Water-Soluble Palladium(II) Catalysts for the Alternating Co- and Terpolymerization of CO and Olefins in Aqueous Phase

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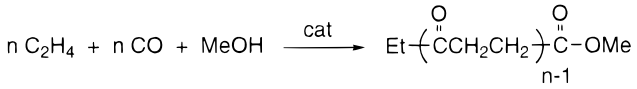
ABSTRACT: The water-soluble diphosphine $(NaO_3S(C_6H_4)CH_2)_2C(CH_2PPh_2)_2$ (Na_2DPPPDS) was employed to prepare the bis-trifluoroacetate Pd(II) complex Pd(Na_2DPPPDS)$(CO_2CF_3)_2$·2THF (**1**). The catalytic performance of **1** in the co- and terpolymerization of CO and ethene and propene in water has been studied in different experimental conditions. In combination with both a protic acid, commonly *p*-toluenesulfonic acid, and an organic oxidant such as 1,4-benzoquinone, **1** forms the most efficient catalyst systems ever reported for the copolymerization of CO and ethene in water. Under comparable conditions, the activity of **1** is similar to that of the industrial Pd(II) 1,3-bis(diphenylphosphino)propane catalysts in MeOH. Unlike the latter which yield a mixture of copolymers bearing diketone, keto-ester, or diester end groups, the copolymers and terpolymers produced with the Na_2DPPPDS-based catalysts have exclusively ketonic end groups for average molecular weights ranging from 10 to 30 kg mol^{-1} depending on the reaction conditions. In situ high-pressure NMR (HPNMR) studies have been performed in actual copolymerization conditions using D_2O as solvent. The only palladium complex visible on the NMR time scale contains the diphosphine ligand and TsO^- or water groups. It is suggested that this palladium complex acts as a reservoir of "(diphosphine)Pd(II)" moieties which are delivered into the catalysis cycle as Pd−H species by reaction with water and/or H^+. A catalysis cycle is proposed on the basis of HPNMR experiments, the structure of the copolymers, and the occurrence of the water-gas-shift reaction.

Introduction

Identifying alternative conditions and solvents in catalytic reactions is one of the major challenges to chemists on the eve of the 21st century. Many chemical processes, even those based on relatively recent technologies, may no longer be acceptable if harmful chemicals and solvents are employed and eventually dispersed in the environment. The immobilization of metal complexes in water for application to aqueous catalysis, including also biphase and supported phase catalysis, is a technique that can address many issues of green chemistry.[1] Water is indeed the most environmentally friendly and cheapest solvent with unique chemical and physical properties. Even the poor solubility of many organic materials and gases in water may represent an environmentally benign feature as the kinetic sluggishness of the reactions can indeed result in increased chemoselectivity while no substantial amount of reagents, products, or byproducts remain in the aqueous phase.[1,2]

Recent applications of aqueous catalysis to industrial processes include the hydroformylation and hydrogenation of olefins,[3] the hydrocyanation of various unsaturated compounds,[4] and the hydrodimerization of butadiene.[5] Other catalytic reactions employing water as solvent are still at the stage of basic research but with actual industrial premises. One of these reactions is the alternating copolymerization of carbon monoxide with alkenes, a process that dates back to the early 1950s when Reppe copolymerized ethene and CO in water with a Ni(II) catalyst at 200 °C and 200 bar to obtain perfectly alternating oligomers.[6] Only recently, however, polyketone materials synthesized by the terpolymerization of CO with ethene and propene have become commercially available with the name of Carilon by Shell.[7,8] The production of ethene/carbon monoxide copolymers is carried out in MeOH at moderated temperature (80−90 °C) in the presence of a catalyst system generally comprising a Pd(II) salt with weakly coordinating counteranions, the diphosphine 1,3-bis(diphenylphosphino)propane (dppp), and a strong protic acid or an organic oxidant (Scheme 1).[8,9]

Scheme 1



The excellent tolerance to water and oxygen of many highly active copolymerization catalysts[8e,9,10] and the development of efficient technologies for the synthesis of water-soluble phosphines[1,2] are largely contributing to stimulate the increasing interest in the design of new palladium systems for the production of polyketone materials by aqueous catalysis. The first of such attempts was reported in 1994 by Jiang and Sen, who copolymerized ethene (or/and propene) with CO in water using the catalyst [Pd(dppp-SO_3K)$(H_2O)_2$]$(BF_4)_2$ prepared in situ by dissolving [Pd$(MeCN)_4$]$(BF_4)_2$ and dppp-SO_3K.[11] The reported productivities were quite low, however (ca. 470 g of C_2H_4/CO copolymer and 170 g of C_2H_4/C_3H_6/CO terpolymer per gram of Pd in 22 and 44 h, respectively). A remarkable increase in productivity was later reported by Sheldon and co-workers, who employed a dppp-SO_3Na ligand of better quality as well as the coaddition of *p*-toluenesulfonic acid to obtain low molecular weight copolymers (6−7 kg mol^{-1}) bearing ketone and acid end groups (Scheme 2).[12] In these conditions, the productivity increased remarkably in the first hour (up to 4 kg of C_2H_4/CO copolymers per gram of Pd), which is still lower, however, than that reported in MeOH in comparable procedures (ca. 6−7 kg).[8,9,13]

