



# Terpolymerisation of 1-olefin and ethene with CO catalysed by the [PdCl<sub>2</sub>(dppp)] complex in methanol as a solvent [dppp = 1,3-bis(diphenylphosphino)propane]

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## ABSTRACT

The catalytic activity of the [PdCl<sub>2</sub>(dppp)] complex in the 1-olefin/ethene (E)/CO terpolymerisation has been studied in MeOH (containing 1000 ppm of H<sub>2</sub>O) as a solvent. The 1-olefins tested were propene (P), 1-hexene (Hex), 1-decene (D) and styrene (S). At 90 °C and 45 atm (E/CO = 1/1), the system [PdCl<sub>2</sub>(dppp)]/TsOH (*p*-toluenesulfonic acid) = 1/8 catalyses efficiently the reactions leading to 5000 g PECO/(g Pd h), 5600 g HexECO/(g Pd h), 5650 g DECO/(g Pd h) and 4100 g SECO/(g Pd h). In particular, it has been studied deeper the effect of Hex and S concentrations on productivities, average molecular weights and melting temperatures of HexECO and SECO, respectively. A mechanism of reaction has been also proposed and discussed, supported by IR, and NMR characterizations.

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## 1. Introduction

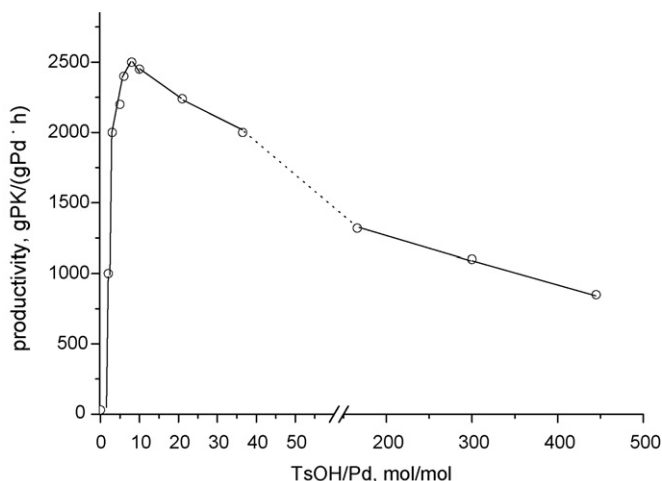
Pd(II)-chelating diphosphine complexes catalyse efficiently the strictly alternating copolymerisation of ethene (E) with CO (ECO) leading to a high molecular weight polymer [1,2]. This class of catalysts is also active for the co- and terpolymerisation of CO with olefins other than ethene thus providing access to a new family of polymers named polyketones (PK). ECO is a highly crystalline material with high melting point ( $T_m = 256^\circ\text{C}$ ), whereas copolymers of CO with alkene others than ethene or terpolymers of CO with two olefins may have different properties depending on the relative characteristics of both alkenes and catalysts [2–7]. Several industries have been showed a keen interest in this new group of polymers, and the propene (P)–E–CO (PECO) terpolymer, which has reduced melting transition ( $T_m$ ) and a much more favorable behavior in blow-molding or in extrusion applications, was the first PK that found entrance into industrial applications, commercialized under the trade name of CARILON<sup>®</sup> by Shell [8] and of KETONEX<sup>®</sup> by BP [9].

Various aspects of the PK catalysis have been reviewed [2,10–14], and the nature of chelating ligand appears fundamental to determine the catalytic activity which is influenced also by the nature of the counter-anions and of the solvent. By comparing the activity of several Pd(II) complexes, it has been found that bidentate bisphosphines are effective for the copolymerisation of ethene, propene, or higher 1-alkenes with CO [15–20], on one hand. On the other hand, nitrogen-based ligands, such as diimine [21–25], bisoxazoline [26,27], phosphine-imine [28,29], and phosphine-phosphite [30–32] have been utilized for the copolymerisation of vinylarenes with CO.

In contrast to the intensive efforts devoted to the copolymer synthesis, however, much less has been reported on terpolymer synthesis. Most of these deal with the terpolymerisation of CO with two aliphatic olefins catalysed by Pd–diphosphine complexes [33,12–15]. The nitrogen-based ligands appear more effective in the terpolymerisation of CO with two aromatic olefins [34] or in the terpolymerisation of CO with one aliphatic and one aromatic olefin [35,28] and only few reports appeared on terpolymerisation of CO with one aliphatic and one aromatic olefin in which are used diphosphine [36,37] or phosphine-phosphite [38] based ligands.

Even if protic or non-protic organic solvents can be used [39–45], in most olefin/CO copolymerisation and terpolymeri-

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**Fig. 1.** Effect of TsOH concentration on the productivity. Run conditions:  $[\text{PdCl}_2(\text{dppp})] = 1.44 \times 10^{-3}$  mmol, MeOH = 80 mL,  $\text{H}_2\text{O} = 1000$  ppm,  $90^\circ\text{C}$ , 45 atm (CO/ethene = 1/1), 1 h.

sation reactions, methanol is employed as a solvent [10–14]. Moreover, in the most relevant cases, there are weakly coordinating anions coordinated to metal, being the strong coordinating anions (for instance Cl) considered less effective [10–14].

