

The Catalytic Copolymerization of Ethene with Carbon Monoxide Efficiently Carried out in Water-Dichloromethane-Sodium Dodecylsulfate Emulsion

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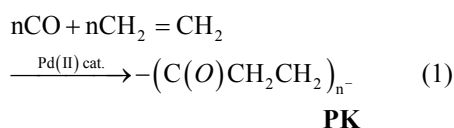
ABSTRACT

The CO-ethene copolymerization has been efficiently carried out in the water/CH₂Cl₂ emulsion by using water insoluble Pd(II) complexes. By using the surfactant SDS very high molecular weight copolymers have been obtained with high productivity (*ca.* 13,000 g/(gPd·h)).

Keywords: Palladium Catalyst; Carbonylation; Copolymerization; Polyketone

1. Introduction

The perfectly alternated poly(1-oxo-trimethylene), commonly called polyketone (PK in reaction 1), is a thermoplastic that has peculiar chemical, physical and mechanical characteristics of considerable interest for a wide range of applications [1-5].



The most active catalyst are cationic Pd(II) complexes having two coordination sites occupied by a chelating diphosphine ligand [6-13]. The catalytic activity (but also the PK molecular weight), however, strongly depends also by the reaction conditions (temperature, pressure of monomers and batch time [14-20]), and by the nature of the solvent [21]. On regard to the solvent, methanol is the most widely used even though water, which represents the ideal choose in terms of sustainability, is used too. The reactions carried out in water, however, usually lead to PK with higher molecular weight in comparison to the polymer obtained in methanol as a solvent [19-22]. As matter of fact, the more active catalysts (used for the reaction in methanol) are inactive or poorly active in water, because unsolvable. Therefore, water-solvable Pd(II)-diphosphine complexes have to be used which some time

shows a lower catalytic activity. These are mainly obtained by sulfonation of the diphosphine ligands (*ca.* 7 kg PK/(gPd·h) [22-28]), but also by fitting the phosphorus atoms with hydroxyl alkyl groups [29,30], or generally by using tenside phosphorus ligands [31].

In some papers it is reported, however, the use of water-insoluble Pd(II) complexes in reactions carried out in emulsion copolymerization (productivity *ca.* 650 g/(gPd·h) of PK) [32], or by using acetic or formic acid as a co-solvent (*ca.* 26,000 g/(gPd·h) of PK) [33].

As a means of implementing the emulsion CO-ethene copolymerization and with the aim to suggest new more sustainable reaction conditions to obtain high molecular weight PK, in the present paper we solubilise the water-insoluble Pd(II)-complexes [PdCl₂(dppp)] (dppp = 1,3-bis(diphenylphosphino)propane) in an water/dichloromethane emulsion, formed by using the commercial sodium dodecylsulfate (SDS), as surfactant.

2. Experimental Section

2.1. Reagents

The complexes [PdX₂(dppp)] X = Cl, TsO (tosilate), OAc (acetate), were prepared as reported in literature [4,7]. Carbon monoxide and ethene were supplied by SIAD Company Italy ("research grade", purity > 99.9%). Dppp, TsOH (p-toluenesulfonic acid), and SDS were Aldrich products.

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2.2. Equipments and Characterization

The catalyst precursor was weighted on a Sartorius Micro balance (precision 0.001 mg). The polymers were analyzed by FTIR and NMR spectroscopies. FTIR spectra were recorded on a Nicolet Magna 750 instrument in KBr powder. The IR spectra show typical stretching signals of CO groups at 1695 cm^{-1} and $-\text{CH}_2-$ groups at 2915 cm^{-1} . 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 1,1,1,3,3,3-hexafluoroisopropanol/ CDCl_3 (10/1) using the Inverse ^1H -Gated Decoupling Technique. The ^{13}C NMR spectra, show 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.

