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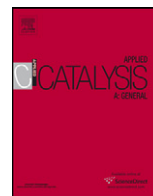
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Influence of formic acid and water on the [Pd(OAc)₂(dppp)] catalyzed ethene–carbon monoxide copolymerization carried out in aprotic organic solvents

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ABSTRACT

The copolymerization of ethene with carbon monoxide catalyzed by [Pd(OAc)₂(dppp)] in an aprotic solvent such as 1,4-dioxane or nitromethane is efficiently promoted both by H₂O and HCOOH and yields a perfectly alternating polyketone (PK). The influence of the concentration of the promoters, pressure and temperature on the catalyst productivity and the limiting viscosity number (LVN) has been studied. The productivity increases with the increase of temperature and pressure. The LVN increases upon increasing the pressure and lowering the temperature. At 363 K and 9.0 MPa, in HCOOH/H₂O/1–4,dioxane (2.7/1.35/1 molar ratio), the productivity is 37.50 kgPK (gPd h)^{−1} (LVN 2.77 dL g^{−1}).

LVN lowers upon increasing the concentration of the acid, suggesting that it is involved in the protonolysis chain-transfer process.

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1. Introduction

The Pd(II)-(chelating-diphosphine) catalyzed copolymerization of ethene with CO to a perfectly alternated copolymer, named polyketone (PK), has been widely studied in the last 30 years [1–11]. The catalytic activity is mostly influenced by the nature of the chelating ligand and the counter anion, although it depends also on the nature of the solvent [1–10]. The copolymerization is carried out preferably in methanol, although in some interesting papers water has been proposed as an alternative solvent [12–17]. We found that the precursors [PdX₂(P–P)] (X = AcO, Cl), inactive in MeOH, turn into highly active catalysts when used in H₂O–AcOH or H₂O–HCOOH [18–25].

Other solvents have also been utilized, such as dichloromethane, THF, toluene, acetonitrile, 1,4-dioxane or acetone, however the productivity is, in each case, was very low [26–28].

Hereafter, we report the results on the [Pd(OAc)₂(dppp)] (dppp = 1,3-bis(diphenylphosphino)propane) catalyzed CO–ethene copolymerization in aprotic solvents (1,4-dioxane and nitromethane) promoted by HCOOH and H₂O.

2. Experimental

2.1. Reagents

1,4-Dioxane, nitromethane (99%), 1,3-bis(diphenylphosphino)propane (dppp), CDCl₃ and 1,1,1,3,3,3-hexafluoroisopropanol (99%) were Aldrich products; formic acid > 99%, (Acros Organics).

The complex [Pd(OAc)₂(dppp)] was prepared as reported in literature [29].

Carbon monoxide and ethene were supplied by SIAD Company ('research grade', purity > 99.9%).

2.2. Equipment

Gas-chromatographic analysis 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; oven: 323 K (2 min) to 473 K at 15 K/min).

FTIR spectra were recorded on a Nicolet Magna 750 instrument in KBr powder.

All the NMR spectra were recorded on a Bruker Avance 300 spectrometer. The ¹H NMR and ¹³C NMR spectra of the polyketone dissolved in 1,1,1,3,3,3-hexafluoroisopropanol/CDCl₃ (10/1) were recorded using the Inverse ¹H-Gated Decoupling Technique.

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Table 1
Selected ^1H NMR and ^{13}C NMR signals of PK.

	^1H NMR (ppm)		^{13}C NMR (ppm)
$-\text{C}(\text{O})\text{CH}_2\text{CH}_2-$	2.77	$-\text{C}(\text{O})\text{CH}_2\text{CH}_2-$	35.73
$-\text{C}(\text{O})\text{CH}_2\text{CH}_3$	1.08	$-\text{C}(\text{O})\text{CH}_2\text{CH}_2-$	212.65
$-\text{C}(\text{O})\text{CH}_2\text{CH}_3$	2.52	$-\text{C}(\text{O})\text{CH}_2\text{CH}_3$	6.91
		$-\text{C}(\text{O})\text{CH}_2\text{CH}_3$	217.04

2.3. Copolymerization

The copolymerizations were carried out as previously described [24,25].

