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Influence of the reaction conditions on the productivity and on the molecular weight of the polyketone obtained by the CO–ethene copolymerisation catalysed by [Pd(TsO)(H_2O)(dppp)](TsO) in MeOH

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Abstract

The influence of the operating conditions on the productivity on the CO–ethene copolymerisation catalysed by the title complex used in combination with TsOH and on the average numerical molecular weight, the limiting viscosity number and the average viscosity molecular weight of the resulting polyketone has been studied.

The productivity, LVN and $\bar{M}_v$ pass through a maximum for a TsOH/Pd ratio = 6/1, whereas $\bar{M}_n$ reaches a plateau and remains practically constant at higher acid concentration. They increase upon increasing the pressures of the monomers when employed in the ratio 1/1 as well as upon increasing the pressure of CO keeping constant the pressure of the other monomer; the productivity as well as $\bar{M}_n$ increase, whereas the LVN and $\bar{M}_v$ pass through a maximum upon increasing the pressure of ethene, keeping constant the pressure of CO. A power law rate equation for the productivity has been obtained.

The productivity decreases whereas the molecular weights increase upon lowering the temperature; the productivity decreases upon increasing the reaction time, whereas the molecular weights are little influenced.

The results are discussed in the light of the copolymerisation mechanism.
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Keywords: Palladium catalyst; Dppp; Carbon monoxide; Ethene; Copolymerisation; Polyketone; Molecular weight

1. Introduction

The discovery in the early 1980s that palladium–phosphine cationic complexes are efficient catalysts for the copolymerisation of carbon monoxide with ethene (E) or a higher α-olefin to yield perfectly alternating polyketones (PK), a new class of exploitable thermoplastics, has attracted since then continuous increasing interest [1–6].

More in general, the products of the carbonylation of an olefin in MeOH, the most used solvent, range from high molecular weight polyketones, to cooligomers down to monocarbonylated derivatives such as ketones and esters. Research efforts have been focused towards the deeper understanding of the key factors that rule the catalysis. The subject has been exhaustively reviewed up to very recently [7–21].

For the CO–E copolymerisation it was proposed that Pd(II)–diphosphine complexes of the type reported in the title are far superior 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 which occur through alternating reversible fast CO and irreversible ethene migratory insertions for thermodynamic and kinetic reasons [1,21–24]. The chain growing process occurs through the formation of five- and six-membered β- and γ-chelate intermediates [16,25,26] and it has been proposed that their formation

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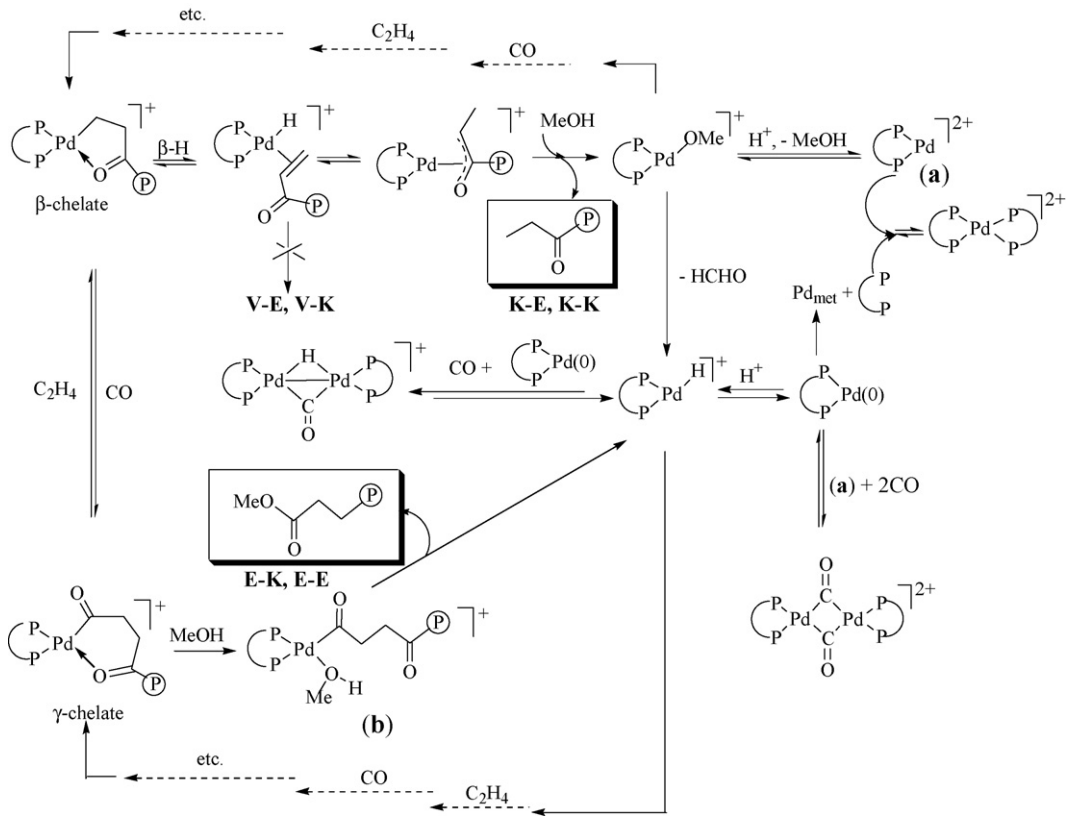