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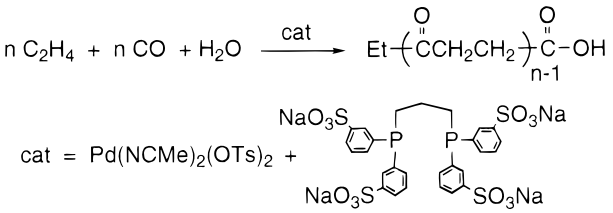
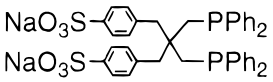
Scheme 2



No information on the catalyst durability, which is the real drawback of the Pd-assisted alkene/CO copolymerization reactions in MeOH, was provided.

In this work are described new water-soluble Pd(II) catalysts for the alternating co- and terpolymerization of CO and ethene or ethene/propene which exhibit improved efficiency, good durability, and capability of producing high molecular weight polyketones bearing exclusively keto end groups. The catalyst precursors contain the ligand $(NaO_3S(C_6H_4)CH_2)_2C(CH_2PPh_2)_2$ (Na_2-DPPPDS) in which the main carbon backbone of dppp is preserved but the polar sulfonate groups are located far away from the phosphorus donors.[14] This type of molecular structure has been designed in order minimize the steric hindrance and the negative charge in the proximity of the donor atoms. As a result, the phosphorus atoms are quite insensitive to the presence of the polar group(s) in the ligand framework and able to coordinate metal ions as efficiently as their nonwater-soluble precursors.[1,2,13,14]



Na_2DPPPDS

A high-pressure NMR (HPNMR) study[13,15] of the C_2H_4/CO copolymerization reaction has been performed, which for the first time has provided a snapshot of what happens in real catalytic conditions.

Experimental Section

All reactions and manipulations were routinely performed, unless otherwise stated, under a nitrogen atmosphere by using standard Schlenk-type techniques. The copolymerization reactions carried out in batch mode were performed with a stainless steel Parr 4565 reactor (100 mL) equipped with a magnetic drive stirrer and a Parr 4842 temperature and pressure controller. The copolymerization reactions carried out at constant pressure were performed with a 250 mL stainless steel autoclave, constructed at the ISSECC-CNR (Firenze, Italy), equipped with a magnetic drive stirrer, a Parr 4842 temperature and pressure controller, and a high-pressure injector. The autoclave was connected to a high-pressure gas reservoir from which an 1:1 ethene/CO mixture was supplied to maintain a constant pressure all over the catalytic reactions. The consumption of the gaseous reagents with time was monitored following the pressure drop in the gas reservoir by means of a pressure transducer. The ligand Na_2DPPPDS was prepared as previously described.[14] 1,4-Benzoquinone (98%), *p*-toluenesulfonic acid monohydrate (98.5+%), and the complexes $[Pd(CO_2CF_3)_2]$ were obtained from Aldrich and used as received. Deionized water was employed in the copolymerization reactions. 1,1,1,3,3,3-Hexafluoropropan-2-ol-d_2 (HFIP-d_2) was purchased from Cambridge Isotope Laboratories, Andover, MA. All the other reagents and solvents were reagent grade and were used as received by commercial suppliers. ^{1}H, ^{13}C-{^{1}H}, and ^{31}P{^{1}H} NMR spectra were obtained on a Bruker ACP 200 spectrometer (200.13, 50.32, and 81.01 MHz, respectively). All chemical shifts are reported in ppm (δ) relative to tetramethylsilane, referenced to the chemical shifts of residual solvent resonances (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P). The 10 mm sapphire NMR tube was purchased from Saphikon, Milford, NH, while the titanium high-pressure charging head was constructed at the ISSECC−CNR (Firenze, Italy).[16] *Note*: *since high gas pressures are involved, safety precautions must be taken at all stages of studies involving high-pressure NMR tubes.* Elemental analyses were performed using a Carlo Erba model 1106 elemental analyzer. Infrared spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrophotometer. Molecular weights of selected polyketone materials were measured on a Waters gel permeation chromatograph equipped with a differential refractometer. Either pure HFIP or a mixture of trichlorobenzene/phenol was used as the solvent, and polystyrene standards were used to calibrate the instrument. Limiting viscosity numbers (LVN) were measured in *m*-cresol at 60 °C in a standard capillary viscosity-measuring device. Differential scanning calorimetry (DSC) experiments were performed on a Perkin-Elmer DSC 7 thermal analyzer at a rate of 20 °C/min. The melting temperatures were taken as peak melting temperatures, and the heats of fusion were calculated from the peak areas. After cooling to ambient temperature at 20 °C/min, a second scan, also at a heating rate of 20 °C/min, was recorded. The degree of crystallinity of the polymers was estimated by wide-angle X-ray scattering (WAXS). The WAXS patterns were recorded with an instrumentation consisting of a Philips PW 1830 X-ray generator providing Cu Kα, Ni filtered (λ = 1.5418 Å) linear beams equipped with a Philips PW 1820 vertical goniometer working in the $\theta-2\theta$ geometry with step scanning motors and proportional detector. The cyclic voltammetric studies were performed in a three-electrode cell having a platinum working electrode surrounded by a platinum-spiral counter electrode and the aqueous saturated calomel reference electrode (SCE) mounted with a Luggin capillary. A BAS 100A electrochemical analyzer was used as a polarizing unit. Controlled potential coulometry was carried out with an Amel 552 potentistat equipped with an Amel 558 integrator.