The average viscosity molecular weight of polymer has been evaluated as Limit Viscosity Number (LVN). The LVN (or $[\eta]$) 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 [34]. 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 25°C . The average viscosity molecular weight (M_w) of the polyketone was derived from the LVN using the Mark-Houwink equation [35].

The solubility of gases was measured using an absorption technique in a high pressure stainless steel autoclave of 300 mL capacity as described in literature [36].

2.3. 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 a typical experiment, 0.724 mg of $[\text{PdCl}_2(\text{dppp})]$ (1.23×10^{-3} mmol) was added to 80 mL of water containing the dosed amount of surfactant and then placed in the autoclave. The mixture was subjected to high shear till a homogeneous liquid is obtained. The autoclave was washed by pressurizing with a 1/1 mixture of $\text{CO}/\text{C}_2\text{H}_4$ (*ca.* 0.5 MPa) and then depressurizing to atmospheric pressure (this cycle was repeated 5 times, at room temperature with stirring). The washed autoclave was pressurized with 0.5 MPa of the gas mixture and heated to 90°C in *ca.* 10 min without stirring. At the reaction temperature the pressure was adjusted to the desired value (typically 4.5 MPa total pressure) and, while stirring, maintained constant throughout the experiment (rate stirring 700 rpm). At the end of the experiment the autoclave was quickly cooled and carefully depressurized. The polymer is insoluble in H_2O and the slurry obtained was filtered, washed several times with acetone and dried under vacuum at 70°C . The dried polymer was weighted and the productivity was calculated as $\text{gPK} \cdot (\text{gPd} \cdot \text{h})^{-1}$; the reproducibility was within *ca.* 5%.

3. Results and Discussion

The water insoluble $[\text{PdCl}_2\text{dppp}]$ complex is used to carry out the CO-ethene copolymerization in the $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ reaction medium. The **Figure 1** shows the influence on the catalytic activity of the $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ ratio and of the SDS addition.

Although CH_2Cl_2 readily dissolves the Pd(II) complex and is also a good solvent for both monomers (comparable to methanol), as suggested by the Henry's law constants in the **Table 1**, we found that the catalyst is

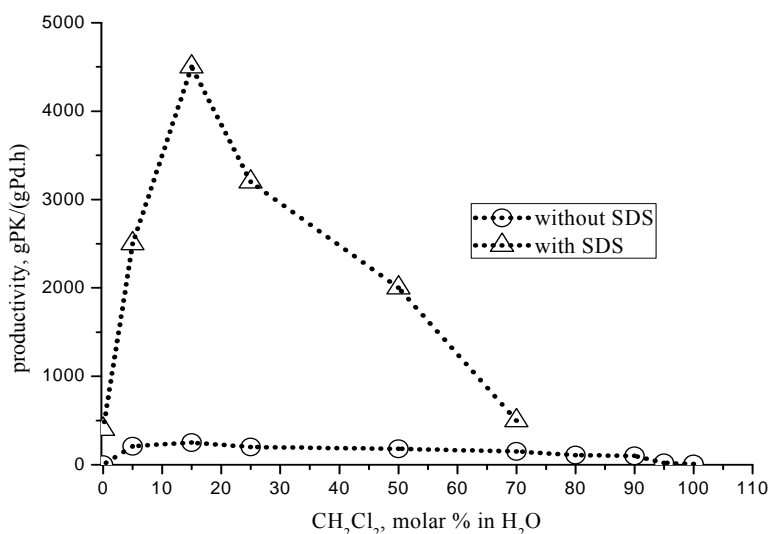


Figure 1. Influence of the $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ on the productivity. Run conditions: $[\text{PdCl}_2(\text{dppp})] = 8.5 \times 10^{-3}$ mmol; O: without SDS; Δ : with SDS 5 mM; volume = 80 mL; $T = 90^\circ\text{C}$; $P = 4.5$ MPa ($\text{CO}/\text{C}_2\text{H}_4 = 1/1$); reaction time = 1 h; stirrer = 700 rpm.

inactive, according with the suggestion that in pure CH_2Cl_2 the initiating Pd-H species cannot form in absence of any H-donors species (for instance H_2O or alcohol, see mechanism).