Only recently in some reports it has been claimed that also the  $[\text{PdX}_2(\text{dppp})]$  complexes having strong coordinating ligands ( $\text{X} = \text{Cl}, \text{OAc}$ ) are highly active in the ECO copolymerisation, if the appropriate solvent is used, for instance  $\text{H}_2\text{O}-\text{CH}_3\text{COOH}$  or  $\text{H}_2\text{O}-\text{MeOH}$  [46,47]. In these papers it has been pointed out the fundamental role played by  $\text{H}_2\text{O}$ : at  $90^\circ\text{C}$  and 45 atm (CO/E = 1/1), the  $[\text{PdCl}_2(\text{dppp})]$  complex, which is inactive in MeOH without addition of  $\text{H}_2\text{O}$ , catalyses the ECO copolymerisation leading to a maximum of productivity [4000 g ECO/(g Pd h)] when  $\text{H}_2\text{O}$  is 20% (molar), which increases up to 6000 g ECO/(g Pd h) when the precursor is used in the presence of *p*-toluenesulfonic acid (TsOH) [47]. The same precursor leads to a productivity of 27,500 g ECO/(g Pd h) when the solvent is  $\text{H}_2\text{O}-\text{CH}_3\text{COOH}$  ( $\text{H}_2\text{O} = 55\%$ , mol/mol) [47].

In the present paper, it has been studied the catalytic activity of  $[\text{PdCl}_2(\text{dppp})]$  complex, having strong coordinating ligands (Cl), in 1-olefins/CO copolymerisation and in 1-olefins/E/CO terpolymerisation, in MeOH as a solvent containing  $\text{H}_2\text{O}$  and TsOH as co-promoters.

Since in literature, there are only few reports on terpolymerisation of ethene, vinylarenes and CO, in which are used phosphine-based ligands, and no data concerning the productivity were reported [35,37], it appears interesting to study also the catalytic activity of  $[\text{PdCl}_2(\text{dppp})]$  in the styrene (S)-E-CO (SECO) terpolymerisation. A mechanism of reaction has been also proposed and discussed.

**Table 2**  
Productivity, LVN and  $T_m$  of PECO, HexECO and DECO terpolymers.

| Monomers           | Polymer | Productivity (g PK/(g Pd h)) | $T_m$ ( $^\circ\text{C}$ ) | LVN (dl/g) | 1-Olefin <sup>a</sup> (mol%) |
|--------------------|---------|------------------------------|----------------------------|------------|------------------------------|
| Ethene/CO          | ECO     | 2500                         | 260                        | 0.30       | –                            |
| Propene/ethene/CO  | PECO    | 5000                         | 216                        | 0.35       | 5.5                          |
| 1-Hexene/ethene/CO | HexECO  | 5530                         | 229                        | 0.45       | 3.6                          |
| 1-Decene/ethene/CO | DECO    | 5650                         | 233                        | 0.60       | 3.4                          |

Run conditions:  $[\text{PdCl}_2(\text{dppp})] = 1.44 \times 10^{-3}$  mmol, TsOH/Pd = 8/1,  $\text{H}_2\text{O} = 1000$  ppm, (MeOH + 1-olefins) = 80 mL,  $\text{mol}_{1\text{-olefin}}/(\text{mol}_{1\text{-olefin}} + \text{mol}_{\text{MeOH}}) = 0.05$ ,  $90^\circ\text{C}$ , 45 atm (E/CO = 1/1), 1 h.

<sup>a</sup> mol% of P, Hex, or D incorporated into the terpolymer.

**Table 1**  
Selected  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  signals of ECO copolymer.

|  | $^1\text{H-NMR}$ |  | $^{13}\text{C-NMR}$ |
|--|------------------|--|---------------------|
| $-\text{C}(\text{O})\text{CH}_2\text{CH}_3$  | 1.08             | $-\text{C}(\text{O})\text{CH}_2\text{CH}_3$  | 6.91                |
| $-\text{C}(\text{O})\text{CH}_2\text{CH}_3$  | 2.52             | $-\text{C}(\text{O})\text{CH}_2\text{CH}_2-$ | 35.73               |
| $-\text{C}(\text{O})\text{CH}_2\text{CH}_2-$ | 2.77             | $-\text{C}(\text{O})\text{OCH}_3$            | 176.31              |
| $-\text{C}(\text{O})\text{OCH}_3$            | 3.72             | $-\text{C}(\text{O})\text{CH}_2\text{CH}_2-$ | 212.65              |
|  |                  | $-\text{C}(\text{O})\text{CH}_2\text{CH}_3$  | 217.04              |

The spectrum was recorded by dissolving the copolymer in a 1,1,1,3,3,3-hexafluoroisopropanol/ $\text{CDCl}_3$  (10/1) solution.

