of temperature on the productivity and on the LVN. Run conditions: $[\text{PdCl}_2(\text{dapp})]$: 8.88×10^{-4} mmol; solvent: $\text{CH}_3\text{COOH} + \text{H}_2\text{O}$, H_2O : 55%; V : 80 mL; 45 atm (dotted line), 110 atm (solid line); $\text{CO/ethene} = 1/1$; 1 h; 700 rpm.

ity ($2500 \text{ gPK}(\text{g Pd h})^{-1}$). At *ca.* 75°C both productivity and LVN are relatively high (*ca.* $15,000 \text{ gPK}(\text{g Pd h})^{-1}$ and *ca.* 7 dL/g).

3.5. Influence of the composition of the solvent under high pressure

In general, the results above discussed are encouraging in order to achieve both high productivity and LVN. We have seen that the composition of the solvent has a strong influence on them. Therefore, we carried out some experiments under constant high pressure and at relatively low temperature (110 atm , 70°C), using a solvent of variable composition. Fig. 9 shows that LVN increases regularly with lowering the concentration of H_2O as found at lower pressure (*cfr.* Fig. 1), whereas the highest productivity is achieved at lower H_2O concentration ($40\text{--}50\%$ versus $55\text{--}65\%$). A reasonable explanation may be the following. In order to achieve high activity it is necessary that the Cl^- anion remains uncoordinated during the catalysis, which is favoured under high pressure of the monomers, which can be achieved at lower concentration of H_2O .

3.6. Influence of reaction time

Figs. 10 and 11 show that when the reaction is carried out for longer reaction times the productivity decreases, whereas LVN increases. The productivity depends on the rate of chain growing

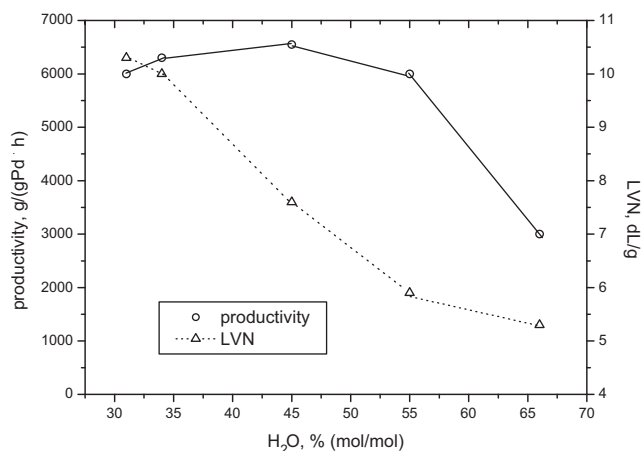


Fig. 9. Influence of H₂O on the productivity and on the LVN. Run conditions: [PdCl₂(dapp)]: 8.88×10^{-4} mmol; solvent: CH₃COOH+H₂O; V: 80 mL; 110 atm; CO/ethene = 1/1; 70 °C; 4 h; 700 rpm.

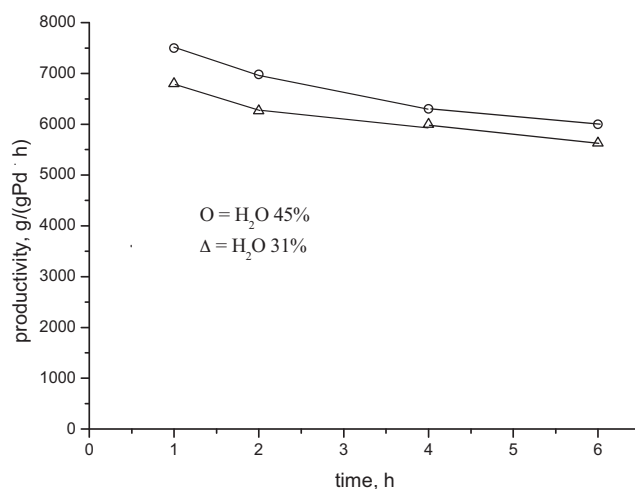
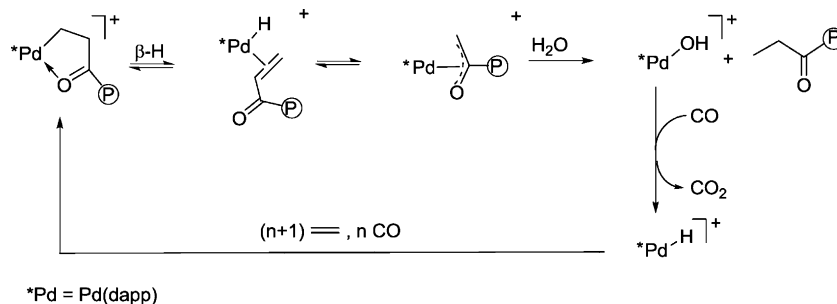