In a typical experiment, 1000 mg of $[\text{Pd}(\text{OAc})_2(\text{dppp})]$ (1.57×10^{-3} mmol) was added to 80 mL of solvent contained in the bottle placed in the autoclave. The autoclave was flushed with a 1/1 mixture of $\text{CO}/\text{C}_2\text{H}_4$ at room temperature with stirring. The autoclave was then pressurized 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 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 depressurized. The polymer was completely precipitated by addition of 100 mL of H_2O and the slurry obtained was filtered, washed with water and acetone and dried under vacuum at 343 K.

The dried polymer was weighed and the productivity was calculated as $\text{kgPK}(\text{gPd h})^{-1}$; the reproducibility was within *ca.* 5%. Low molecular weight products eventually formed were detected through GC analysis of the liquid phase.

The IR spectra show typical stretching signals of CO groups at 1695 cm^{-1} and $-\text{CH}_2-$ groups at 2915 cm^{-1} .

The ^{13}C NMR spectra, shows a single carbonyl absorption at 212.65 ppm ($-\text{C}(\text{O})\text{CH}_2\text{CH}_2-$) and a single resonance for the $-\text{CH}_2-$ groups at 35.73 ppm ($-\text{C}(\text{O})\text{CH}_2\text{CH}_2-$) in the ratio 1:2 due to the exclusive perfectly alternated structure [1]. The most relevant signals are reported in Table 1.

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

The average viscosity molecular weight of polymer has been evaluated as Limit Viscosity Number (LVN) measurements. The LVN of a dilute PK solution was determined by using the Huggins relationship between the viscosity number and the polymer concentration by extrapolation to zero concentration [30]. The PK solution was prepared in *m*-cresol as a solvent and the viscosity was measured by using a Cannon–Fenske type capillary viscosimeter, thermostated at 298 K.

The average viscosity molecular weight (M_w) of the polyketone was derived from the LVN using the Mark–Houwink equation [31].

$$[\eta]_{m\text{-cresol}, 298\text{ K}} = 1.01 \times 10^{-4} \bar{M}_w^{0.85}$$

3. Results and discussion

3.1. Promoting effect of HCOOH

The promoting effect of HCOOH has been studied in two aproctic organic solvents having significant different polarity, such as 1,4-dioxane ($\epsilon = 2.3$) and nitromethane ($\epsilon = 39.4$). In both solvents the catalytic activity passes through a maximum when HCOOH increases (Fig. 1).

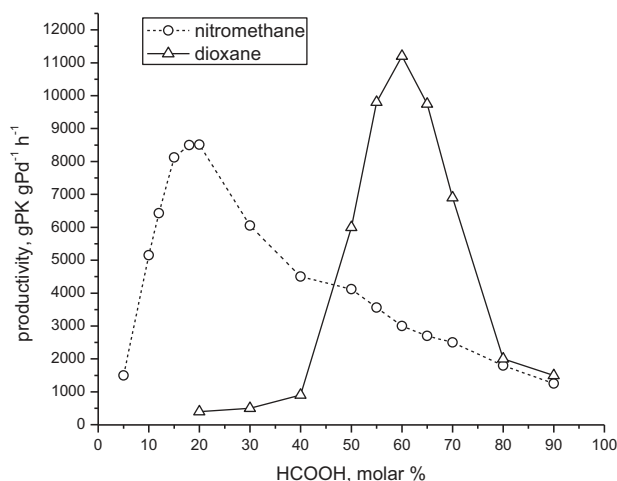


Fig. 1. Influence of HCOOH concentration on the productivity in nitromethane and 1,4-dioxane. Run conditions: $[\text{Pd}(\text{OAc})_2(\text{dppp})] = 1.57 \times 10^{-3}$ mmol; $\text{TsOH}/\text{Pd} = 100/1$ (molar ratio); volume of the reaction medium (solvent + HCOOH) 80 mL; 363 K; 4.5 MPa ($\text{CO}/\text{C}_2\text{H}_4 = 1/1$); 1 h; 700 rpm.