Preparation of $Pd(Na_2DPPPDS)(CO_2CF_3)_2\cdot 2THF$ (1). A solid sample of the diphosphine ligand Na_2DPPPDS (215 mg, 0.27 mmol) was added to a stirred solution of $[Pd(CO_2CF_3)_2]$ (83 mg, 0.25 mmol) in MeOH (30 mL) at room temperature. After 30 min, the resulting yellow solution was concentrated to 10 mL under vacuum. Portionwise addition of THF (30 mL) led to the precipitation of **1** in quantitative yield. Anal. Calcd (found) for $C_{53}H_{52}F_6Na_2O_{12}P_2PdS_2$: C, 50.0 (49.5); H, 4.1 (4.2). IR (Nujol mull): ν(C=O) 1684 (s) cm^{-1}. ^{31}P{^{1}H} NMR (MeOH-d_4): δ 18.7 (s, $w_{1/2}$ = 17 Hz). ^{1}H NMR (MeOH-d_4): δ 7.7−6.8 (m, 28 H, Ph and $(C_6H_4)SO_3Na$), 2.54 (s, 4 H, C$H_2(C_6H_4)SO_3$Na), 2.44 (d, 4 H, J(HP) = 8.7 Hz, CH_2P). ^{13}C{^{1}H} NMR (MeOH-d_4, 20 °C, 50.32 MHz): 166.1 (q, J(CF) = 38.6 Hz, CO_2CF_3), 145.8 (s), 141.0 (s), 140.1 (d, J(CP) = 10.5 Hz), 135.7 (s), 132.8 (d, J(CP) = 26.1 Hz), 130.4 (s), 130.1 (s), 127.4 (s), 107.1 (q, J(CF) = 279.5 Hz, CO_2CF_3), 32.9 (br d, J(CP) = 19.1 Hz).

Ethene−CO Copolymerization. Autoclave Experiments. The reaction conditions and the results of these experiments are summarized in Tables 1 and 2. Typically, a solution of 1,4-benzoquinone (BQ, 90 mg, 0.83 mmol) in water (95 mL) was introduced by suction into a 250 mL autoclave previously evacuated by a vacuum pump. A solution of both **1** (11.8 mg, 1.04×10^{-2} mmol) and *p*-toluenesulfonic acid (TsOH, 40 mg, 0.21 mmol) in water (5 mL) was introduced into the injector of the autoclave under nitrogen. The autoclave was first pressurized with a 1:1 mixture of C_2H_4 and CO to 600 psi at room temperature and then immersed into an oil bath preheated to 85 °C. When the reaction mixture reached the reaction temperature, the catalyst solution in the injector was introduced into the reaction chamber by a nitrogen pressure of 60 psi higher than the pressure inside the reaction vessel. During the reaction the pressure level was kept constant at ca. 750 psi by continuous feeding of an equimolar mixture of C_2H_4 and CO from the high-pressure reservoir. The reaction mixture was then stirred (1400 rpm) for the required reaction time. The reaction was stopped by cooling the autoclave to

Table 1. Alternating Copolymerization of Ethene and CO Catalyzed by 1 in Water for 1 h[a]

entry	P_{tot} (psi)[b]	TsOH (equiv)	PH_2 (psi)[c]	Na_2DPPPDS (equiv)	BQ (equiv)	productivity[d]	productivity[d,e]	entry[e]
1	600	300				4.8	4.8	1a
2	600	20			80	4.8	7.0	2a
3	600	300	40		80	5.8		
4	600	20	40		80	4.8		
5	600	20		2	80	6.1	2.4	5a
6[f]	600	20		2	80	5.3		
7	900	20			80	5.5		
8	900	300	40		80	6.6		
9	900	20		2	80	7.2		
10[f]	900	20		2	80	6.6		

[a] Reaction conditions: H_2O, 100 mL; catalyst **1**, 1.04×10^{-2} mmol; temperature, 85 °C; stirring rate, 1400 rpm. [b] Initial pressure of C_2H_4/CO (1:1). [c] Initial pressure of H_2. [d] Expressed as kg of copolymer (g of Pd × h)$^{-1}$. [e] Reaction conditions: MeOH, 100 mL; catalyst **2**, 1.04×10^{-2} mmol; TsOH, 2 equiv; BQ and dppp, as in the related runs in H_2O; initial pressure of C_2H_4/CO (1:1), 600 psi; temperature, 85 °C; stirring rate, 1400 rpm. [f] 1,4-Dioxane/H_2O 1:1 (v:v), 100 mL.