On the other hand, in pure H_2O the catalyst is inactive too, probably due to the poor solubility of the Pd(II) complex, which floats on the solvent. By mixing CH_2Cl_2 - H_2O together, in the absence of any surfactant, two stable immiscible phases readily form where under vigorous stirring the catalyst become active. The productivity was *ca.* 150 - 200 gPK/(gPd h), at CH_2Cl_2 concentration within the range of 15 - 20 molar %.

The addition of a dosed amount of the surface active agent SDS increases the catalytic activity, which passes through a maximum of *ca.* 4500 gPK/(gPd h) at CH_2Cl_2 20 molar %.

The surfactant favors the formation of droplets in which the monomers and the catalyst are highly partitioned (see solubility) into the CH_2Cl_2 phase relatively to the aqueous phase. It can form CH_2Cl_2 droplets in water (O/W emulsion) or *vice versa* H_2O droplets in CH_2Cl_2 (W/O emulsion).

In any cases the formation of an emulsion leads to an increase of the contact area between the two phases fa-

voring, therefore, the catalysis which occurs at the CH_2Cl_2 / H_2O interfaces (H_2O or TsOH have to react on the metal center, see the **Figure 2**).

The **Figure 1** shows that at CH_2Cl_2 higher than 20 molar % the productivity decreases, suggesting a correlation with the phase inversion. According to this, under W/O emulsion conditions (high CH_2Cl_2 concentration) the catalyst and the monomers are diluted in the organic bulk with a negative consequence on the reaction kinetic.

The addition of the acid promoter (TsOH) to the SDS- CH_2Cl_2 / H_2O (20 molar %) emulsion increases the productivity up to a plateau of *ca.* 8000 g/(gPd·h) (**Figure 3**).

As widely described in literature, the addition of acid promoters avoids the catalyst deactivation to inactive or

Table 1. Henry's law constant measured at 90°C in different solvents.

Solvent	$H_{\text{CO}(90^\circ\text{C})}$	$H_{\text{ethene}(90^\circ\text{C})}$
	MPa	MPa
Methanol	248.6	51.6
Dichloromethane	236.0	52.1
Water	5540.0	1538.8