Scheme 1. Proposed CO–E copolymerisation mechanism, with some side reactions of $[PdH(P–P)]^+$.

contributes also to the perfect alternation [25]. Termination occurs *via* protonolysis or methanolysis, with reformation of the $Pd–OCH_3^+$ or $Pd–H^+$ species that start the catalysis (Scheme 1) [21,24].

In "cationic" complexes the charge of the metal center is balanced by a non-coordinating anion, so that they present "free" coordination sites easily available to the reacting molecules. The coordinating capacity depends not only on the nature of the anion, but also on that of the solvent. Thus the activity of the catalysts $[PdX_2(dppp)]$ ($X^- = TfO^-$, TsO^-, TFA^-, AcO^-, Cl^-) in MeOH is comparable when X^- is weakly coordinating like TfO^-, TsO^-, TFA^- (productivity *ca.* 7000–6000 g polymer/(gPd h) at 90 °C, 4.5 MPa, CO/E = 1/1), whereas when X = AcO or Cl the catalysts are ineffective [24]; the latest ones become very active when used in H_2O-AcOH (27000 g polymer/(gPd h), under the conditions just reported and 40–50% H_2O molar ratio) [27,28].

In general, the properties of a co-polymer depend not only on the nature of the monomers and on their relative concentration and distribution along the polymer chain, but also on the average molecular weight and on the distribution of the molecular weights. Copolymers in which the monomers are present in only one ratio and in a unique distribution along the polymer chain, as is the case of a perfectly alternating CO–E copolymer, can find different applications depending, in particular, on the average molecular weight.

With a catalytic system based on one given ligand and one given counter anion the molecular weight can be influenced by the operating conditions, i.e. concentration of activating agents, temperature, pressure, monomer ratio, solvent, and batch time. In spite of the importance of controlling the molecular weight through the operating conditions, to our knowledge a few studies have appeared up to now. A thesis work reported the catalytic activity of $[Pd(TFA)_2(dppp)]$/TFAH (TFAH = CF_3COOH) in MeOH. It was found that, under typical reaction conditions (85 °C, 7.0 MPa, CO/E 1/1), upon increasing the TFAH/Pd upto 25/1 the productivity increases to a plateau of *ca.* 10,000 g PK/(gPd h) and that the numeric average molecular weight of the PK obtained reaches a plateau ($\bar{M}_n$ *ca.* 11,000 g/mol) when the above ratio is >4. Moreover, it was found that upon increasing the partial pressure of the monomers in the range normally experienced (1.0–7.0 MPa), both productivity and viscosity increase. It was proposed a power rate equation in which the reaction order for the activity of CO and of E is 0.83 and 0.48, respectively [29].

Using a catalyst system formed *in situ* from $Pd(AcO)_2$, dppp and TFAH in ratio 1/1/2, a kinetic model has been developed for the initial rate of copolymerisation, the consumption of the two monomers and the molecular weight characteristics of the resulting copolymer as a function of the total pressure up to 4.0 MPa, CO/E = 1/1, at 90 °C in MeOH [30].

The CO–E copolymerisation kinetics was also studied by using the precursor $[Pd(TsO)(H_2O)(dppp)](TsO)$ in MeOH under the usual conditions. For the initial rate the reaction orders were found to be 0.63 and 0.72 for the CO and E activity and for

the pressure 0.55 and 0.67, respectively. No data on the viscosity or molecular weight were reported [31,32].

In an attempt to find how productivity and molecular weight are correlated, here we present the influence of the operating conditions on productivity of the precursor [Pd(TsO)(H_2O)(dppp)](TsO) in combination with TsOH, in MeOH as a solvent, and on the molecular weight and viscosity of the PK obtained.

2. Experimental

2.1. Reagents

Methanol was purchased from Baker; 1,3-bis(diphenylphosphino)propane (dppp), 1,1,1,3,3,3-hexafluoroisopropanol (99%) and $CDCl_3$ were Aldrich products. The complex [Pd(TsO)(H_2O)(dppp)](TsO) was prepared as reported in Ref. [33]. Carbon monoxide and ethene were supplied by SIAD Company ('research grade', purity >99.9%).