## 2. Results and discussion

### 2.1. Ethene/CO and 1-olefin/CO copolymerisations

The  $[\text{PdCl}_2(\text{dppp})]$  complex has been used as catalyst precursor in the copolymerisation of CO with ethene, propene, 1-hexene (Hex), and 1-decene (D). It has been reported that  $[\text{PdCl}_2(\text{dppp})]$  catalyses efficiently the ECO copolymerisation in  $\text{H}_2\text{O}-\text{MeOH}$  ( $\text{H}_2\text{O} = 20\%$ ) as a solvent pointing out the fundamental role played by  $\text{H}_2\text{O}$  and the acid (TsOH) to determinate the catalytic activity (see Introduction [47]). Unfortunately, in such a solvent the olefins tested form two immiscible phases forcing us to use only 1000 ppm of  $\text{H}_2\text{O}$  in MeOH to favor the formation of Pd-H active species and at the same time a suitable homogeneous reaction medium both for copolymerisation and terpolymerisation experiments. In the case of ECO copolymerisation the low  $\text{H}_2\text{O}$  concentration reduces the catalytic activity to 150 g PK/(g Pd h) with formation of Pd metal in trace amount, that's why we use also TsOH as promoter [47], which stabilizes the hydride species against deprotonation [12–14]. Quite interesting, by increasing the TsOH concentration, the productivity passes through a maximum of 2500 g PK/(g Pd h) when TsOH/Pd is 8/1 (mol/mol) and then slightly decreases at higher TsOH/Pd ratio down to 800 g PK/(g Pd h) when TsOH/Pd is 450/1 (mol/mol) (see Fig. 1).

The ECO copolymer was characterised by IR and NMR spectroscopies. The IR spectrum shows typical stretching signals of CO groups at  $1695\text{ cm}^{-1}$  and  $-\text{CH}_2-$  groups at  $2915\text{ cm}^{-1}$ .

The  $^{13}\text{C-NMR}$  spectrum 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. The end-groups analysis indicates the presence of both  $-\text{C}(\text{O})\text{OCH}_3$  (176.31 ppm) and  $-\text{C}(\text{O})\text{CH}_2\text{CH}_3$  groups (217.04 ppm) according to the reaction mechanism proposed in the literature [10–14]. Selected  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  signals and the assignments are reported in Table 1.

However, the  $[\text{PdCl}_2(\text{dppp})]/\text{TsOH}$  (1/8) catalytic system shows an activity very poor in the PCO, HexCO and DCO copolymerisation yielding only soluble co-oligomers, detected through the GC analysis. The poor productivity and low molecular weights suggest a propagation rate significantly slower than in the case of ECO copolymerisation which competes with termination one.

**Table 3**  
Selected NMR data for PECO, HexECO and DECO terpolymers.

|  | <sup>1</sup> H-NMR |  | <sup>13</sup> C-NMR |
|--|--------------------|--|---------------------|
| <b>PECO</b>  |                    |  |                     |
| –C(O)CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>       | 0.93               | –C(O)CH(CH <sub>3</sub> )CH <sub>2</sub> –                 | 15.81               |
| –C(O)CH <sub>2</sub> CH <sub>3</sub>                       | 1.06               | –C(O)CH <sub>2</sub> CH <sub>2</sub> –                     | 35.75               |
| –C(O)CH(CH <sub>3</sub> )CH <sub>2</sub> –                 | 1.13               | –C(O)CH(CH <sub>3</sub> )CH <sub>2</sub> –                 | 41.42               |
| –C(O)CH <sub>2</sub> CH <sub>3</sub>                       | 2.52               | –C(O)CH(CH <sub>3</sub> )CH <sub>2</sub> –                 | 45.21               |
| –C(O)CH <sub>2</sub> CH <sub>2</sub> –                     | 2.77               |  |                     |
| –C(O)CH(CH <sub>3</sub> )CH <sub>2</sub> –                 | 2.81               | –C(O)OCH <sub>3</sub>                                      | 176.31              |
| –C(O)CH(CH <sub>3</sub> )CH <sub>2</sub> –                 | 3.15               | –C(O)CH <sub>2</sub> CH <sub>2</sub> –                     | 212.66              |
| –C(O)OCH <sub>3</sub>                                      | 3.72               | –C(O)CH(CH <sub>3</sub> )CH <sub>2</sub> –                 | 214.22              |
| –C(O)C(CH <sub>3</sub> )=CH <sub>2</sub>                   | 6.15               | –C(O)CH <sub>2</sub> CH <sub>3</sub>                       | 217.04              |
| <b>HexECO</b>  |                    |  |                     |
| –C(O)CH(R)CH <sub>2</sub> –                                |                    | –C(O)CH <sub>2</sub> CH <sub>2</sub> –                     | 35.71               |
| <b>R</b> = (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> | 0.93               | –C(O)CH(R)CH <sub>2</sub> –                                | 46.08               |
| <b>R</b> = (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> | 1.34               | –C(O)CH(R)CH <sub>2</sub> –                                | 42.89               |
| –C(O)CH <sub>2</sub> CH <sub>3</sub>                       | 1.08               | –C(O)CH(R)CH <sub>2</sub> –                                |                     |
| –C(O)CH <sub>2</sub> CH <sub>3</sub>                       | 2.25               | <b>R</b> = (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> | 21.71–36.16         |
| –C(O)CH <sub>2</sub> CH <sub>2</sub> –                     | 2.79               | <b>R</b> = (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> | 12.26               |
| –C(O)CH(R)CH <sub>2</sub> –                                | 2.57               |  |                     |
| –C(O)CH(R)CH <sub>2</sub> –                                | 2.90               | –C(O)OCH <sub>3</sub>                                      | 176.31              |
| –C(O)OCH <sub>3</sub>                                      | 3.72               | –C(O)CH <sub>2</sub> CH <sub>2</sub> –                     | 212.61              |
|  |                    | –C(O)CH(R)CH <sub>2</sub> –                                | 213.89              |
|  |                    | –C(O)CH <sub>2</sub> CH <sub>3</sub>                       | 217.04              |
| <b>DECO</b>  |                    |  |                     |
| –C(O)CH <sub>2</sub> CH <sub>3</sub>                       | 1.07               | –C(O)CH(R)CH <sub>2</sub> –                                | 44.58               |
| –C(O)CH <sub>2</sub> CH <sub>3</sub>                       | 2.27               | –C(O)CH(R)CH <sub>2</sub> –                                | 42.89               |
| –C(O)CH(R)CH <sub>2</sub> –                                | 2.55               |  |                     |
| –C(O)CH <sub>2</sub> CH <sub>2</sub> –                     | 2.79               | –C(O)CH(R)CH <sub>2</sub> –                                |                     |
| –C(O)CH(R)CH <sub>2</sub> –                                | 2.95               | <b>R</b> = (CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub> | 18.71–35.16         |
| –C(O)OCH <sub>3</sub>                                      | 3.71               | <b>R</b> = (CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub> | 12.26               |
| –C(O)CH(R)CH <sub>2</sub> –                                |                    | –C(O)OCH <sub>3</sub>                                      | 176.31              |
| <b>R</b> = (CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub> | 1.31               | –C(O)CH <sub>2</sub> CH <sub>2</sub> –                     | 212.55              |
| <b>R</b> = (CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub> | 0.91               | –C(O)CH(R)CH <sub>2</sub> –                                | 214.90              |
|  |                    | –C(O)CH <sub>2</sub> CH <sub>3</sub>                       | 217.04              |