Table 2. Alternating Copolymerization of Ethene and CO Catalyzed by 1 in Water for 3 h[a]

entry	P_{tot} (psi)[b]	TsOH (equiv)	PH_2 (psi)[c]	Na_2DPPPDS (equiv)	BQ (equiv)	productivity[d]	productivity[d,e]	entry[e]
1	600	300				2.6	4.3	1a
2	600	20			80	2.8	5.4	2a
3	600	300	40		80	2.9		
4	600	20		2	80	3.7		
5[f]	600	20		2	80	4.9		

[a] Reaction conditions: H_2O, 100 mL; catalyst **1**, 1.04×10^{-2} mmol; temperature, 85 °C; stirring rate, 1400 rpm. [b] Initial pressure of C_2H_4/CO (1:1). [c] Initial pressure of H_2. [d] Expressed as kg of copolymer (g of Pd × h)$^{-1}$. [e] Reaction conditions: MeOH, 100 mL; catalyst **2**, 1.04×10^{-2} mmol; TsOH, 2 equiv; BQ as in the related runs in H_2O; initial pressure of C_2H_4/CO (1:1), 600 psi; temperature, 85 °C; stirring rate, 1400 rpm. [f] 1,4-Dioxane/H_2O 1:1 (v:v), 100 mL.

Table 3. Terpolymerization of Ethene, Propene, and CO Catalyzed by 1 in Water[a]

entry	propene (g)	Na_2DPPPDS (equiv)	time (h)	productivity[b]
1	1		3	2.8
2	2		3	2.8
3	2		1	5.1
4	2	2	3	3.4
5	2	2	1	5.9
6[c]	2	2	3	4.7
7[c]	2	2	1	7.4
8	5		3	2.7
9	7		3	1.9

[a] Reaction conditions: H_2O, 100 mL; catalyst **1**, 1.04×10^{-2} mmol; TsOH, 20 equiv; BQ, 80 equiv; initial pressure of C_2H_4/CO (1:1), 600 psi; temperature, 85 °C; stirring rate, 1400 rpm. [b] Expressed as kg of copolymer (g of Pd × h)$^{-1}$. [c] 1,4-Dioxane/H_2O 1:1 (v:v), 100 mL.

room temperature by means of an ice−water bath. After the unreacted gases were released, the formed insoluble ethene−carbon monoxide copolymer was filtered off, washed with methanol, and dried in a vacuum oven at 70 °C to give a white powder. Anal. Calcd (found) for $(COCH_2CH_2)_n$: C, 64.3 (64.1); H, 7.2 (7.1). IR (powder sample in KBr pellet): 3391 (w), 2912 (m), 1694 (vs), 1408 (s), 1333 (s), 1259 (m), 1056 (s), 811 (m), 592 (m). ^{1}H NMR (HFIP-d_2): δ 2.80 (s, CH_2C(O)CH_2), 2.55 (q, J(HH) = 7.5 Hz, C(O)CH_2CH$_3$), 1.07 (t, J(HH) = 7.5 Hz, C(O)CH$_2$CH_3). ^{13}C{^{1}H} NMR (HFIP-d_2): δ 219.0 (*C*(O)CH$_2$CH$_3$), 215.1 (CH$_2$*C*(O)CH$_2$), 37.5 (*C*H$_2$C(O)*C*H$_2$), 8.3 (C(O)CH$_2$*C*H$_3$).

Ethene−Propene−CO Terpolymerization. Autoclave Experiments. The reaction conditions and the results of these experiments are summarized in Table 3. Terpolymerization reactions were carried out following a procedure analogous to that reported above for the copolymerization. The required amount of propene was introduced in the autoclave just before pressurizing with the C_2H_4/CO mixture. IR (powder sample in KBr pellet): 3391 (w), 2912 (m), 1694 (vs), 1408 (s), 1333 (s), 1259 (m), 1056 (s), 811 (m), 592 (m). ^{1}H NMR (HFIP-d_2): δ 3.05 (m, CH$_2$C*H*(CH$_3$)), 2.80 (s, CH_2C(O)CH_2), 2.55 (q, J(HH) = 7.5 Hz, C(O)CH_2CH$_3$), 1.15 (d, J(HH) = 6.5 Hz, CH$_2$CH(CH_3)), 1.07 (t, J(HH) = 7.5 Hz, C(O)CH$_2$CH_3). ^{13}C{^{1}H} NMR (HFIP/C_6D_6, 9:1, v:v): δ 216.9 (*C*(O)CH$_2$CH$_3$), 214.2 (CH$_2$*C*(O)CH(CH$_3$)), 212.7 (CH$_2$*C*(O)CH$_2$), 44.9 (C(O)*C*H$_2$CH(CH$_3$)), 41.2 (C(O)CH$_2$*C*H(CH$_3$)), 35.5 (*C*H$_2$C(O)*C*H$_2$), 34.3 (*C*H$_2$C(O)CH(CH$_3$)), and 15.5 (C(O)CH$_2$CH(*C*H$_3$)), 6.6 (C(O)CH$_2$*C*H$_3$).