2.2. Equipment

The catalyst precursor was weighted on a Sartorious Microbalance (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: N_2, 0.2 ml/min; oven: 50 °C (2 min) to 200 °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 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, 2.00 mg of [Pd(TsO)(H_2O)(dppp)](TsO) (2.54×10^{-3} mmol) and TsOH (TsOH/Pd = 6/1) were dissolved in 80 ml of MeOH (500 ppm H_2O) contained in the bottle placed in the autoclave. The autoclave was washed by pressurising with a 1/1 mixture of CO/C_2H_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 363 K in *ca.* 10 min without stirring. The pressure was then adjusted to the desired value (typically 4.5 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 carefully depressurised. The slurry product was filtered, washed with MeOH and dried under vacuum at 343 K.

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

2.4. Number-average molecular weight ($\bar{M}_n$) determination, limiting viscosity number (LVN) measurements and viscosity-average molecular weight ($\bar{M}_v$) calculation

The number-average molecular weight has been calculated from the ratio of intensity of the signal of the chain protons to the methyl protons of the keto-end group.

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 [34]. 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 viscosity-average molecular weight (hereafter named molecular weight) of the polyketone was derived from the LVN using the Mark-Houwink equation [35]:

$$[\eta]_{\text{m-cresol},25^\circ\text{C}} = 1.01 \times 10^{-4} \bar{M}_v^{0.85} \quad (1)$$

3. Results and discussion

The CO–E copolymerisation has been carried out under conditions slightly different from those previously reported. The pre-formed catalyst precursor [Pd(TsO)(H_2O)(dppp)](TsO) has been used instead of forming it *in situ* from Pd(AcO)$_2$ and dppp in the presence of two equivalents of TsOH [24,36]. This is because the pre-formed precursor guarantees better that the components the catalytic system are in the required 1/1/2 stoichiometric ratio, which cannot be assured when formed *in situ* due to the relatively small amounts of components that have to be weighted. Moreover, at difference from what reported in the kinetics studies [31,32], in most of experiments the precursor has been used together with six equivalents of TsOH because preliminary experiments showed that in this case the catalytic activity passes through a maximum and the results are more reproducible. In addition, all experiments have been carried out using MeOH having 500 ppm of H_2O because in a previous study it has been shown that the optimal H_2O concentration is in the range of 500–1000 ppm when the total pressure is in the range of 4.5–6.0 MPa (CO/E = 1/1) at 363 K [36], which are the conditions close to the ones experienced in the present study.

3.1. Influence of the TsOH/Pd ratio

Under the conditions reported in Fig. 1, productivity, $\bar{M}_n$, $\bar{M}_v$ and LVN increase upon increasing the TsOH/Pd ratio upto 6/1 (see also Fig. 2).

The productivity depends on the rate of chain growing and on their number, the latter related to concentration of the species

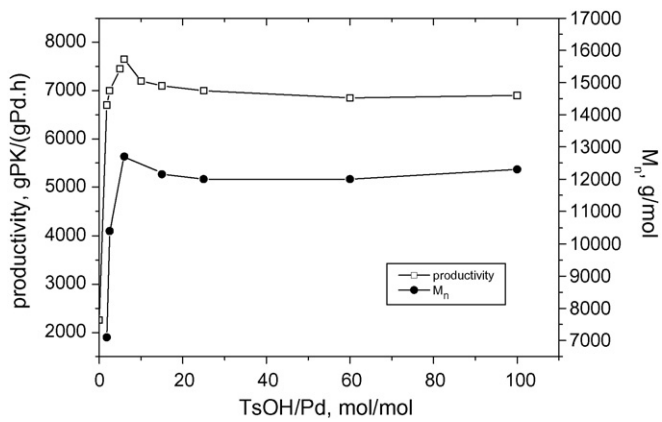

Fig. 1. Effect of the TsOH/Pd ratio on productivity and $\bar{M}_n$. Run conditions: [Pd(TsO)(H_2O)(dppp)](TsO) 2.0 mg (2.54×10^{-3} mmol); MeOH 80 ml (H_2O 500 ppm); P 4.5 MPa (CO/E 1/1); T 363 K; reaction time 1 h; stirrer speed 700 rpm.

that start the catalysis. The promoting effect of the acid at relatively low ratios may be due to its capacity to stabilise the Pd–H^+ species that initiates the catalysis, preventing deprotonation and decomposition that ultimately ends in the formation of inactive palladium metal and of free ligand that inhibits the activity of the complexes still undecomposed [36]. In addition the acid may activate/destabilise the γ- or β-chelate intermediates through which catalysis occurs (Scheme 1), thus favouring the process of the insertion of the monomers and hence of chain growing. The decreasing of productivity at higher acid concentration suggests that the TsO^- anion competes with the monomers for the coordination.