HCOOH can influence the catalysis because of several effects: (i) it can provide a higher concentration of the $\text{Pd}(\text{II})-\text{H}^+$ initiator (see below) preventing deprotonation that ultimately leads to inactive Pd metal [5]; (ii) it may activate/destabilize the β - and the γ -chelate of the growing chain by protonating the oxygen atom coordinated to the metal, thus favouring the chain growing process [32]; (iii) it causes an increase of the polarity of the reaction medium (HCOOH , $\epsilon = 59$), which could favour the formation of more reactive “cationic” species. At high HCOOH concentration, however, the productivity decreases. This might be due (i) to the increase of the concentration of the conjugate base of the acid, HCOO^- , which competes with the monomers for the coordination on the metal centre and (ii) to the lowering of the solubility of the monomers (see Table 2), measured as previously described [18,19,25].

In both solvents LVN decreases by increasing the HCOOH concentration (Fig. 2), in contrast with what observed in $\text{H}_2\text{O}-\text{AcOH}$ [21,23]. The trend suggests a direct involvement of the acid in the

Table 2
Henry's law constants for CO and ethene in different reaction media.

Solvent	H_{CO} (MPa)	H_{ethene} (MPa)
HCOOH	1.5×10^3	3.47×10^2
H_2O	8.2×10^3	1.25×10^3
1,4-Dioxane	3.2×10^2	3.4×10^1
Nitromethane	4.6×10^2	3.86×10^1

HCOOH (mol%)	1,4-Dioxane		Nitromethane	
	H_{CO} (MPa)	H_{ethene} (MPa)	H_{CO} (MPa)	H_{ethene} (MPa)
5	346.5	38.2	488.7	43.9
10	374.7	42.1	519.8	48.6
20	438.2	54.6	585.9	59.1
40	599.8	86.4	745.7	93.3
80	1120.6	218.8	1205.0	224.4

H_2O^a (mol%)	1,4-Dioxane ^a		Nitromethane ^a	
	H_{CO} (MPa)	H_{ethene} (MPa)	H_{CO} (MPa)	H_{ethene} (MPa)
10	478.5	55.0	651.2	61.2
20	662.2	78.5	869.0	86.3
40	1186.6	161.4	1270.1	173
60	2165.0	332.0	2284.3	347.9
80	4635.8	682.6	4894.2	695.8

^a The solvent mixture contains 5% of HCOOH.

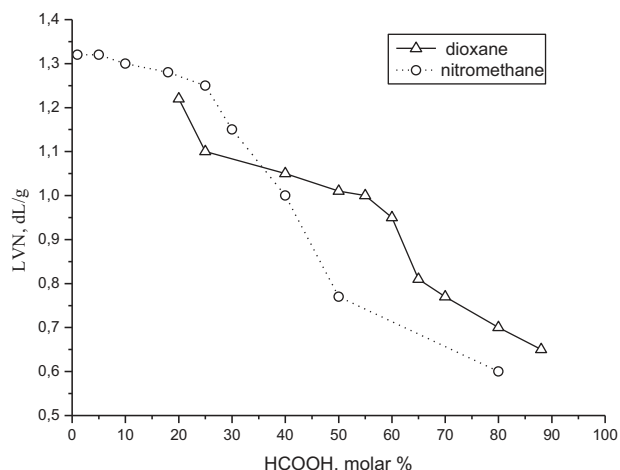


Fig. 2. Influence of HCOOH on the LVN in 1,4-dioxane and nitromethane. Run conditions: those of Fig. 1.

chain termination step (see below). In addition, it can be due to the lowering of the solubility of the monomers.

In order to further improve the catalyst performance, we tested also the influence of H₂O, which can be a hydride source for the catalyst [23–25].

3.2. Promoting effect of H₂O in the solvent

The influence of H₂O on the productivity has been evaluated in the presence of the acid in a low concentration (5 mol%), enough to avoid catalyst deactivation (Pd metal formation). Fig. 3 shows that the productivity passes through a maximum of 6.50 and 11.50 kgPK (gPd h)⁻¹ when H₂O ca. 40 and 60 mol% in nitromethane or 1,4-dioxane, respectively.

The promoting effect of H₂O accords with the literature [18–23], whereas the decrease of productivity at high H₂O concentration, is probably imputable to the lowering of monomers solubility in H₂O (Table 2).