The spectra were recorded by dissolving the terpolymer in a 1,1,1,3,3,3-hexafluoroisopropanol/CDCl<sub>3</sub> (10/1) solution.

## 2.2. 1-Olefin/ethene/CO terpolymerisation

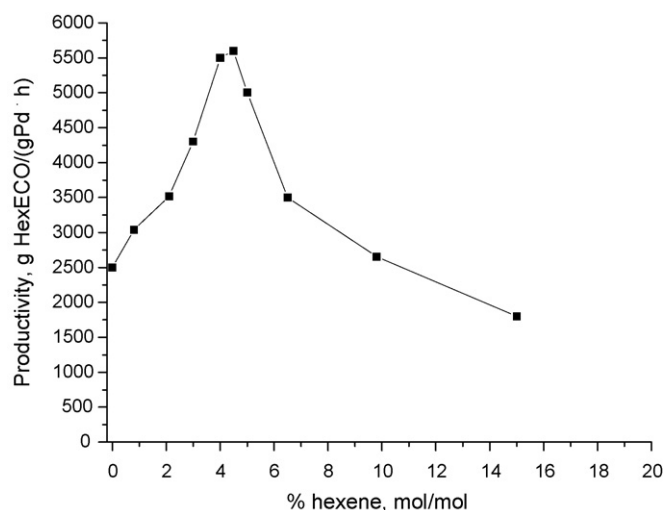
Table 2 shows the productivities together with the melting temperatures ( $T_m$ ), the limiting viscosity numbers (LVNs) and the mol% of olefin incorporated in the polymers obtained by carrying out the terpolymerisations of E and CO with P, Hex, and D.

Quite interesting, the productivities are very close to the values reported in literature for terpolymerisations catalysed by Pd(II)–(dppp) complexes having weakly coordinating ligands [6].

In all cases a white polymer was obtained, indicating that no decomposition of the catalyst to Pd metal occurred. The lowering of  $T_m$ , with respect to  $T_m$  of ECO, indicates the formation of terpolymers [3] which have been further characterised by IR, <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopies.

All the IR spectra show the typical stretching signals of carbonyl groups of polyketone ECO as a strong absorption band at about 1695 cm<sup>–1</sup> (KBr) and the strong absorption band of the –CH<sub>2</sub>– groups at about 2915 cm<sup>–1</sup>. However, the solids were definitively identify as PECO, 1-hexene/ethene/CO (HexECO), and DECO terpolymers by the <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra. Table 3 shows some selected signals and the assignments, which are in good agreement with the values reported in the literature [48,49].