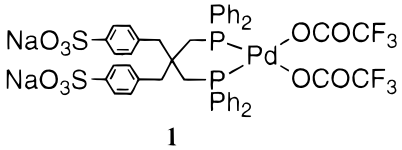
Ethene−CO Copolymerization. In Situ High-Pressure NMR Experiments. (A) D_2O. A 10 mm sapphire HPNMR tube was charged with a solution of **1** (17.7 mg, 1.56×10^{-2} mmol) and a 20-fold excess of TsOH in D_2O (2 mL) under nitrogen. The tube was pressurized with an equimolar mixture of C_2H_4 and CO to 600 psi at room temperature and then placed into a NMR probe at 20 °C. The reaction was followed by variable-temperature ^{31}P{^{1}H} and ^{1}H NMR spectroscopy over the temperature range from 20 to 85 °C. After 2 h at 85 °C, the tube was cooled to room temperature and removed from the probe head. The formed copolymer appeared as an off-white solid floating over a colorless solution.

(B) D_2O/1,4-Dioxane. A 10 mm sapphire HPNMR tube was charged with a solution of **1** (17.7 mg, 1.56×10^{-2} mmol) in a 1:1 mixture of D_2O/1,4-dioxane (2 mL) under nitrogen and then placed into a NMR probe at 20 °C (^{31}P{^{1}H} NMR singlet at δ 19.2). The catalyst solution was treated sequentially with TsOH (15 mg, 0.08 mmol), BQ (34 mg, 0.32 mmol), and a 1:1 mixture of C_2H_4/CO (600 psi). The reaction was analogously followed by variable-temperature ^{31}P{^{1}H} and ^{1}H NMR spectroscopy over the temperature range from 20 to 85 °C.

A detailed description of these HPNMR studies is given in a forthcoming section.

Results and Discussion

Preparation and Characterization of the Pd(II) Catalyst Precursor. The reaction of Na_2DPPPDS with [Pd(CO$_2$CF$_3$)$_2$] in MeOH yields the complex Pd(Na_2DPPPDS)(CO$_2$CF$_3$)$_2$·2THF (**1**) in analytically pure form.



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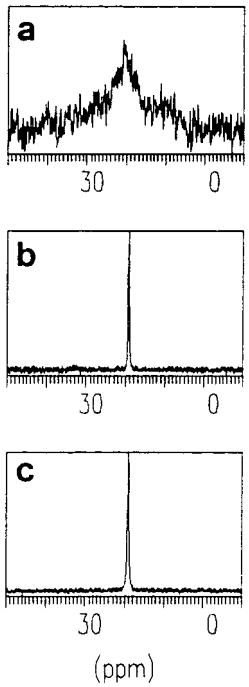


Figure 1. $^{31}P\{^1H\}$ NMR spectra (81.01 MHz, 20 °C) of **1** in different solvent media: D_2O (a); 1,4-dioxane/D_2O (1:1, v:v) (b); MeOH-d_4 (c).

Complex **1** appears as an off-white, hygroscopic powder which readily dissolves in polar solvents such as H_2O and MeOH in which no appreciable decomposition at room temperature is observed by NMR spectroscopy within 24 h. However, aquo species most probably form upon dissolution of **1** in water as shown by the $^{31}P\{^1H\}$ NMR spectrum in D_2O (Figure 1a). The very broad and complex line shape of the spectrum indeed suggests that the hydration of the metal center is accompanied by intramolecular and intermolecular exchange reactions of water molecules and, most likely, by the formation of μ-OH dimeric species.[17] Appreciable narrowing of the $^{31}P\{^1H\}$ NMR signal due to the magnetically equivalent phosphorus nuclei occurs by adding 1,4-dioxane (1:1, v:v) to the water solution of **1** (singlet at 19.2 ppm, $w_{1/2} = 21$ Hz, Figure 1b). A relatively narrow signal features also the $^{31}P\{^1H\}$ NMR spectrum of **1** in MeOH singlet at 18.7 ppm ($w_{1/2} = 17$ Hz, Figure 1c).