Fig. 4 shows the influence of H₂O on the LVN, which is in the range 1.18–1.20 dL g⁻¹, corresponding to an average viscosity molecular weight (M_w) of 61–62 kg mol⁻¹. It is interesting to note that LVN is practically unaffected by the concentration of H₂O and by the aprotic organic solvent used.

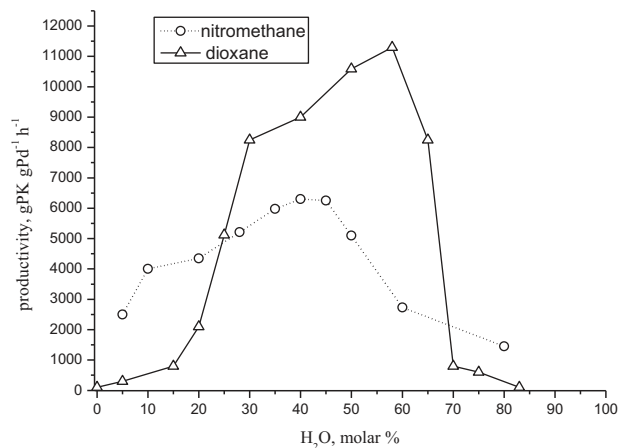


Fig. 3. Influence of H₂O on the productivity in 1,4-dioxane and nitromethane. Run conditions: [Pd(OAc)₂(dppp)] = 1.57 × 10⁻³ mmol; volume of the reaction medium 80 mL; HCOOH 5 mol%; 363 K; 4.5 MPa (CO/C₂H₄ = 1/1); 1 h; 700 rpm.

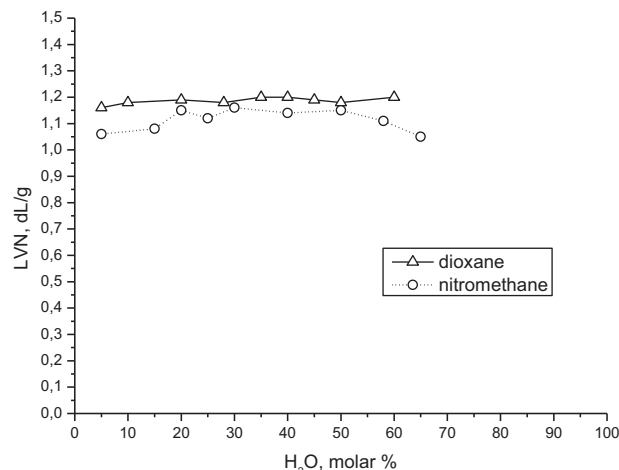


Fig. 4. Influence of H₂O on the LVN in 1,4-dioxane and nitromethane. Run conditions: those of Fig. 3.

3.3. Optimization of the HCOOH/H₂O/1,4-dioxane ratio

Since in 1,4-dioxane a higher productivity is obtained, we optimized the HCOOH/H₂O ratio under the conditions of the maximum of Fig. 3 (56 mL of 1,4-dioxane). The productivity increases from ca. 11.50 up to ca. 18.35 kgPK (gPd h)⁻¹ when the molar ratio H₂O/HCOOH is ca. 2/1, corresponding to the molar fraction 0.67 mol H₂O/mol(H₂O + HCOOH) in Fig. 5.

Furthermore, by keeping constant H₂O/HCOOH = 2/1 molar ratio, the productivity passes through a maximum of ca. 21.00 kgPK (gPd h)⁻¹ when HCOOH/H₂O/1,4-dioxane is ca. 2.7/1.35/1 (1,4-dioxane is ca. 20 mol%, Fig. 6). Under such reaction conditions the LVN is 1.28 dL g⁻¹, corresponding to 67.13 kg mol⁻¹. Productivity and LVN are significantly higher than those obtainable with “cationic” [Pd(TsO)(H₂O)(dppp)](TsO) in MeOH [32].

It is interesting to note that without 1,4-dioxane (solvent is H₂O/HCOOH, 2/1 molar ratio), the productivity decreases to ca. 11.00 kgPK (gPd h)⁻¹, and that in pure 1,4-dioxane no catalytic activity is observed.