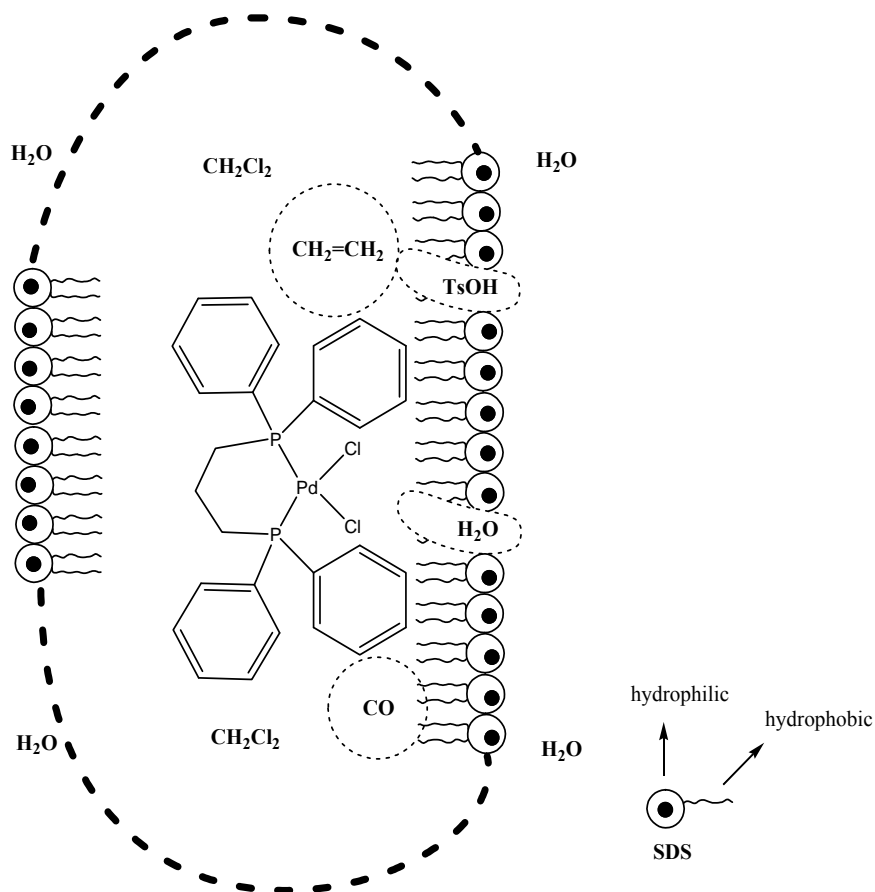


Figure 2. Schematic representation of CH_2Cl_2 droplet in water.

less active Pd(0) species, Pd metal included, which normally occurs under the reductive conditions of the reaction [6-12].

The **Figure 4** shows that by optimizing the SDS concentration, the productivity passes through a maximum, which was *ca.* 13,000 gPK/(gPd·h) at SDS concentration of *ca.* 10 mM.

The increase of productivity confirms that the catalysis is favored by the formation of an increasing amount of stable droplets (critical micelle concentration is 8.3 mM for SDS at 25°C [37]). As matter of facts, the emulsion

increases the O/W interface area, where the Pd(II) activation can occur more efficiently (see **Figure 2**).

At SDS concentration higher than *ca.* 10 mM, however, the decrease of productivity suggests the influence of two possible phenomena: the droplets coalescence and the formation of foams [38]. The surfactant can favor the coalescence which causes a decrease of the O/W interface area and, at the same time, can favor the formation of foams, negative for the catalysis as the reaction medium becomes inefficiently stirred and reaction rates limited by diffusion phenomena.

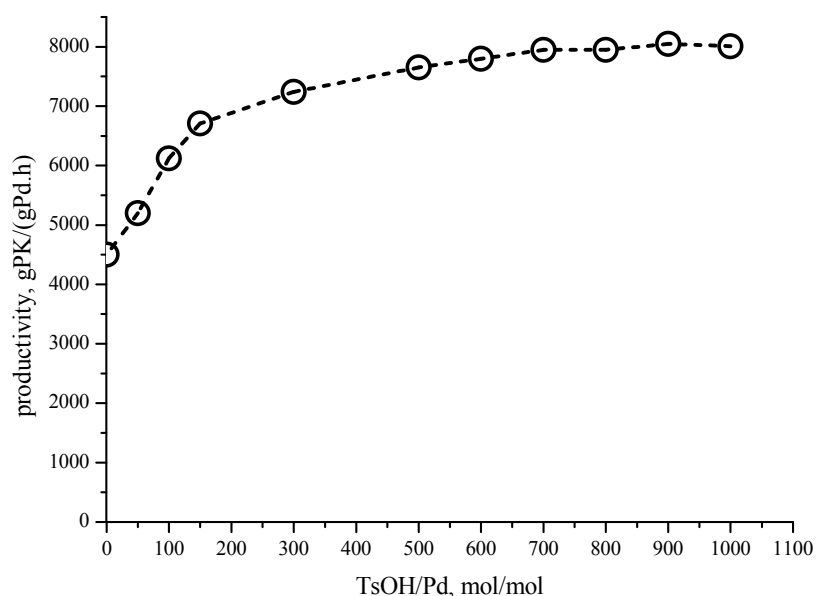


Figure 3. Influence of *p*-toluenesulfonic acid concentration on the productivity. Run conditions: $[\text{PdCl}_2(\text{dppp})] = 8.5 \times 10^{-3}$ mmol; SDS: 5 mM; volume = 80 ml; T = 90°C; P = 4.5 MPa (CO/C₂H₄ = 1/1); reaction time = 1 h; stirrer = 700 rpm.