Fig. 10. Influence of reaction time on the productivity. Run conditions: [PdCl₂(dapp)]: 8.88×10^{-4} mmol; solvent: CH₃COOH+H₂O; V: 80 mL; 110 atm (CO/ethene 1/1); 70 °C; 1 h; 700 rpm.

and on their concentration, the latter is related to the concentration of the Pd–H⁺ species that starts the catalysis. LVN depends on the rate of chain growing relative to the rate of the chain termination process. The fact that the lowering of productivity occurs with concomitant increasing of LVN suggests that after the chain-transfer termination step the regeneration of active Pd–H⁺ species

becomes less efficient and/or that the copolymer inhibits the insertion of the monomers more than the protonolysis chain transfer process. The lowering of the productivity may be caused also by the difficulty of maintaining efficient the stirring of the PK/solvent slurry as the amount of PK, since this presents a relatively low apparent density and conglomerates a relatively large fraction of the



Scheme 2. Termination step for the CO–E copolymerization.

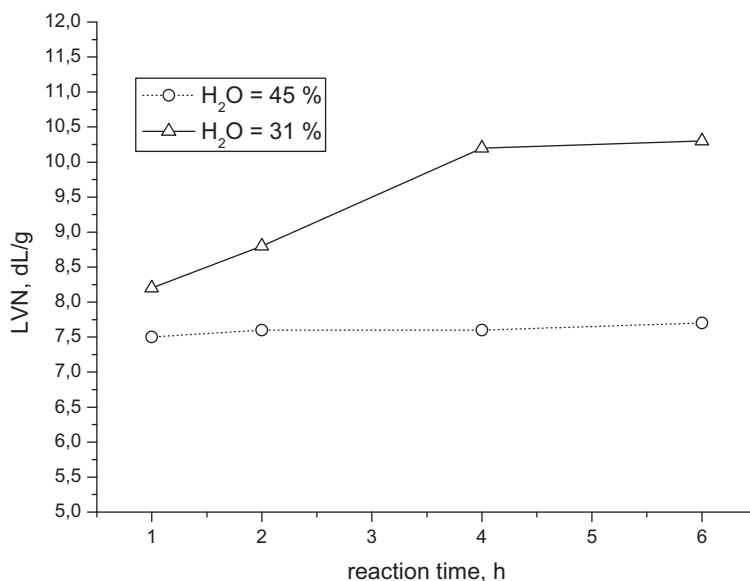


Fig. 11. Influence of reaction time on the LVN. Run conditions: [PdCl₂(dapp)]: 8.88×10^{-4} mmol; solvent: CH₃COOH+H₂O; V: 80 mL; 110 atm (CO/ethene 1/1); 70 °C; 1 h; 700 rpm.

Table 1

Influence of temperature. Run conditions: [PdCl₂(dapp)]: 8.88 × 10⁻⁴ mmol; solvent: CH₃COOH + H₂O, H₂O: 40%; V: 80 mL.

Total pressure (atm)	T (°C)	Reaction time (h)	Productivity (g/g Pd h)	LVN (dL/g)
110	60	4	4000	11.1
110	70	4	6100	10.3
110	80	2	10,500	8.5
110	90	2	20,300	4.5

solvent to the point that after 4 h of reaction most of the solvent appears to be absorbed into the copolymer.

In conclusion, high LVN can be achieved under high pressure at relatively low temperature and H₂O concentration, though at the expenses of the productivity. This may be improved upon increasing the temperature as shown in Table 1.