Also the initial increasing of $\bar{M}_n$, $\bar{M}_v$ and LVN may also be due to acid activation/destabilisation of the γ- or β-chelate intermediates. That the acid may destabilise the oxo-chelates *via* proton interaction with the donating oxygen has been suggested also to explain the significant change of selectivity in the carbonylation of E to diethyl ketone catalysed by the system $Pd(AcO)_2$/dtbpe/TfOH (dtbpe = 1,2-bis(di-*t*-butylphosphino)ethane) in MeOH, as a significant amount of oligomers/copolymers forms when the acid is used in excess (TfOH/Pd = 10/1) [37].

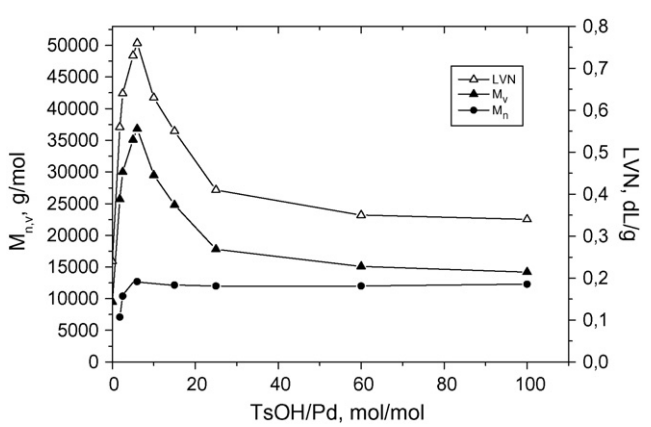

Fig. 2. Effect of the TsOH/Pd ratio on $\bar{M}_n$, $\bar{M}_v$ and LVN. Run conditions: see Fig. 1.

Beyond the TsOH/Pd ratio 6/1, $\bar{M}_n$ remains practically constant, as found for the $Pd(AcO)_2$/dppp/TFAH system [29]. Chain transfer occurs *via* protonolysis and methanolysis [24]. Chain transfer *via* β-hydride elimination can be excluded because vinyl-ester and vinyl-ketone end groups were not detected by $^{13}C\{^1H\}$ and ^1H NMR analysis.

The acid may favor protonolysis if a direct splitting of a Pd-alkyl occurs. Instead, it has been found that protonolysis involves a pre-equilibrium of the β-chelate with its enolate isomer by a β-H elimination/hydride migration and protonation to the more nucleophilic oxygen atom to give an enol, which rearranges to the ketone [38–40]. Therefore, a lowering of the molecular weight of the copolymer should be expected upon increasing the acid concentration. However, for the catalytic system $[Pd(TFA)_2(dppp)]$/TFAH it was also found that $\bar{M}_n$ is not effected upon increasing the acid/Pd ratio in the range of 4–100 [38]. It was concluded that the above protonation is not the slow step of the protonolysis process [40]. This is confirmed also by our results as $\bar{M}_n$ is little effected beyond the TsOH/Pd = 6/1.

Studies on the methanolysis of model complexes of the type $[Pd(COMe)(P–P)]^+$ in which the diphosphine ligand is *trans* or *cis* coordinated led to the conclusion that methanolysis requires a vacant coordination site to coordinate MeOH *cis* to the acyl ligand [41,42]. In addition it has been found that excess acid influences the methanolysis of $[Pd(COCH_3)(CO)(dppp)](CF_3SO_3)$ as the highest reaction rate is observed in the presence of nine equivalents of triflic acid. It has been suggested that the acid might activate the acetyl group, thus enhancing the electrophilicity of the carbonyl atom. That the reaction becomes slower when a larger excess of acid is used it might be that the anion of the acid competes with MeOH for the coordination [42].

In the present case the acid may promote the process of propagation, as already mentioned, as well as the termination step by methanolysis, by activation of the acetyl group of intermediate (**b**) (Scheme 1). Fig. 1 shows that, at relatively low TsOH/Pd ratios, the acid efficiently promotes the polymerization degree, whereas at higher concentrations $\bar{M}_n$ is little influenced.

In contrast, $\bar{M}_v$ significantly lowers *ca.* 40% upon increasing the TsOH/Pd ratio from 6/1 to 100/1 (Fig. 2), indicating the occurrence of a less random more efficient chain transfer mechanism.

The following considerations may explain the influence of the acid on $\bar{M}_v$. In general when termination occurs though more than one mechanism a higher polydispersity is observed [43]. Methanolysis leads to the formation of an ester end group and of a Pd–H species, which starts the next catalytic cycle ("hydride cycle") and will lead to the formation of a keto group at the other end of the PK chain. Protonolysis yields a keto end group and a Pd–OCH_3 species, which starts another catalytic cycle ("methoxy cycle"), which will lead to an ester end group. When the two cycles cross there is formation of chains having the same end groups, ester–ester and keto–keto. For a matter of electronic balance the ester/keto end groups ratio results 1/1 (as found by NMR analysis of all the samples of PK obtained under all the conditions experienced in the present study).