The electrochemical behavior of **1** has been studied in H_2O, H_2O/1,4-dioxane, or MeOH solutions using $LiClO_4$ as supporting electrolyte. Compound **1** in water solution undergoes a reduction step at $E_p = -0.36$ V (vs SCE) that shows features of chemical reversibility coupled to electrode adsorption phenomena. A similar reduction behavior is exhibited in a 1:1 (v:v) H_2O/1,4-dioxane mixture ($E_p = -0.42$ V), whereas the complex is irreversibly reduced at $E_p = -0.20$ V in MeOH with subsequent formation of palladium metal. Even though these adsorption phenomena did not allow us to perfom reliable controlled potential coulometric experiments, the reduction step most likely involves one electron as observed for the nonsulfonated derivative $Pd\{(PhCH_2)_2C(CH_2PPh_2)_2\}(CO_2CF_3)_2$ which in MeOH undergoes a chemically reversible Pd(II)/Pd(I) reduction step at $E^{\circ\prime} = -0.67$ V.[13] The slightly negative reduction potential in H_2O anticipates the instability of **1** in the reducing environment of the CO/C_2H_4 copolymerization reaction. On the other hand, the chemical reversibility of the reduction step forecasts an effective reoxidation by an appropriate chemical oxidant (see below).

Copolymerization of Ethene and CO in Water. Following a partial optimization process, the catalytic performance of **1** for the copolymerization of ethene and CO in water was tested under the experimental conditions reported in Table 1. Besides summarizing the results obtained for 1 h runs, Table 1 also reports a few selected data obtained in our high-pressure reactor ensemble with the catalyst precursor $Pd(dppp)(CO_2CF_3)_2$ (**2**) in MeOH.[13]

Our typical values of temperature (85 °C), catalyst concentration (ca. 10^{-4} M), and total pressure (600 psi) are in the usual range of highly efficient catalytic systems based on $Pd(dppp)X_2$ precursors (X = unidentate ligand) in MeOH.[8,9,13] In water, however, a much higher concentration of protic acid was required for having productivities comparable to those in MeOH. For example, **1** yielded 4.8 kg of polyketone (g of Pd × h)$^{-1}$ in the presence of 300 equiv of TsOH, while the same productivity with the catalyst precursor **2** in MeOH was obtained with 2 equiv of acid (entries 1 and 1a). Only with the coaddition of 80 equiv of BQ could the concentration of acid significantly be reduced in the aqueous reactions with no decrease in productivity (entry 2). In these conditions, however, **2** in MeOH was more active by ca. 45% (entry 2a). The activity gap between **1** and **2** could effectively be reduced and even canceled by various modifications of the aqueous catalytic system. The simple addition of H_2 (40 psi) to the catalytic mixture raised the productivity from 4.8 to 5.8, but a high concentration of TsOH was required (entries 3 and 4). Unlike the analogous reaction in MeOH (entry 5a), the most beneficial effect on the polymerization rate was produced by the addition of 2 equiv of free ligand which gave 6.1 kg of polyketone (g of Pd × h)$^{-1}$ (entry 5). Under these conditions, the use of a 1:1 mixture of H_2O and 1,4-dioxane as solvent produced a lower amount of copolymer (entry 6). These productivity values are the highest ever reported for C_2H_4/CO copolymerization reactions in water.[11,12] Finally, increasing the C_2H_4/CO pressure from 600 to 900 psi increased the productivity following the same experimental trend: 5.5, 6.6, and 7.2 kg of polyketone (g of Pd × h)$^{-1}$ were obtained in the presence of the coreagent systems TsOH/BQ, TsOH/BQ/H_2, and TsOH/BQ/free ligand, respectively (entries 7−9). Again, the addition of 1,4-dioxane resulted in a slight decrease of productivity as compared to the case of the analogous reaction in pure water (entry 10).

To test the catalyst durability in the various experimental conditions investigated, the reaction time was prolonged to 3 h while maintaining a constant pressure of 600 psi (Table 2).

Consistent with a slow but effective deactivation of the catalyst, the productivities were invariably lower than those found for the 1 h runs. As an example, 2.6 (entry 1), 2.8 (entry 2), 2.9 (entry 3), and 3.7 kg of polyketone (g of Pd × h)$^{-1}$ (entry 4) were obtained following the optimization procedure described above. Notably, the use of a 1:1 mixture of H_2O and 1,4-dioxane in combination with the addition of 2 equiv of free ligand gave a productivity value of 4.9 (entry 5), which is only slightly lower than that found with **2** in MeOH (entry 2a).