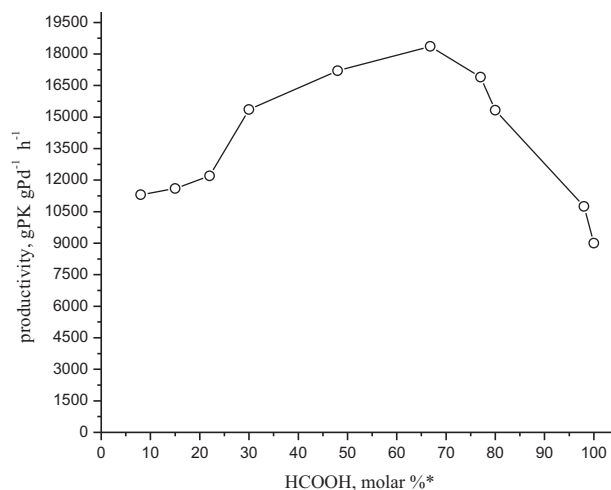


Fig. 5. Effect of the relative concentration of HCOOH-H₂O on the productivity in 1,4-dioxane. Run conditions: [Pd(OAc)₂(dppp)] = 1.57 × 10⁻³ mmol; volume of the reaction medium 80 mL, 1,4-dioxane 56 mL; 363 K; 4.5 MPa (CO/C₂H₄ = 1/1); 1 h; 700 rpm. * [mol HCOOH / (mol HCOOH + mol H₂O)] × 100.

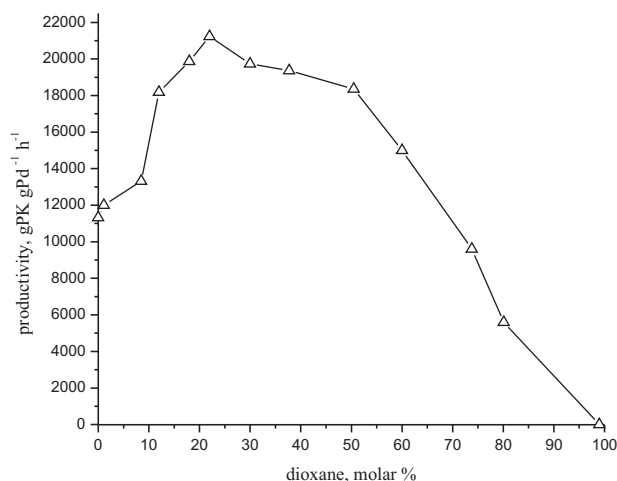


Fig. 6. Effect of 1,4-dioxane mol% at constant H₂O/HCOOH molar ratio on the productivity. Run conditions: [Pd(OAc)₂(dppp)] = 1.57 × 10⁻³ mmol; volume of the reaction medium 80 mL; H₂O/HCOOH = 2/1 (molar ratio); 363 K; 4.5 MPa (CO/C₂H₄ = 1/1); 1 h; 700 rpm.

3.4. Influence of temperature on productivity and LVN

The influence of temperature on the productivity and LVN has been tested in the range 333–363 K under 4.5 MPa (CO/ethene 1/1). Table 3 shows that the productivity increases by increasing the temperature, whereas the LVN decreases. The apparent activation energy of 12.7 kcal mol⁻¹, evaluated by the Arrhenius plot, accords with a reaction under kinetic control [33,34].

3.5. Influence of the pressure on productivity and LVN

The productivity and the LVN increase by increasing the total pressure. Under 9.0 MPa, CO/ethene = 1/1, 37.50 kgPK (gPd h)⁻¹ are obtained having LVN 2.77 dL g⁻¹ (M_W = 166.48 kg mol⁻¹) (Fig. 7).