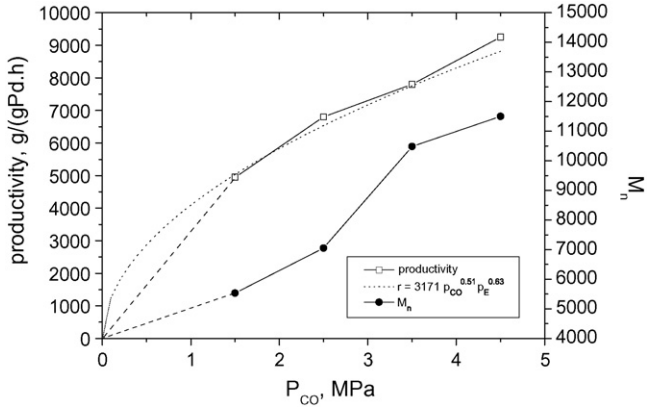

Fig. 3. Effect of the CO partial pressure on productivity and $\bar{M}_n$ at E constant pressure. Run conditions: [Pd(TsO)(H_2O)(dppp)](TsO) 2.00 mg (2.54×10^{-3} mmol); TsOH/Pd 6/1 (mol/mol); MeOH 80 ml (H_2O 500 ppm); E partial pressure 1.5 MPa; T 363 K; reaction time 1 h; stirrer speed 700 rpm.

Going back to the effect of the acid on $\bar{M}_v$, we can only speculate as to why this decreases upon increasing the acid concentration. We suggest that upon increasing the acid concentration, the "hydride cycle" prevails on the other one starting from a Pd–OCH_3 species, because this is less stable at high concentration of acid. Therefore, upon increasing the acid concentration catalysis shifts toward one single mechanism and consequently termination too. This would explain the lowering of $\bar{M}_v$ upon increasing the acid concentration.

3.2. Influence of the pressure of one monomer at constant pressure of the other monomer

The influence of the pressure of CO and of E has been studied using TsOH and the catalyst precursor in the ratio 6/1, which assure satisfactory reproducibility and higher productivity. The productivity increases with increasing the pressure of one monomer (Figs. 3 and 4), similarly to what found when the precursor is used in absence of acid [31,32].

Eqs. (2) and (3) fit satisfactorily well the data of productivity as a function of the pressure of one monomer, keeping constant

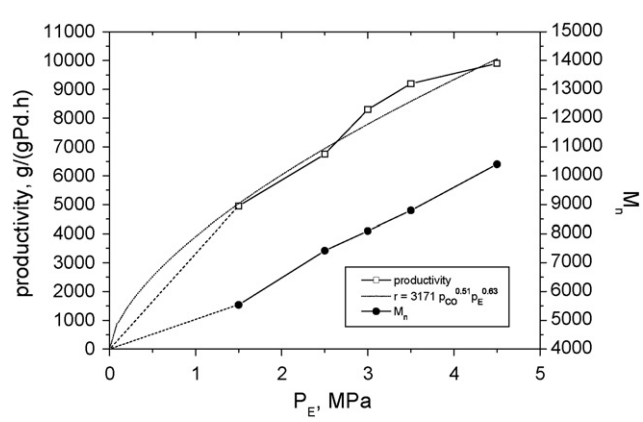

Fig. 4. Effect of the E partial pressure on productivity and $\bar{M}_n$ at CO constant pressure. Run conditions: [Pd(TsO)(H_2O)(dppp)](TsO) 2.00 mg (2.54×10^{-3} mmol); TsOH/Pd 6/1 (mol/mol); MeOH 80 ml (H_2O 500 ppm); CO partial pressure 1.5 MPa; T 363 K; reaction time 1 h; stirrer speed 700 rpm.

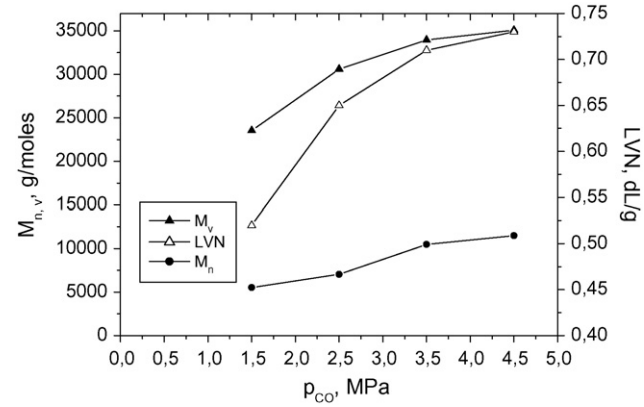

Fig. 5. Effect of the CO partial pressure on $\bar{M}_n$, $\bar{M}_v$ and LVN at E constant pressure. Run conditions: see Fig. 3.

the pressure of the other monomer.