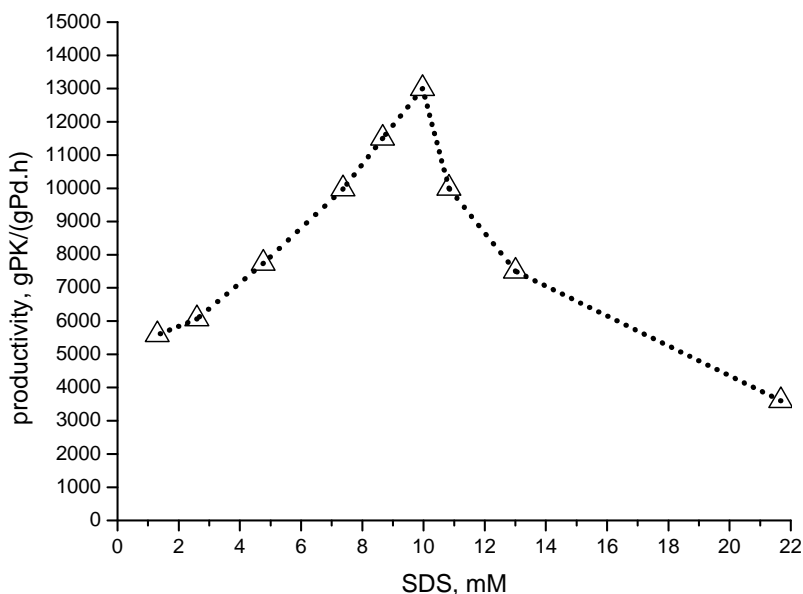


Figure 4. Influence of SDS concentration on the productivity. Run conditions: $[\text{PdCl}_2(\text{dppp})] = 8.5 \times 10^{-3}$ mmol; O: TsOH/Pd: 800/1, mol/mol; volume = 80 ml; T = 90°C; P = 4.5 MPa (CO/C₂H₄ = 1/1); reaction time = 1 h; stirrer = 700 rpm.

The PK obtained had a Limiting Viscosity Number (LVN) of 1.8 dL/g which is higher respect to the LVN obtained in methanol (0.5 dL/g). **Table 2** shows the LVN and the respective viscosity average molecular weight of the PKs obtained in different solvents.

Among the solvents used in the **Table 2**, the SDS/CH₂Cl₂/H₂O emulsion copolymerization leads to the highest LVN, suggesting the following considerations on the reaction mechanism. It is accepted that in water the neutral Pd(II)-H intermediate is firstly generated from the precursor by a reaction strictly related to the water gas shift [6-12], and then converted into the catalytically active cationic Pd(II)-H⁺ species by a water-controlled solvolysis process [8] (**Scheme 1**, reactions **a-b**).

The fast migratory insertion of ethene into the Pd-H bond starts the copolymerization (Step **c**). The alternate and successive insertions of CO and ethene lead to the growth of the polymer chain (Steps **d-e**): the chain-swollen drops quickly turn into insoluble polymer particles and the final result is a dispersion of PK particles in water.

Termination occurs, as proposed in literature [6-12], via protonolysis with H₂O of the Pd-(CH₂CH₂-polymer)⁺ species (Step **f**), which gives the PK and the Pd-OH⁺ species. The latter can insert CO to form the Pd-C(O)OH⁺ intermediate (Step **g**), which gives β-hydride elimination with CO₂ evolution (Step **h**). The active Pd-H⁺ species are formed again, which restart the catalytic cycle.