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References

- [1] E. Drent, P.H.M. Budzelaar, *Chem. Rev.* 96 (1996) 663.
- [2] A. Sommazzi, F. Garbassi, *Prog. Polym. Sci.* 22 (1997) 1547.
- [3] C. Bianchini, A. Meli, W. Oberhauser, *J. Chem. Soc. Dalton Trans.* (2003) 2627.
- [4] R.A.M. Robertson, D.J. Cole-Hamilton, *Coord. Chem. Rev.* 225 (2002) 67.
- [5] A. Sen (Ed.), *Catalytic Synthesis of Alkene-Carbon Monoxide Copolymers and Cooligomers*, Kluwer Academic Publishers, Dordrecht, 2003.
- [6] G. Cavinato, L. Toniolo, A. Vavasori, *Topics in organometallic chemistry*, in: M. Beller (Ed.), *Catalytic Carbonylation Reactions*, vol. 18, Springer, 2006, p. 125.
- [7] V.N. Zudin, G.N. Ill'inich, V.A. Likhobov, Yu.I. Yermakow, *J. Chem. Soc. Chem. Commun.* (1984) 545.
- [8] W.P. Mul, A.W. van der Made, A.A. Smaardijk, E. Drent, in: A. Sen (Ed.), *Catalytic Synthesis of Alkene-Carbon Monoxide Copolymers and Cooligomers*, Kluwer Academic Publishers, Dordrecht, 2003, p. 87 (Chapter 4).
- [9] P.W.N.M. van Leeuwen, M.A. Zuideveld, B.H.G. Swennenhuis, Z. Freixa, P.C.J. Kamer, K. Goubitz, J. Fraanje, M. Lutz, A.L. Spek, *J. Am. Chem. Soc.* 125 (2003) 5523.
- [10] R.I. Pugh, E. Drent, *Adv. Synth. Catal.* 344 (2002) 837.
- [11] W. Clegg, G.R. Eastham, M.R.J. Elsegood, R.P. Tooze, X.L. Wang, K. Whiston, *J. Chem. Soc. Chem. Commun.* (1999) 1877.
- [12] E. Drent, J.A.M. van Broekhoven, M.J. Doyle, *J. Organomet. Chem.* 417 (1991) 235.
- [13] A. Vavasori, L. Toniolo, G. Cavinato, F. Visentin, *J. Mol. Catal. A: Chem.* 204–205 (2003) 295.
- [14] A. Fabrello, A. Vavasori, F. Dall'Acqua, L. Toniolo, *J. Mol. Catal. A: Chem.* 276 (2007) 211.
- [15] A. Vavasori, L. Toniolo, G. Cavinato, *J. Mol. Catal. A: Chem.* 215 (2004) 63.
- [16] A. Vavasori, A. Bellieni, L. Ronchin, F. Dall'Acqua, L. Toniolo, G. Cavinato, *J. Mol. Catal. A: Chem.* 263 (2007) 9.
- [17] C. Bianchini, A. Meli, W. Oberhauser, P.W.N.M. van Leeuwen, M.A. Zuideveld, Z. Freixa, P.J. Kamer, A.L. Spek, O.V. Gusev, M. Kal'sin, *Organometallics* 22 (2003) 2409.
- [18] C. Bianchini, P. Brueggeller, C. Claver, G. Czermak, A. Dumfort, A. Meli, W. Oberhauser, E.J. Garcia Suarez, *J. Chem. Soc. Dalton Trans.* (2006) 1877.
- [19] C. Bianchini, A. Meli, W. Oberhauser, A.M. Segarra, C. Claver, E.J. Garcia Suarez, *J. Mol. Catal. A: Chem.* 265 (2007) 292.
- [20] R. Taniguchi, J. Kato, T. Komatsu, Patent US 7666975 B2 by Asahi Kasei Fibers Corp., Japan (2010).
- [21] <http://ep.espacenet.com/>.
- [22] J.R. Doyle, P.E. Slade, H.B. Joanassen, *Inorg. Synth.* 6 (1960) 216.
- [23] M.L. Huggins, *J. Am. Chem. Soc.* 64 (1942) 2716.
- [24] B.J. Lommerts, D.J. Sikkema, *Macromolecules* 33 (2000) 7950.
- [25] V.N. Zudin, V.D. Chinakov, V.M. Nekipelov, V.A. Rogov, V.A. Likhobov, Yu.I. Yermakow, *J. Mol. Catal.* 52 (1989) 27.
- [26] W.P. Mul, H. Oosterbeek, G.A. Beitel, G.J. Kramer, E. Drent, *Angew. Chem. Int. Ed.* 39 (2000) 1848.
- [27] E.G. Chepaikin, A.P. Bezruchenko, A.A. Leshcheva, G.N. Boiko, *Russ. Chem. Bull.* 43 (1994) 360.
- [28] E.G. Chepaikin, A.P. Bezruchenko, A.A. Leshcheva, *Kinet. Katal.* 40 (1999) 313.
- [29] M.A. Zuideveld, P.C.J. Kamer, P.W.N.M. van Leeuwen, P.A.A. Klusener, H.A. Stil, C.F. Roobeek, *J. Am. Chem. Soc.* 120 (1998) 7977.
- [30] P.W.N.M. van Leeuwen, in: A. Sen (Ed.), *Catalytic Synthesis of Alkene-Carbon Monoxide Copolymers and Cooligomers*, Kluwer Academic Publishers, Dordrecht, 2003, p. 141 (Chapter 6).
- [31] W.P. Mul, E. Drent, P.J. Jansens, A.H. Kramer, M.H.W. Sonnemans, *J. Am. Chem. Soc.* 123 (2001) 5350.