$$\text{productivity} = k_{co} p_{co}^{\alpha} \quad (2)$$

$$\text{productivity} = k_E p_E^{\beta} \quad (3)$$

where $k_{co} = 4016$ gPK (gPd h $MPa^{0.51}$)$^{-1}$, $\alpha = 0.51$, $k_E = 3780$ gPK (gPd h $MPa^{0.63}$)$^{-1}$ and $\beta = 0.63$

By combining Eqs. (2) and (3) a power rate low in both CO and E can be derived:

$$\text{productivity} = k p_{co}^{\alpha}\, p_E^{\beta} \quad (4)$$

Considering that Eq. (2) has been obtained for a pressure of ethene of 1.5 MPa and that Eq. (3) has been obtained for a pressure of CO of 1.5 MPa, one obtains for Eq. (4): $k = 3241$ gPK (gPd h $MPa^{1.14}$)$^{-1}$ from Eq. (2) and $k = 3101$ gPK (gPd h $MPa^{1.14}$)$^{-1}$ from Eq. (3), in good agreement 3171 gPK (gPd h $MPa^{1.14}$)$^{-1}$ is the average value used to fit the data in Fig. 5.

Both $\bar{M}_n$ and $\bar{M}_v$ increase with increasing the pressure of CO, however, the increment of $\bar{M}_v$ becomes smaller at higher pressure, i.e. as the ratio CO/E becomes significantly >1 (Fig. 5). Again, this may be associated with the possibility that upon increasing the pressure of CO one termination mechanism (the one involving a γ-chelate, since this forms after the insertion of CO) becomes more important.

Upon increasing the pressure of E, $\bar{M}_n$ regularly increases (Fig. 4), whereas the viscosity and $\bar{M}_v$ pass through a maximum (Fig. 6). Moreover, it can be observed that at higher pressure of ethene the difference between $\bar{M}_v$ and $\bar{M}_n$ is smaller. These observations suggest that the polydispersity becomes smaller at high pressure of the olefin.

Once more, an explanation on the origin of decreasing the polydispersity might be found considering the chain-transfer termination steps. Under high pressure of ethene, it is reasonable to suppose that the β-chelates intermediates, which form after the insertion of ethene, may be present in a relatively higher concentration than when the copolymerisation is carried out under low pressure of the olefin. The lowering of LVN and $\bar{M}_v$ observed at higher pressure of E might be related to a shift towards one prevailing termination mechanism.

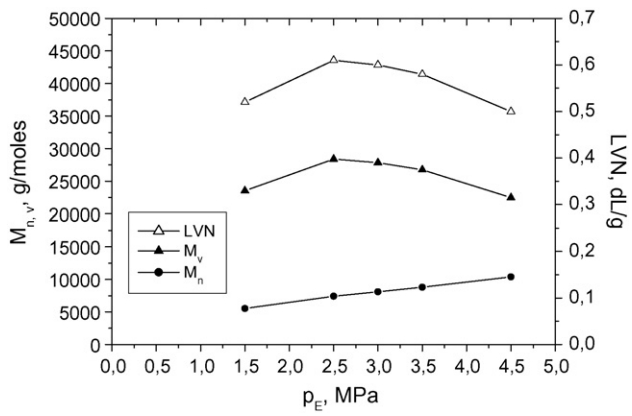

Fig. 6. Effect of the E partial pressure on $\bar{M}_n$, $\bar{M}_v$ and LVN at CO constant pressure. Run conditions: see Fig. 5.

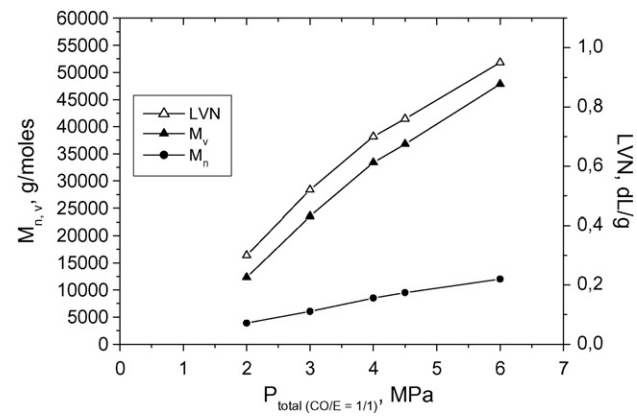

Fig. 8. Effect of total pressure on $\bar{M}_n$, $\bar{M}_v$ and LVN at constant CO/E ratio. Run conditions: see Fig. 7.

3.3. Influence of the total pressure using the monomers in the ratio 1/1

By using the monomers in the ratio 1/1 the productivity increases roughly linearly with increasing the total pressure (Fig. 7) in agreement with the results just presented and with Eq. (4). As expected, $\bar{M}_n$ increases regularly. Not only, also the viscosity and $\bar{M}_v$ increase almost linearly upon increasing the pressure of both monomers (Fig. 8), suggesting that when the monomers are used in a balanced ratio, termination does not occur predominantly *via* only one mechanism.