Plotting the consumption of the gaseous reagents vs time for 3 h reactions clearly shows that the catalyst activity reaches a maximum during the first 30 min and then steadily decreases (run 4, Figure 2). In contrast, the catalyst activity remains almost constant over the

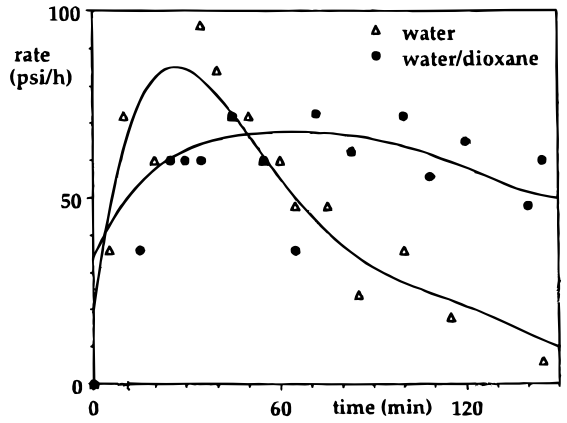


Figure 2. Gas consumption during CO/C_2H_4 copolymerization reactions catalyzed by **1** in different solvent media.

whole reaction time when a 1:1 mixture of 1,4-dioxane/water is employed as solvent (run 5, Figure 2). This evidence suggests that the larger productivity in water/1,4-dioxane is due not only to the major solubility of the gaseous reactants but also to the greater stability of the catalyst system.

Additional pieces of experimental evidence accumulated over the course of the copolymerization reactions catalyzed by **1** in water are outlined below.

Unlike the reactions in MeOH catalyzed by **2**,[8,9,13] the presence of a strong protic acid was of mandatory importance for the occurrence of the copolymerizations in water. In our hands, TsOH ($pK_a = -2.7$)[18] was invariably more efficient than TFA ($pK_a = 0$) to assist the copolymerization reactions, and for this reason it was successively employed in all the catalytic runs. Indeed, with no acid, almost no reaction took place (0.4 kg of polyketone (g of Pd × h)$^{-1}$). In the absence of a protic acid, even the addition of 80 equiv of BQ did not lead to appreciable catalytic activity (1.8 kg of polyketone (g of Pd × h)$^{-1}$). The amount of 300 equiv of acid (3×10^{-2} M, Tables 1 and 2) with respect to the catalyst precursor corresponds to a peak of catalytic activity obtained from a study in which, following analogous experimental conditions, the concentration of acid was varied from 2×10^{-4} to 2×10^{-1} M. A similar procedure was carried out also to determine the optimal concentrations of the TsOH/BQ mixture (20/80 equiv). Once the optimal concentrations of acid and organic oxidant were fixed up at 85 °C, the temperature was varied from 65 to 125 °C, but only a detrimental effect was obtained. The last parameter to be otimized was the catalyst concentration. To our surprise, a decrease in productivity was observed for catalyst concentrations higher than 10^{-4} M while only a very slight decrease was observed for lower concentrations down to 5×10^{-5} M. Indeed, for a concentration of 3×10^{-4} M the productivity decreased by ca. 30%. The present catalytic system tolerates the presence of air in the reactor, but the initial introduction of 20 psi of O_2 into the reactor gave a 10% decrease in productivity.

To verify whether the water-gas-shift (WGS) reaction is catalyzed by **1** concomitantly to the C_2H_4/CO copolymerization as occurs for the catalyst [Pd(dppp-SO_3K)-$(H_2O)_2$]$(BF_4)_2$,[11] the gaseous phases of some reactions were carefully discharged into aqueous solutions saturated with $Ba(OH)_2$. As a result, the precipitation of an appreciable amount of $BaCO_3$ was observed in all cases.

The occurrence of the WGS reaction was also confirmed by the observation that the pH value (2.8) of the water solution of any standard catalytic run with 20 equiv of TsOH and 80 equiv of BQ remained practically unchanged at the end of the reaction despite the apparent consumption of protons by BQ to form hydroquinone.

Terpolymerization of Ethene, Propene, and CO in Water. On the basis of the optimal reaction conditions determined for the copolymerization runs, the palladium complex **1** was successfully employed as catalyst precursor for the terpolymerization of CO with ethene and propene in water (Table 3). In line with previous experiments in MeOH,[8,9] the yield of terpolymer was found to inversely depend on the amount of propene in the reactor. In particular, the productivity was comparable to that obtained for the ethene/CO copolymer only for runs carried out in the presence of a low amount of propene (≤2 g). For higher concentrations of propene, the productivity decreased (runs 8, 9 vs runs 1, 2), but the incorporation of propene in the polymeric chains was concomitantly enhanced (up to 5% with respect to ethene) (see below). This behavior is typical for terpolymerization reactions catalyzed by Pd−(diphosphine) complexes in MeOH.[8] Like the ethene/CO copolymerization, the addition of 2 equiv of free ligand and/or the use of 1,4-dioxane as cosolvent was found to exert a beneficial effect on the polymerization rate at comparable propene concentrations (runs 2, 3 vs runs 4, 5 and 6, 7, respectively). Moreover, consistent with a progressive, although slow, deactivation of the catalyst with time, the productivities of the 1 h runs were higher than those observed for the corresponding runs prolonged to 3 h.

