



# Influence of formic acid and water on the $[\text{Pd}(\text{OAc})_2(\text{dppp})]$ 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  $[\text{Pd}(\text{OAc})_2(\text{dppp})]$  in an aprotic solvent such as 1,4-dioxane or nitromethane is efficiently promoted both by  $\text{H}_2\text{O}$  and  $\text{HCOOH}$  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  $\text{HCOOH}/\text{H}_2\text{O}/1\text{-}4,\text{dioxane}$  (2.7/1.35/1 molar ratio), the productivity is  $37.50 \text{ kgPK}(\text{gPd h})^{-1}$  (LVN  $2.77 \text{ dL g}^{-1}$ ).

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  $[\text{PdX}_2(\text{P-P})]$  ( $\text{X} = \text{AcO}, \text{Cl}$ ), inactive in MeOH, turn into highly active catalysts when used in  $\text{H}_2\text{O}-\text{AcOH}$  or  $\text{H}_2\text{O}-\text{HCOOH}$  [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  $[\text{Pd}(\text{OAc})_2(\text{dppp})]$  ( $\text{dppp} = 1,3\text{-bis}(\text{diphenylphosphino})\text{propane}$ ) catalyzed CO–ethene copolymerization in aprotic solvents (1,4-dioxane and nitromethane) promoted by  $\text{HCOOH}$  and  $\text{H}_2\text{O}$ .

## 2. Experimental

### 2.1. Reagents

1,4-Dioxane, nitromethane (99%), 1,3-bis(diphenylphosphino)propane (dppp),  $\text{CDCl}_3$  and 1,1,1,3,3,3-hexafluoroisopropanol (99%) were Aldrich products; formic acid > 99%, (Acros Organics).

The complex  $[\text{Pd}(\text{OAc})_2(\text{dppp})]$  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,  $30 \text{ m} \times 0.35 \mu\text{m} \times 0.53 \mu\text{m}$  column (detector: FID; carrier gas:  $\text{N}_2$ , 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  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of the polyketone dissolved in 1,1,1,3,3,3-hexafluoroisopropanol/ $\text{CDCl}_3$  (10/1) were recorded using the Inverse  $^1\text{H}$ -Gated Decoupling Technique.

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