These results, together with those reported in Figs. 3–6, suggest that the monomers compete for coordination on the metal centre on both the process relevant to the incorporation of the monomers into the growing chain and the process of chain-transfer.

3.4. Influence of the pressure of the monomers at constant total pressure

Fig. 9 shows how the productivity varies upon varying the CO/E ratio, keeping constant the total pressure, 6.0 MPa. The highest productivity is achieved when the monomers are used in the ratio close to 1/1.

From the data of Figs. 3 and 4 it has been shown that the copolymerisation rate can be expressed by Eq. (4), plotted in Fig. 5, in good agreement with the experimental data.

The viscosity, too, passes through a maximum when the monomers are balanced, in agreement with the previous observations.

3.5. Influence of the temperature

Since a PK of high molecular weight is obtained, the rate of the propagation process is higher than the rate of the termination one and the activation energy of the first process is lower than the activation energy of the other. Therefore upon lowering the temperature a PK of higher molecular weight, and hence of higher viscosity, is expected, though at the expense of the productivity. Table 1 reports the results obtained at three different temperatures, which are in agreement what foreseen.

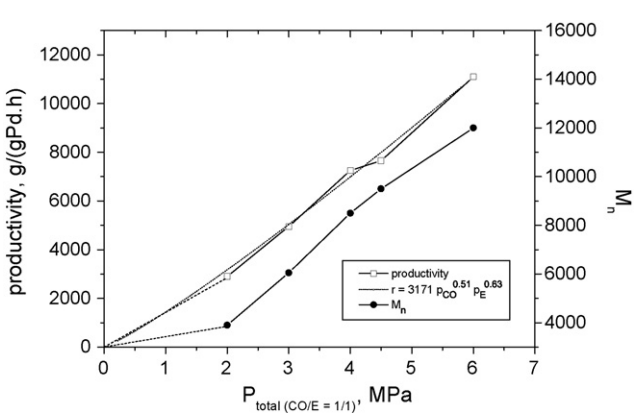

Fig. 7. Effect of total pressure on productivity and $\bar{M}_n$ at constant CO/E ratio. Run conditions: [Pd(TsO)(H_2O)(dppp)](TsO) 2.00 mg (2.54×10^{-3} mmol); TsOH/Pd 6/1 (mol/mol); MeOH 80 ml (H_2O 500 ppm); CO/E 1/1; T 363 K; reaction time 1 h; stirrer speed 700 rpm.

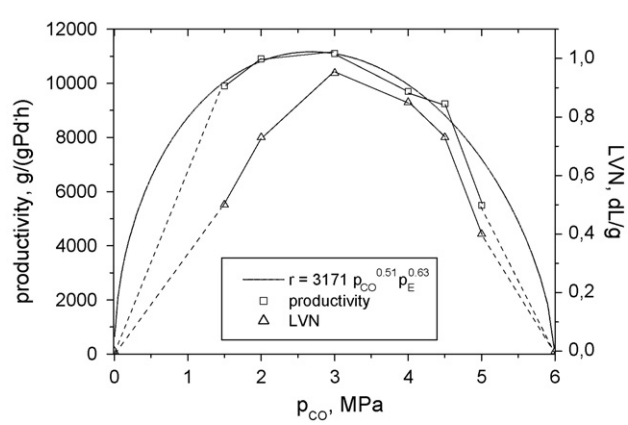

Fig. 9. Effect on productivity and LVN of the CO/E ratio at constant total pressure. Run conditions: [Pd(TsO)(H_2O)(dppp)](TsO) 2.0 mg (2.54×10^{-3} mmol); TsOH/Pd 6/1 (mol/mol); MeOH 80 ml (H_2O 500 ppm); total pressure 6.0 MPa; T 363 K; reaction time 1 h; stirrer 700 rpm.

Table 1
Effect of temperature on productivity, LVN and $\bar{M}_v$

T (K)	Productivity gPK/(gPd h)	LVN (dL/g)	$\bar{M}_v$ (g/mol)
343	2500	1.00	50,800
353	4200	0.88	43,700
363	7650	0.76	36,800

Run conditions: [Pd(TsO)(H_2O)(dppp)](TsO) 2.0 mg (2.54×10^{-3} mmol); MeOH 80 ml; H_2O 500 ppm, TsOH/Pd 6/1 (mol/mol); P 45 MPa (CO/E 1/1); reaction time 1 h; stirrer speed 700 rpm.