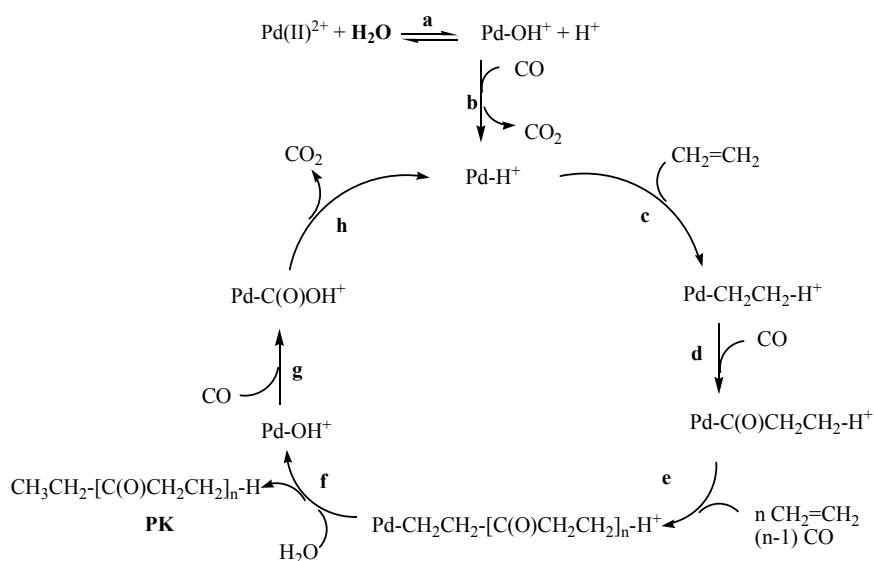
According with the literature and supported by the NMR analysis, which indicate the presence of only

-C(O)CH₂CH₃ end-groups, in the SDS/CH₂Cl₂/H₂O emulsion the termination can occur only through reaction with H₂O (protonolysis) or with the acid. Protonolysis with H₂O or TsOH are slower than with methanol and under emulsion condition occur mostly at the interface, being H₂O and TsOH in the bulk, out of the droplets in the O/W emulsion. On the contrary, the propagation occurs inside the droplets where the monomers concentration is higher (see introduction) in accord with the high productivity obtained. Furthermore, the high propagation rate together with the slow termination rate favor the formation of PKs with high average molecular weight.

Table 2. LVN and viscosity average molecular weight of PK in different solvents.

Solvent	LVN	MW
	dL/g	g/mol
Methanol	0.5	22,215
SDS/CH ₂ Cl ₂ /H ₂ O	1.8	100,258
dioxane/H ₂ O	1.20	62,223
nitromethane/H ₂ O	1.18	61,000
HCOOH/H ₂ O (70%)	0.63	29,156
CH ₃ COOH/H ₂ O	0.93	46,102

Run conditions: O: [PdCl₂(dppp)] = 8.5 × 10⁻³ mmol; volume = 80 ml; T = 90°C; P = 4.5 MPa (CO/C₂H₄ = 1/1); reaction time = 1 h; stirrer = 700 rpm.



where:

Pd(II): the catalyst precursor, PdCl₂dppp

Pd- : P(II) complex where the ligands are omitted to simplify the schematic representation.

PK: *alt*-poly(1-oxo-trimethylene)

Scheme 1. Proposed reaction mechanism.

4. Conclusion

The catalyzed CO-ethene copolymerization has been efficiently performed in a SDS/H₂O/CH₂Cl₂ emulsion by using Pd(II) water insoluble complexes. The optimization of such reaction systems shows a catalytic activity higher (ca. 13,000 g/(gPd·h)) than in methanol as a solvent (ca. 8000 g/(gPd·h)). The best catalyst performance was reached with SDS 10 mM and 20 molar % of CH₂Cl₂ in H₂O. Under conditions of the maximum productivity the PK obtained showed a molecular weight higher than in methanol (LVN was 1.8 dL/g respect to 0.5 dL/g in methanol).

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