In all NMR spectra, the dominant resonances for the ECO units indicates the presence in the polymer backbone mainly of long sequences of ECO units together with minor amount of XCO (X = P, Hex, D) units. The 1-olefin (mol%) incorporated in the terpolymer has been estimated from the relative integration of the character-



**Fig. 2.** Effect of 1-hexene concentration on the productivity. Run conditions: [PdCl<sub>2</sub>(dppp)] = 1.44 × 10<sup>–3</sup> mmol, TsOH/Pd = 8/1, (MeOH + 1-hexene) = 80 mL, H<sub>2</sub>O = 1000 ppm, 90 °C, 45 atm (CO/ethene = 1/1), 1 h.

istic XCO (X = P, Hex, D) and ECO signals in the <sup>1</sup>H-NMR spectra [20].

The end-groups analysis shows mainly the presence of –C(O)CH<sub>2</sub>CH<sub>3</sub> and –C(O)OCH<sub>3</sub> and vinyl end-groups (detected only in PECO), in accord with the mechanism proposed above.

### 2.2.1. 1-Hexene/ethene/CO terpolymerisation

Among the alkyl 1-olefins tested (P, Hex, D), we took into deeper consideration only 1-hexene. Fig. 2 shows that by increasing the concentration of Hex the productivity passes through a maximum value of 5600 g HexECO/(g Pd h) when the olefin is ca. 4.5% (mol/mol). A further increase of its concentration causes a decrease of productivity down to 1800 g HexECO/(g Pd h) when Hex is 15% (mol/mol).

The Henry's law constants (Table 4) for CO and E, measured in pure MeOH and in pure Hex, shows that both the monomers are soluble more in Hex than in MeOH.

These findings suggest that upon increasing the Hex concentration in MeOH two main effects are possible: (i) it increases also the E and CO solubility, thus the ECO propagation rate increases [50], which gives higher productivity of HexECO terpolymer, (ii) when Hex is higher than 4.5%, the terpolymerisation rate (measured as productivity) decreases probably because it increases the competition of monomers (E, Hex and CO) for the coordination to the metal and at the same time increases the incorporation of Hex in the polymer chain, which is much slower than ethene insertion (see copolymerisation experiments and [14]).

We measure also the limity viscosity number, which is correlated to the average molecular weight of the polymer, and the melting temperature ( $T_m$ ) of terpolymers (see Fig. 3 and Table 5). LVN increases by increasing Hex concentration and passes through a maximum of 0.58 dL/g when Hex is ca. 4.0%. At higher Hex concentration LVN decreases down to 0.28 dL/g at 15% Hex. On the other

**Table 4**  
Henry's law constants for CO and ethene measured at 90 °C in different solvents.

| Solvent  | Henry constant (atm) |        |
|----------|----------------------|--------|
|          | CO                   | Ethene |
| MeOH     | 2710                 | 513    |
| 1-Hexene | 1418                 | 405    |
| Styrene  | 2050                 | 393    |

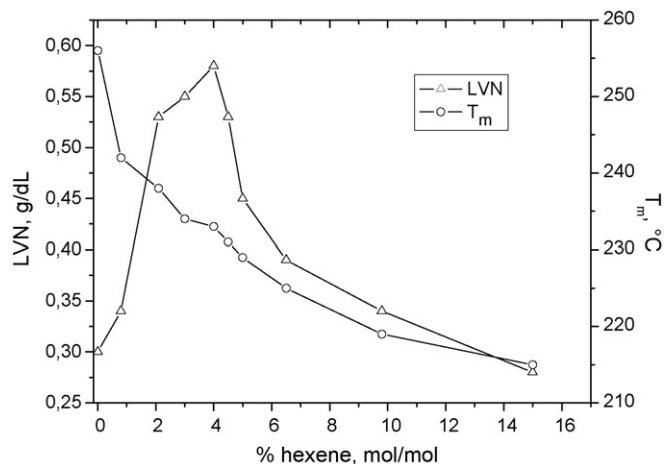


Fig. 3. Effect of 1-hexene concentration on the LVN and on the  $T_m$ . Run conditions: see Fig. 2.

hand, in the same range of olefin concentration,  $T_m$  decreases from 256 °C ( $T_m$  of ECO) down to 215 °C, where the Hex mol% incorporated in the polymer is ca. 5.1, in good agreement with the values reported in the literature [3,14,51–53].

The trends of LVN and  $T_m$  agree with points (i) and (ii) used to describe the trend of productivity. It is plausible that the first increase of molecular weight observed is due to a higher propagation rate of ECO blocks with respect to the HexCO ones and/or chain transfer. When Hex concentration is higher than 4.5% (mol/mol), the decrease of LVN observed confirm point (ii) because the decrease of propagation rate favors also the termination step with formation of short polymer chain. On the other hand, the decrease of  $T_m$  observed by increasing the Hex concentration, accords with a progressive increase of HexCO units along the polymer chain (or at the end) [3,54], also at low Hex concentration, where the productivity and LVN increase.

