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Terpolymerization of propene and ethene with carbon monoxide catalyzed by [$PdCl_2$(dppf)] in HCOOH–H_2O as a solvent [dppf = 1,1′-bis(diphenylphosphino)ferrocene]

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ABSTRACT

The [$PdCl_2$(dppf)] complex efficiently catalyzes the terpolymerization of propene and ethene with carbon monoxide in HCOOH–H_2O as a solvent, when H_2O concentration ranges between 50 and 65 molar %. The productivity, the melting temperature and the viscosity average molecular weight of the terpolymer depend on the propene concentration and on the reaction time.

The NMR analysis of the polymer composition indicates the presence along the chain mainly of ethene–CO units together with a low percent of propene–CO units.

A reaction mechanism is proposed and discussed.

1. Introduction

Pd(II)-chelating diphosphine complexes efficiently catalyze the strictly alternating co- and ter-polymerization of CO with aliphatic 1-olefins, providing access to a new family of engineering thermoplastics named polyketones (PK) [1–3].

In contrast to the intensive efforts devoted to ethene (E)–carbon monoxide (ECO) copolymerization, much less has been reported on terpolymerization of two olefins with carbon monoxide [1–12], although industries have shown more interest for terpolymers than for copolymers, as documented by the high number of patents in this field. This is because the ECO copolymer is a highly crystalline material with high melting point (T_m), whereas the terpolymers have lower melting points, making them more easily processable [13–19]. As matter of fact, the first commercialized PK, was the propene (P)–ethene–CO (PECO) terpolymer (trade name CARILON® by Shell [20] and KETONEX® by BP [21]). Currently, several industries are showing renovated keen interest in these terpolymers, searching for new catalytic systems more efficient and selective in particular for applications in the field of lubricants (oligomers) and/or in the field of fibers (high molecular weight). In general, for fiber production both high productivity of the catalyst and high average molecular weight of the polymer are required.

Among the main aspects that rule the Pd(II)-catalysis the nature of the chelating ligand, of the counter-anion and of the solvent plays a key role [1–3,22–25]. Methanol is the most used solvent in which case the counter-anions must be weakly coordinating in order to ensure high productivity.

We recently reported that by using reaction media such as H_2O–MeOH, H_2O–CH_3COOH or H_2O–HCOOH also Pd(II)-complexes having strongly coordinating ligands efficiently catalyze the reaction [26–30]. For example, we have found that the [$PdCl_2$(dppp)] complex efficiently catalyzes the terpolymerization with propene (P), 1-hexene (Hex), 1-decene (D) or styrene (S) with CO (5000 gPECO/(gPd h), 5600 gHexECO/(gPd h), 5650 gDECO/(gPd h) and 4100 gSECO/(gPd h), in MeOH as a solvent containing H_2O and TsOH as co-promoters [6].

In addition, it is reported that the CO–ethene copolymerization catalyzed by a cationic Pd(II)-dppf based catalyst, using MeOH as a solvent, gives PKs of low molecular weight, together with co-oligomers and other carbonylated products of even lower molecular weight such as dimethyl 4-oxoheptanoate, dimethyl succinate, methyl 4-oxohexanoate and methyl propanoate [31]. Under the same experimental conditions, but in CH_3COOH–H_2O as a solvent, we achieved a remarkable increase of the catalytic activity together with an increase of the average molecular weight [29].

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More recently, interesting results have been obtained in HCOOH–H_2O as a solvent in which the catalyst shows both a higher catalytic activity and a higher ECO molecular weight also using strongly coordinating counter anions. As matter of fact, we reported that the [$PdCl_2$(dppf)] complex in such a solvent efficiently catalyzes the ethene–CO (ECO) copolymerization leading to high molecular weight polymer with a productivity of 20,200 gECO/(gPd h), at 90 °C, 45 atm (CO/E = 1/1), and H_2O *ca.* 50 molar % [32]. It is worth to point out that both [$Pd(OAc)_2$(dppf)] and [$PdCl_2$(dppf)] are inactive in MeOH. This prompted us to extend the use of H_2O–organic acid as a solvent to the terpolymerization of ethene and another olefin with CO.

In this paper, we report on the catalytic activity of the [$PdCl_2$(dppf)] precursor in the PECO terpolymerization carried out in H_2O–HCOOH as a solvent. The effect of the operative conditions on the productivity and on the viscosity average molecular weight has been studied. A reaction mechanism has been also proposed and discussed.