3.6. On the chain-transfer process

It should be stated first that the copolymer presents exclusively keto-end groups. This feature was found also for other catalytic systems used in a H₂O–AcOH or H₂O–HCOOH mixture [18–25]. The nature of the ending groups depends on the chain-transfer process. When H₂O–AcOH was used as a solvent, it was proposed that this process involves protonolysis with H₂O with formation of a Pd(II)–OH species, that generates the Pd–hydride initiator after CO insertion followed by CO₂ evolution (Scheme 1, steps c, e, and f). All this may hold also in the present case when H₂O is added to 1,4-dioxane or nitromethane with dissolved 5% HCOOH (Scheme 1, steps a–d) and also when only HCOOH is added, because some H₂O might be present in the solvent. However, in this latter case, considering that the LVN significantly lowers upon increasing the concentration of the acid (cf. Fig. 2), the chain-transfer process might occur through protonolysis with the acid, with formation of the PK and of a Pd(II)-formate species [35] which would generate the Pd(II)–H initiator after β-hydride transfer and CO₂ evolution (Scheme 1, steps c' and g). This suggestion is supported by an

Table 3
Influence of temperature on the productivity and LVN.

T (K)	Productivity (kgPK (gPd h) ⁻¹)	LVN (dL g ⁻¹)
333	12.14	1.95
343	15.11	1.82
353	18.10	1.41
363	21.00	1.28

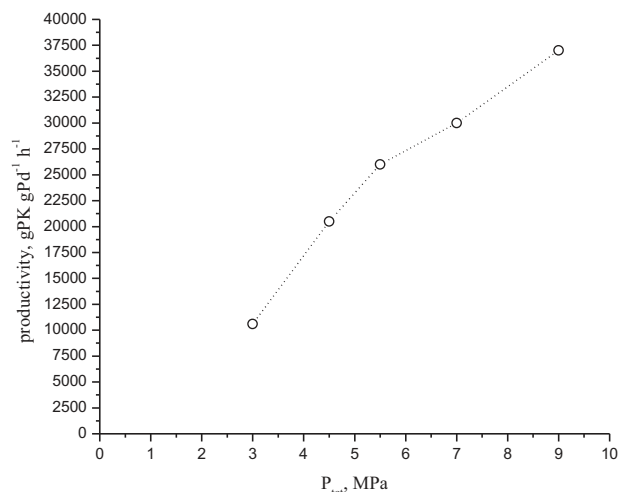
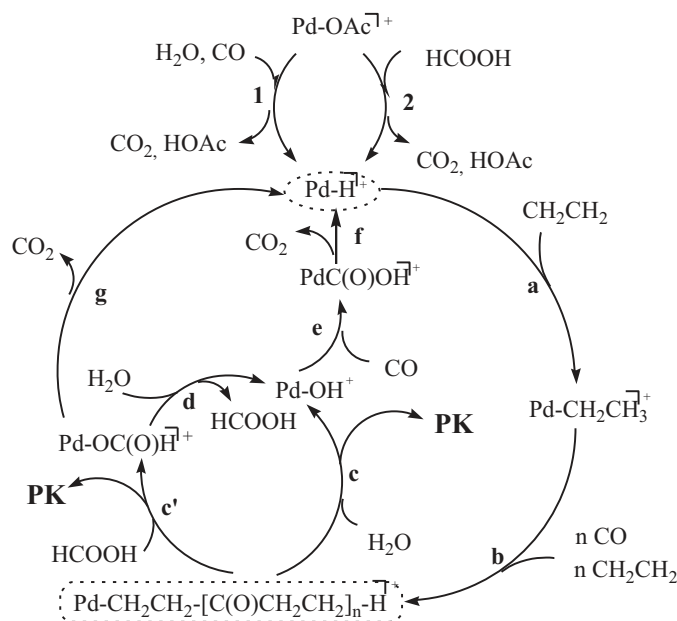


Fig. 7. Influence of total pressure on the productivity. Run conditions: [Pd(OAc)₂(dppp)] = 1.57 × 10⁻³ mmol; volume of the reaction medium 80 mL; 1,4-dioxane/H₂O/HCOOH = 2.7/1.35/1 (molar ratio); 363 K; CO/C₂H₄ = 1/1; 1 h; 700 rpm.