The  $^1\text{H-NMR}$  and the  $^{13}\text{C-NMR}$  analysis of the polymer confirm the formation of HexECO terpolymers (see Table 3). The  $^1\text{H-NMR}$  spectrum shows signals at 1.08 ppm ( $\text{CH}_3\text{CH}_2\text{CO-}$ ), 2.25 ppm ( $\text{CH}_3\text{CH}_2\text{CO-}$ ) and 3.72 ppm ( $\text{CH}_3\text{OCO}$ ) and the  $^{13}\text{C-NMR}$  spectrum shows signals at 217.04 ppm [ $\text{CH}_3\text{CH}_2\text{C}(\text{O})$ ] and at 176.31 ppm [ $\text{CH}_3\text{OC}(\text{O})$ ] which indicate the presence of mainly  $\text{CH}_3\text{CH}_2\text{CO-}$  and  $\text{CH}_3\text{OCO-}$  end-groups. The signals at 0.93 ppm and at 1.34 ppm in the  $^1\text{H-NMR}$  spectrum, and the signals at 12.26, 21.71–36.16, 42.89 and 46.08 ppm in the  $^{13}\text{C-NMR}$  spectrum indicate the presence of HexCO units along and/or at the end of polymer chain.

Table 5  
Effect of the 1-hexene concentration on the productivity,  $T_m$ , and LVN.

| 1-Hexene %, (mol/mol) | Productivity (g HexECO/(g Pd h)) | LVN (dL/g) | $T_m$ (°C) |
|-----------------------|----------------------------------|------------|------------|
| –                     | 2500                             | 0.30       | 256        |
| 0.8                   | 3038                             | 0.34       | 242        |
| 2.1                   | 3520                             | 0.53       | 238        |
| 3.0                   | 4300                             | 0.55       | 234        |
| 4.0                   | 5500                             | 0.58       | 233        |
| 4.5                   | 5600                             | 0.53       | 231        |
| 5.0                   | 5000                             | 0.45       | 229        |
| 6.5                   | 3500                             | 0.39       | 225        |
| 9.8                   | 2654                             | 0.34       | 219        |
| 15.0                  | 1800                             | 0.28       | 215        |

Run conditions:  $[\text{PdCl}_2(\text{dppp})] = 1.44 \times 10^{-3}$  mmol,  $\text{TsOH}/\text{Pd} = 8/1$ ,  $\text{H}_2\text{O} = 1000$  ppm,  $(\text{MeOH} + 1\text{-hexene}) = 80$  mL, 90 °C, 45 atm ( $\text{CO}/\text{ethene} = 1/1$ ), 1 h.

Table 6  
Effect of styrene concentration on the SECO productivity, LVN and  $T_m$ .

| Styrene % (mol/mol) | Productivity (g SECO/(g Pd h)) | LVN (dL/g) | $T_m$ (°C) |
|---------------------|--------------------------------|------------|------------|
| –                   | 2500                           | 0.30       | 256        |
| 0.1                 | 3030                           | 0.30       | 252        |
| 0.5                 | 3780                           | 0.31       | 245        |
| 0.8                 | 4000                           | 0.32       | 241        |
| 1.0                 | 4100                           | 0.32       | 235        |
| 1.3                 | 3930                           | 0.30       | 233        |
| 2.3                 | 3240                           | 0.29       | 231        |
| 4.8                 | 2100                           | 0.27       | 225        |
| 17.5                | 1059                           | 0.25       | 206        |

Run conditions:  $[\text{PdCl}_2(\text{dppp})] = 1.44 \times 10^{-3}$  mmol,  $\text{TsOH}/\text{Pd} = 8/1$ ,  $\text{H}_2\text{O} = 1000$  ppm,  $(\text{MeOH} + \text{styrene}) = 80$  mL, 90 °C, 45 atm ( $\text{CO}/\text{ethene} = 1/1$ ), 1 h.

### 2.3. Styrene/ethene/CO terpolymerisation

The  $[\text{PdCl}_2(\text{dppp})]/\text{TsOH}$  (1/8) system does not catalyse the copolymerisation of styrene with CO, but the reaction of styrene and ethene with carbon monoxide leads to a white solid which melts at 225 °C. Since the lowering of  $T_m$  can indicate the formation of a terpolymer, we look deeper into investigation of the system.

In Table 6 are reported the effects of the increase of styrene concentration in MeOH on productivity, LVN and  $T_m$ . The productivity passes through a maximum of 4100 g SECO/(g Pd h) when styrene is about 1% (mol/mol), see Fig. 4.

In Table 4 are reported also the Henry's law constants for CO and E measured in pure styrene at 90 °C. Since the solubility of monomers is higher in styrene than in MeOH, on the light also of the above discussion (see Section 2.2.1.), the two opposite effects (i) and (ii) can explain the maximum of the productivity observed in Fig. 4.

Table 6 and Fig. 5 show that the melting temperature,  $T_m$ , decreases by increasing the styrene concentration in MeOH from 256 °C (ECO copolymer) to 206 °C, when concentration of styrene was 17.5% (mol/mol), and LVN passes through a maximum of 0.32 dL/g at styrene concentration of 1% (mol/mol). These findings, analogously to the above discussion, suggest an increasing presence of SCO units along or at the end of polymer chains by increasing the styrene concentration in the solvent (at  $T_m = 206$  °C, S in the polymer is ca. 3.2 mol%), which determinates, together with the higher solubility of E and CO in the reaction medium, also the trend of the LVN shown in Fig. 5 (see Section 2.2.1.).

