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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 H_2O 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/H_2O/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.

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 [PdX$_2$(P-P)] (X = AcO, Cl), inactive in MeOH, turn into highly active catalysts when used in H_2O—AcOH or H_2O—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 H_2O.

2. Experimental

2.1. Reagents

1,4-Dioxane, nitromethane (99%), 1,3-bis(diphenylphosphino)propane (dppp), $CDCl_3$ 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: N_2, 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 ^{1}H NMR and ^{13}C NMR spectra of the polyketone dissolved in 1,1,1,3,3,3-hexafluoroisopropanol/$CDCl_3$ (10/1) were recorded using the Inverse ^{1}H-Gated Decoupling Technique.

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

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

2.3. Copolymerization

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

In a typical experiment, 1000 mg of [Pd(OAc)$_2$(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 CO/C_2H_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 kgPK(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 –CH$_2$– groups at 2915 cm^{-1}.

The ^{13}C NMR spectra, shows a single carbonyl absorption at 212.65 ppm (—**C**(O)CH$_2$CH$_2$—) and a single resonance for the —CH$_2$— groups at 35.73 ppm (—C(O)**C**H$_2$**C**H$_2$—) 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].

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

3. Results and discussion

3.1. Promoting effect of HCOOH

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

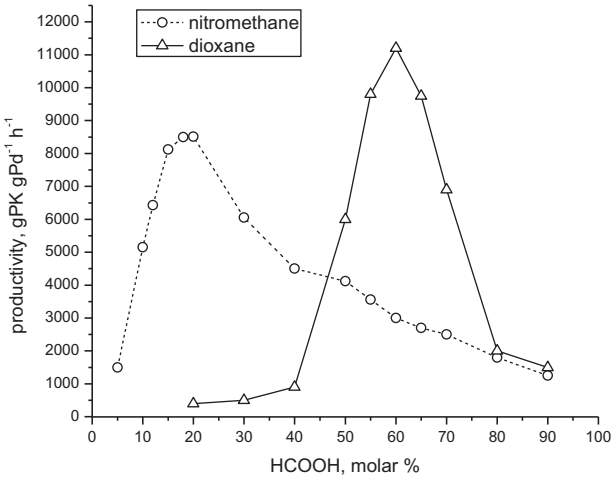

Fig. 1. Influence of HCOOH concentration on the productivity in nitromethane and 1,4-dioxane. Run conditions: [Pd(OAc)$_2$(dppp)] = 1.57×10^{-3} mmol; TsOH/Pd = 100/1 (molar ratio); volume of the reaction medium (solvent + HCOOH) 80 mL; 363 K; 4.5 MPa (CO/C_2H_4 = 1/1); 1 h; 700 rpm.

HCOOH can influence the catalysis because of several effects: (i) it can provide a higher concentration of the Pd(II)—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, $\varepsilon = 59$), 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 H_2O—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.