experiment carried out under the conditions of the maximum productivity in 1,4-dioxane in the presence of HCOOH (cf. Fig. 1), but also in the presence of 5% of acetic anhydride, which has been added in order to eliminate H₂O from the reaction medium. After 1 h reaction 1.1 g of PK were recovered, productivity 10.6 kgPK (gPd h)⁻¹, LVN = 0.93 dL g⁻¹. The fact that in H₂O–AcOH or H₂O–HCOOH the LVN increases upon increasing the acid concentration [21–23] is also in favour of the suggestion that under the conditions of Fig. 2 the chain-transfer process occur through protonolysis with formic acid. The comparison of Fig. 1 with Fig. 2 suggests further comments. It shows that the LVN decreases with the increase of HCOOH concentration also in the range of HCOOH concentration where the productivity increases. As far as the molecular weight is concerned, it depends on the rate of the chain growing process with respect to the process of the chain termination. As mentioned above, the acid



where: PK is CH₃CH₂–[C(O)CH₂CH₂]_n–H

Scheme 1. Proposed pathways for the activation of the catalytic precursor and for the chain-transfer process.

may destabilize the β - and γ -chelate rings, thus favouring the chain growing process [36]. However, the decrease of the solubility of the monomers upon increasing the acid concentration has an opposite effect. We have just shown that the acid is involved in the termination step. This might be another reason why LVN lowers. With methanol, it has demonstrated that the termination process occurs via an enolate formation step from a β -chelate, which is slower than the subsequent methanol protonolysis [37]. If this holds also with the reaction media of Fig. 2, then the protonolysis will be effective to a minor extent upon increasing HCOOH concentration. This means that the lowering of the LVN is mainly due to the lowering of the concentration of the monomers.

Steps 1 and 2 of Scheme 1 show how the precursor may be activated to the hydride that starts the first catalytic cycle.

4. Conclusion

HCOOH efficiently promotes the catalytic activity of [Pd(OAc)₂(dppp)] in 1,4-dioxane (11.20 kgPK (gPd h)⁻¹, CO/ethene 1/1, 4.5 MPa, 363 K) and nitromethane (8.5 kgPK (gPd h)⁻¹, CO/ethene 1/1, 4.5 MPa, 363 K). LVN linearly decreases by increasing the HCOOH concentration in both solvents, which suggests a direct involvement of the acid in the chain termination step, although an additional effect can be due to the lowering of the solubility of the monomers.

Furthermore, it has been found that also H₂O, under acid conditions, efficiently promotes the reaction in the same solvents. A combination of both promoters leads to the best results. The highest productivity has been obtained in HCOOH/H₂O/1-4,dioxane in the molar ratio 2.7/1.35/1 (ca. 37.50 kgPK (gPd h)⁻¹, LVN of 2.77 dL g⁻¹, at 363 K under 9.0 MPa of CO/ethene = 1/1).