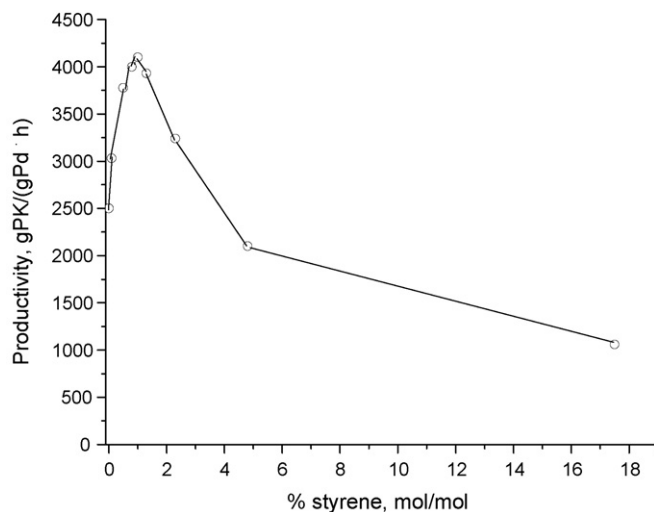


Fig. 4. Effect of styrene concentration on the productivity. Run conditions:  $[\text{PdCl}_2(\text{dppp})] = 1.44 \times 10^{-3}$  mmol,  $\text{TsOH}/\text{Pd} = 8/1$ ,  $(\text{MeOH} + \text{styrene}) = 80$  mL,  $\text{H}_2\text{O} = 1000$  ppm, 90 °C, 45 atm ( $\text{CO}/\text{ethene} = 1/1$ ), 1 h.





The absorbances at 137.51, 128.91, 128.20, and 126.11 ppm were attributable to the phenyl group,  $-\text{C}(\text{O})\text{CH}(\text{Ph})\text{CH}_2$ . The signal at 6.93 ppm ( $\text{CH}_3\text{CH}_2\text{CO}$ ), 216.94 ppm ( $\text{CH}_3\text{CH}_2\text{CO}-$ ), 203.64 ppm ( $\text{PhCH}=\text{CHCO}$ ) and at 176.29 ppm ( $\text{CH}_3\text{OCO}$ ) suggest three termination pathways [48,49,55].

It is interesting to note that the termination of the polymer chain is caused mostly by alcoholysis of an acyl group leading ester end-group whereas the  $\beta$ -hydride elimination which leads to a styryl end-group is an effective alternative, which accords with the termination routes proposed [see mechanism].

#### 2.4. Proposed catalytic cycle

The mechanism proposed in literature for the olefin/E/CO terpolymerisation by palladium catalysis closely resembles that proposed for olefins/CO copolymerisation [2–15,56–61].

In methanol as a solvent, two possible species Pd–H and Pd–C(O)OCH<sub>3</sub> (see Scheme 1) may initiate the copolymerisation [2–15].

The precursor [PdCl<sub>2</sub>(dppp)] is activated according to Scheme 1, where both MeOH and H<sub>2</sub>O can react with the Pd(II) complex to form, in the presence of CO the active species. MeOH reacts with a Pd(II) complex to form, in the presence of CO, both the active Pd–C(O)OCH<sub>3</sub> and Pd–H species [2–15], whereas H<sub>2</sub>O gives only Pd–H species through a reaction strictly related to the water gas shift, where H<sub>2</sub>O react with the complex to gives a Pd–OH intermediate which upon insertion of CO forms the Pd–COOH species. The latter easily eliminates CO<sub>2</sub> to form the Pd–H active species [13,46,47]. The presence in solution of an acid increases the productivity probably by stabilizing the Pd–H intermediate towards decomposition to inactive Pd(0) species [46,47,58].

The insertion of an olefin into a Pd–H bond or into Pd–C(O)OCH<sub>3</sub> species to form a Pd–alkyl intermediate represent two initiation steps of the catalysis [2–14,57–61].

Chain propagation towards the formation of terpolymers involves the alternating insertion of CO and an olefin (ethene or the second alkene present in the reaction mixture) into the Pd–alkyl and into a Pd–acyl bond, respectively. Due to the higher stability of the Pd(II)–CO bond compared to the 1-alkene complex, the coordination and migratory insertion of carbon monoxide into a Pd–alkyl species is faster than the alkene insertion, which is the rate limiting step in this polymerisation reaction [10–14]. Since double CO-insertion seems to be energetically disfavored a strictly alternating CO/olefin terpolymer results. The terpolymer chains are formed by ECO and XCO units (X = P, Hex, D, S), in amounts ruled by the relative rates of the insertion of the two olefins into the Pd–acyl bond [62,63].

All the proposed chain transfer polymer forming steps reform (directly or after reaction with CO, see Scheme 1) the active Pd–H and Pd–C(O)OCH<sub>3</sub> species, which restart the polymer growing cycle.