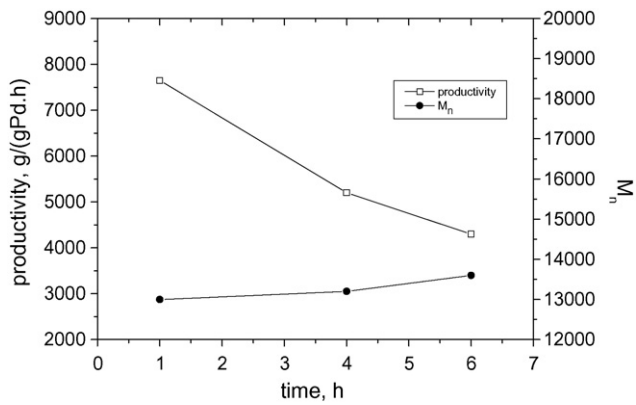

Fig. 10. Effect of the reaction time on productivity and $\bar{M}_n$. Run conditions: [Pd(TsO)(H_2O)(dppp)](TsO) 2.0 mg (2.54×10^{-3} mmol); TsOH/Pd 6/1 (mol/mol); MeOH 80 ml (H_2O 500 ppm); P 4.5 MPa (CO/E 1/1); T 363 K; stirrer speed 700 rpm.

3.6. Influence of the batch time

After 6 h run the productivity lowers of *ca.* 45% of that achieved after 1 h, whereas $\bar{M}_n$, $\bar{M}_v$ and LVN are little affected (Figs. 10 and 11), thus indicating the number of growing chains and/or the rate of chain growing lower too, whereas the chain length and polydispersity are little affected. The lowering of productivity suggests that the chain transfer process is not so efficient in reproducing the active species that restart the catalytic cycle and/or that the copolymer inhibits to some extent the catalysis.

By studying model reactions of protonolysis or methanolysis of Pd-alkyl or Pd-acyl bonds, it has been found that these reactions occur with formation of less active of the type $[(P–P)Pd(\mu\text{-}H)(\mu\text{-}H)Pd(P–P)]^{2+}$, $[(P–P)Pd(\mu\text{-}H)(\mu\text{-}CO)Pd(P–P)]^{+}$, $[(P–P)Pd(\mu\text{-}CO)_2Pd(P–P)]^{2+}$, or $[Pd(P–P)]_2{}^{2+}$ and of bis-chelate $[Pd(P–P)_2]^{2+}$ [14,37]. The dimers show a lower activity, though it can be restored when used in the presence of excess acid or of an organic oxidant, such as benzoquinone [44–46].

Also bis-chelates show a lower activity [45]. In the present case their formation is unlikely, because they form when partial decomposition to palladium metal occurs, which is accompanied by formation of the free ligand, which gives the bis-chelate with the remaining undecomposed species. In fact, even after 6 h of reaction the polymer is recovered as a white-snow powder, suggesting that no decomposition to black palladium occurs.

Using the catalytic system $Pd(AcO)_2$/dapp/TFAH (dapp = 1,3-bis(dianysilphosphino)propane) in the ratios 1/1.05/3, the lowering of productivity observed with run time was not ascribed to the formation of dimeric or bis-chelate species analogous to the ones just reported. It was found that the polymer presents a bimodal molecular weight distribution and that the average molecular weight increases with run time. In addition, it was observed that the copolymer particle size and agglomeration increase during the copolymerisation run and that the fractions of larger size had a higher molecular weight. It was suggested that the catalyst works in part absorbed on the surface, producing a PK of lower molecular weight, and in part trapped inside the pores of the particle, producing a higher PK [47].

The particles and agglomerates obtained with the $Pd(AcO)_2$/dapp/TFAH catalytic system after 16 h reaction were much larger than in the present case (40–400 μm versus 10–30 μm). Thus it is likely that this is the reason why the molecular weight is not significantly affected by the batch time.

The lowering of productivity may be caused also by the possibility that as the amount of copolymer increases the stirring of the slurry becomes less efficient. The apparent density of the copolymer is rather low, the copolymer conglobates significant amounts of MeOH, to the point that after some hours of reaction most of the solvent is absorbed into the spongy copolymer.

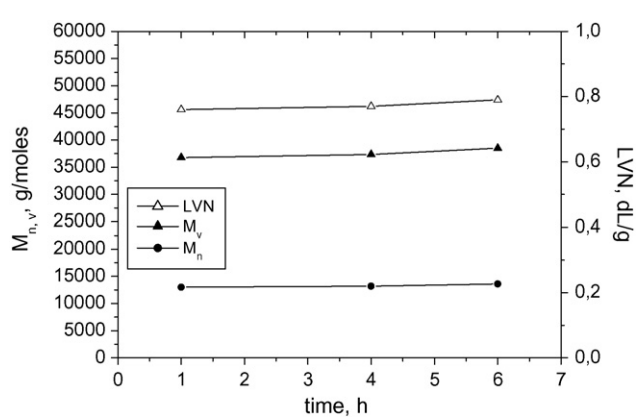

Fig. 11. Effect of the reaction time on $\bar{M}_n$, $\bar{M}_v$ and LVN. Run conditions: see Fig. 10.

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