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References

- [1] E. Drent, J.A.M. van Broekhoven, M.J. Doyle, *J. Organomet. Chem.* 417 (1991) 235–251.
- [2] E. Drent, P.H.M. Budzelaar, *Chem. Rev.* 96 (1996) 663–682.
- [3] E. Drent, J.A.M. van Broekhoven, P.H.M. Budzelaar, in: B. Cornils, W.A. Herrmann (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, vol. 1, Wiley-VCH, Weinheim, Germany, 1996.
- [4] A. Sommazzi, F. Garbassi, *Prog. Polym. Sci.* 22 (1997) 1547–1605.
- [5] C. Bianchini, A. Meli, *Coord. Chem. Rev.* 225 (2002) 35–66.
- [6] A. Sen (Ed.), *Catalytic Synthesis of Alternating Alkene–Carbon Monoxide Copolymers*, Kluwer, Amsterdam, 2003.
- [7] G.P. Belov, E.V. Novikova, *Russ. Chem. Rev.* 73 (2004) 267–291.
- [8] P.W.N.M. van Leeuwen, *Homogeneous Catalysis: Understanding the Art*, Kluwer Academic Publisher, Dordrecht, The Netherlands, 2004.
- [9] G. Cavinato, L. Toniolo, A. Vavasori, in: S.M. Beller (Ed.), *Topics in Organometallic Chem.: Catalytic Carbonylation Reactions*, vol. 18, Springer-Verlag, Berlin Heidelberg, 2006, pp. 125.
- [10] P.W.N.M. van Leeuwen, Z. Freixa, in: L. Kollár (Ed.), *Modern Carbonylation Methods*, Wiley-VCH, Weinheim, Germany, 2008.
- [11] O.M. Chukanova, K.A. Alpherov, G.P. Belov, *J. Mol. Catal. A: Chem.* 325 (2010) 60–64.
- [12] Z. Jiang, A. Sen, *Macromolecules* 27 (1994) 7215–7216.
- [13] G. Verspui, G. Papadogianakis, R.A. Sheldon, *Chem. Commun.* (1998) 401.
- [14] C. Bianchini, H.M. Lee, A. Meli, S. Moneti, V. Patinec, G. Petrucci, F. Vizza, *Macromolecules* 32 (1999) 3859–3866.
- [15] G. Verspui, F. Schanssema, R.A. Sheldon, *Appl. Catal. A: Gen.* 198 (2000) 5–11.
- [16] G. Verspui, F. Schanssema, R.A. Sheldon, *Angew. Chem. Int. Ed.* 30 (2000) 804–806.
- [17] S. Mecking, J.P. Claverie, in: B. Rieger, L.S. Baugh, S. Kacker, S. Striegler (Eds.), *Late Transition Metal Polymerisation Catalysis*, Wiley-VCH, Weinheim, Germany, 2003.
- [18] A. Vavasori, L. Toniolo, G. Cavinato, F. Visentin, *J. Mol. Catal. A: Chem.* 204–205 (2003) 295–303.
- [19] A. Vavasori, L. Toniolo, G. Cavinato, *J. Mol. Catal. A: Chem.* 215 (2004) 63–72.
- [20] G. Cavinato, A. Vavasori, L. Toniolo, L. Ronchin, F. Dall'Acqua, A. Dolmella, *Inorg. Chim. Acta* 358 (2005) 4555–4562.
- [21] A. Vavasori, A. Bellieni, L. Ronchin, F. Dall'Acqua, L. Toniolo, G. Cavinato, *J. Mol. Catal.* 263 (2007) 9–14.
- [22] A. Vavasori, L. Ronchin, L. Toniolo, *Appl. Catal. A: Gen.* 389 (2010) 108–113.
- [23] A. Vavasori, F. Dall'Acqua, G. Cavinato, L. Toniolo, *J. Mol. Catal.* 332 (2010) 158–164.
- [24] A. Vavasori, G. Cavinato, L. Toniolo, *J. Mol. Catal. A: Chem.* 191 (2003) 209–215.
- [25] A. Vavasori, L. Toniolo, L. Ronchin, *J. Mol. Catal. A: Chem.* 363–364 (2012) 398–403.
- [26] H.-K. Luo, Y. Kuo, X.-W. Wang, D.-G. Li, *J. Mol. Catal. A: Chem.* 151 (2000) 91–113.
- [27] C. Bianchini, A. Meli, W. Oberhauser, A.M. Segarra, C. Claver, E.J. Garcia Suarez, *J. Mol. Catal. A: Chem.* 265 (2007) 292–305.
- [28] J. Schwarz, E. Herdtweck, W.A. Herrmann, M.G. Gardiner, *Organometallics* 19 (2000) 3154–3160.
- [29] F. Benetollo, R. Bertani, G. Bombieri, L. Toniolo, *Inorg. Chim. Acta* 233 (1995) 5–9.
- [30] M.L. Huggins, *J. Am. Chem. Soc.* 64 (1942) 2716–2718.
- [31] B.J. Lommerts, D.J. Sikkema, *Macromolecules* 33 (2000) 7950–7954.
- [32] A. Fabrello, A. Vavasori, F. Dall'Acqua, L. Toniolo, *J. Mol. Catal. A: Chem.* 276 (2007) 211–218.
- [33] P.A. Ramachandran, R.V. Chaudhari, *Three Phase Catalytic Reactors*, Gordon and Breach, New York, 1983.
- [34] L. Toniolo, S.M. Kulkarni, D. Fatutto, R.V. Chaudhari, *Ind. Eng. Chem. Res.* 40 (2001) 2037–2045.
- [35] J.T. Lee, H. Alper, *Chem. Commun.* (2000) 2189.
- [36] C. Bianchini, A. Meli, W. Oberhauser, *Dalton Trans.* (2003) 2627–2635.
- [37] 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) 7977–7978.