Several chain terminations pathways are possible: (a) methanolysis, due to reaction of MeOH with a Pd–C(O)P species (Pd–acyl intermediate; P = growing polymer) which leads to a EK or EE terpolymer (E = ester end-group, K = keton end-group) and the Pd–H active species; (b) protonolysis, involves a Pd–CH<sub>2</sub>CHR–C(O)P species (Pd–alkyl intermediate) and MeOH and/or H<sub>2</sub>O. The reaction with MeOH yields EK or KK terpolymers and the active species Pd–C(O)OCH<sub>3</sub> whereas the reaction with H<sub>2</sub>O gives the EK and KK terpolymers and the Pd–OH species which inserts CO to form the Pd–COOH intermediate: the latter gives the active species Pd–H by elimination of CO<sub>2</sub>. (c) Termination by  $\beta$ -hydrogen elimination involves a Pd–CH<sub>2</sub>CHR–C(O)P species to form EV and/or KV (V = vinyl) terpolymers and the Pd–H active species.

Unlike ECO copolymerisation, the mayor pathway to chain termination in SCO alternating copolymerisation in methanol consists of a fast  $\beta$ -hydrogen elimination from the last inserted styrene unit [64]. Generally, this pathway prevails over the termination path by methanolysis, whereas in the ECO only termination by methanolysis is accepted. However, the SCO copolymer has higher tendency than PCO and higher 1-alkenes to terminate by  $\beta$ -hydride elimination [64].

According to this, the NMR characterizations of terpolymers shows ketones and methyl esters end-groups but also vinyl-end groups.

### 3. Experimental

#### 3.1. Reagents

Palladium(II) chloride was purchased from Engelhard Italiana SRL; 1,3-bis(diphenylphosphino)propane (dppp), 1,1,1,3,3,3-hexafluoroisopropanol (99%), methanol (H<sub>2</sub>O = 100 ppm), CDCl<sub>3</sub>, 1-hexene, 1-decene and styrene were Aldrich products. Carbon monoxide, ethene and propene were supplied by SIAD Company ('research grade', purity >99.9%).

The complex [PdCl<sub>2</sub>(dppp)] was prepared as reported in the literature [65].

#### 3.2. Equipment

The catalyst precursor was weighted on a Sartorius Micro balance (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  $\mu\text{m}$  × 0.53  $\mu\text{m}$  column (detector: FID; carrier gas: N<sub>2</sub>, 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 by dissolving the polymers in a 1,1,1,3,3,3-hexafluoroisopropanol/CDCl<sub>3</sub> (10/1) solution. The <sup>13</sup>C-NMR spectra of the polyketone were recorded using the Inverse <sup>1</sup>H-Gated Decoupling Technique.

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

The melting temperatures of polymers have been determined on a PerkinElmer Differential Scanning Calorimetry (mod. DSC 7) instrument.

#### 3.3. Copolymerisations and terpolymerisations

The polymerisation 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 gaseous monomers (E and CO) were supplied to the autoclave in the ratio 1/1 from a gas reservoir connected to the autoclave through a constant pressure regulator whereas the liquid monomers were mixed with the solvent before running the reactions.

In a typical experiment, 0.850 mg of [PdCl<sub>2</sub>(dppp)] ( $1.44 \times 10^{-3}$  mmol) was added to 80 mL of solvent (MeOH + olefin) contained in the bottle placed in the autoclave. The autoclave was washed by pressurising with a 1/1 mixture of CO/C<sub>2</sub>H<sub>4</sub> (ca. 5 atm) and then depressurising to atmospheric pressure (this cycle was repeated five times, at room temperature with stirring). The autoclave was then pressurised with 5 atm of the gas mixture and

then heated to 90 °C in ca. 10 min without stirring. The pressure was then adjusted to the desired value (typically 45 atm, 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 depressurised. The polymer was completely precipitate by addition of 100 mL of H<sub>2</sub>O and the slurry obtained was filtered, washed with water and acetone and dried under vacuum at 70 °C.

The dried polymer was weighted and the productivity was calculated as g PK/(g Pd h); the reproducibility was within ca. 5%.

### 3.4. Limiting viscosity number measurements

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 [66]. 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.

### 3.5. Solubility measurements

The solubility of the monomers in the solvent of reaction was measured by an absorption technique. In a typical experiment a known volume of solvent ( $V_S = 80$  mL) was charged into the autoclave used for the copolymerisation reaction and heated to a desired temperature (90 °C). After the thermal equilibrium was attained, the void space above the liquid was carefully washed (without stirring the solvent) with a monomer and pressurised to a desired value ( $P_A$ ) by supplying the monomer from a tank reservoir of 12.0 mL volume ( $V_r$ ) maintained at constant temperature ( $T$ ). The initial pressure in the reservoir ( $P_i$ ) was adjusted at  $P_i > P_A$ . The liquid in the autoclave was then vigorously stirred till the pressure of the reservoir dropped to a constant final value,  $P_f$ . The moles of A absorbed are  $n_{A,abs} = V_r(P_i - P_f)(zRT)^{-1}$  and the molar fraction of A in the solvent is  $X_A = n_{A,abs} / (n_{A,abs} + n_{solvent})^{-1}$ .

The Henry's law constant  $H$  (MPa) has been calculated as  $H = P_A X_A^{-1}$  for  $P_A \rightarrow 0$ .

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