2. Experimental

2.1. Reagents

Palladium(II) chloride was purchased from Engelhard Italy SRL; 1,1′-bis(diphenylphosphino)ferrocene (dppf), 1,1,1,3,3,3-hexafluoroisopropanol (99%), methanol (H_2O = 100 ppm) and $CDCl_3$ were Aldrich products. Carbon monoxide, ethene and propene were supplied by SIAD Company ('research grade', purity >99.9%).

The complex [$PdCl_2$(dppf)] was prepared as reported in literature [33].

2.2. Equipment

The catalyst precursor was weighted on a Sartorius Micro balance.

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 μm × 0.53 μm column (detector: FID; carrier gas: N_2, 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/$CDCl_3$ (10/1). The ^{13}C NMR spectra of the polyketone were recorded using the Inverse ^1H-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 Perkin Elmer Differential Scanning Calorimeter (mod. DSC 7) instrument.

2.3. Terpolymerization

The polymerizations were carried out by using a Hastelloy C autoclave of 280 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 free volume available to the liquid and to the gas phase was 250 mL. 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 monomer was mixed with the solvent before running the reactions.

Table 1
Most relevant ^{13}C NMR and ^1H NMR signals for PECO terpolymer.

	^1H NMR		^{13}C NMR
–C(O) $CH_2CH_2CH_3$	0.93	–C(O)CH(CH_3)CH_2 –	15.81
–C(O)CH_2CH_3	1.06	–C(O)CH_2CH_2–	35.75
–C(O)CH(CH_3)CH_2–	1.13	–C(O)CH(CH_3)CH_2 –	41.42
–C(O)CH_2CH_3	2.52	–C(O)CH(CH_3)CH_2 –	45.21
–C(O)CH_2CH_2–	2.77		
–C(O)CH(CH_3)CH_2–	2.81	–C(O)CH_2CH_2–	212.66
–C(O)CH(CH_3)CH_2–	3.15	–C(O)CH(CH_3)CH_2 –	214.22
–C(O)C(CH_3)=CH_2	6.15	–C(O)CH_2CH_3	217.04

In a typical experiment, [$PdCl_2$(dppf)] (1.54×10^{-3} mmol) was added to 70 mL of H_2O–HCOOH (H_2O = 60 molar % calculated as mol H_2O/(mol H_2O + mol HCOOH × 100) in the bottle placed in the autoclave. The autoclave was washed by pressurizing with a 1/1 mixture of CO/C_2H_4 (*ca.* 0.5 MPa) and then depressurizing to atmospheric pressure: this cycle was repeated 5 times, at room temperature. Then 10 mL of liquid propene was added to the reactor containing the catalyst and the H_2O–HCOOH mixture. The autoclave was pressurized with 0.5 MPa of the CO/E mixture and then heated to 90 °C in *ca.* 10 min without stirring. The pressure was then adjusted to the desired value (typically 4.5 MPa, total pressure by admitting CO and E in the ratio 1/1) while stirring. The pressure was maintained constant throughout the experiment (1 h, stirring rate 700 rpm) by continuously supplying the E/CO = 1/1 monomers. At the end of the experiment the autoclave was quickly cooled and carefully depressurized. GC analysis showed that no light product was formed. The polymer was completely precipitate by addition of 100 mL of H_2O, filtered, washed with water and acetone and dried under vacuum at 70 °C.

The dried polymer was weighted and the productivity was calculated as gPECO/(gPd h).

2.4. Polymers characterization

All the terpolymers have been characterized by IR and NMR spectroscopies. The IR spectra show typical stretching absorptions of CO groups at 1695 cm^{-1} and of –CH_2– groups at 2915 cm^{-1}. Table 1 shows some selected ^1H NMR e ^{13}C NMR signals and the assignments are in good agreement with the values reported in literature [34,35].

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 [36]. 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.

The T_m of terpolymers was determined by the DSC calorimetric curves.

3. Results and discussion

The [$PdCl_2$(dppf)] complex in H_2O–HCOOH catalyzes the terpolymerization of propene and ethene with CO (Scheme 1) leading to a productivity of 7350 gPECO/(gPd h) under the typical experimental conditions reported in Section 2. This productivity is far superior to the productivity of [$Pd(H_2O)_2$(dppf)]$(TsO)_2$ in MeOH for the CO–ethene copolymerization [31]. No data have been reported for the terpolymerization with this catalyst. However, it may be foreseen that this catalyst is even less active for the terpolymerization, because it is expected that in the presence of propene the rate of terpolymerization may be slower than that of the CO–ethene copolymerization.

The influence of the H_2O/HCOOH molar ratio, of the amount of liquid propene initially charged and of the reaction time on the