The use of water as reaction medium for the terpolymerization of CO, ethene, and propene has previously been reported by Sen using [Pd(dppp-SO_3K)-$(H_2O)_2$]$(BF_4)_2$.[11] In conditions of much higher gas pressure (500 psi of CO, 500 psi of C_2H_4, and 38 g of propene in a 125 mL bomb) and of lower temperature (50 °C), this catalyst precursor gave a productivity of 0.004 kg of terpolymer (g of Pd × h)$^{-1}$, which is dramatically lower than that obtainable with catalyst **1** (up to 5.9 kg of terpolymer (g of Pd × h)$^{-1}$ (run 5).

A major contribution to the much greater catalytic activity of the present water-soluble catalysts as compared to that of the dppp-SO_3K-based Pd(II) catalysts, especially in the terpolymerization reactions, is certainly provided by the minor steric crowding at the Pd center as the two sulfonate groups in Na_2DPPPDS are positioned far away from the phosphorus donors, whereas the four sulfonate groups in dppp-SO_3K wrap the metal center. The different overall charge of the complex species resulting from the presence of either two or four sulfonate groups in the ligands may also play a relevant role in determining the catalyst efficiency and/or catalytic mechanism. For example, the kinetic instability of the "(Na_2DPPPDS)Pd−COOH" moiety, which determines the selective formation of diketone polymers (see below), is most likely electronic in nature.

Copolymerization of Ethene and CO. In Situ HPNMR Studies. The C_2H_4/CO copolymerization catalyzed by **1** in water was studied in an HPNMR tube under experimental conditions that were as close as possible to those employed in the batch reactions. The only significant differences were a higher concentration of the catalyst precursor for a better resolution and acquisition of the NMR spectra and, obviously, a lower stirring rate. The mass transfer of gases from the

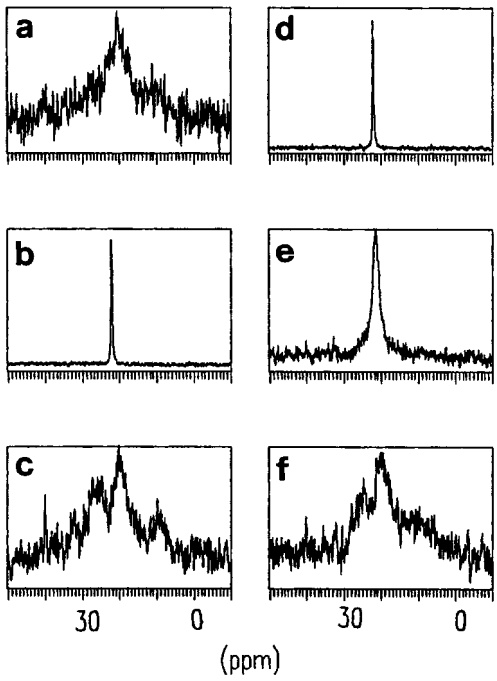


Figure 3. Selected $^{31}P\{^1H\}$ HPNMR spectra (sapphire tube, D_2O, 20−85 °C, 81.01 MHz) recorded during a CO/C_2H_4 copolymerization reaction assisted by **1** in the presence of 20 equiv of TsOH and a CO/C_2H_4 pressurre of 600 psi: at room temperature (a); first heating to 85 °C (b); cooling to room temperature (c); second heating to 85 °C (d); cooling to 60 °C (e); cooling to room temperature (f).

headspace of the 10 mm NMR tubes is generally efficient enough to replenish the solution which is being depleted of the reagents by the catalyst.[13,15] In particular, the amount of gaseous reagents in the headspace of the tubes was large enough to maintain a high concentration of C_2H_4/CO in the solution (^1H NMR evidence for ethene) in conditions of slow rate like those determined by the high catalyst concentration employed in the HPNMR experiments (vide infra). A sequence of selected $^{31}P\{^1H\}$ NMR spectra is reported in Figure 3 for a reaction in D_2O catalyzed by **1** in the presence of a 20-fold excess of TsOH and of 600 psi of an equimolar mixture of C_2H_4 and CO.

The spectrum shown in Figure 3a refers to the catalytic system at room temperature. The spectrum is similar to that of the catalyst precursor without CO, C_2H_4, or acid indicating that, at room temperature, none of these reagents drastically modify the ligand environment at palladium which most likely comprises water and TsO^- ligands in rapid exchange. This was confirmed by independent experiments in which CO, C_2H_4, and TsOH were separately added to D_2O solutions of **1**. Heating the tube to 85 °C results in a remarkable line narrowing, singlet at 22.1 ppm ($w_{1/2}$ = 28 Hz) (Figure 3b) as well as the formation of the polyketone which, owing to its low density, accumulates over the liquid surface. Cooling the tube down to 20 °C and heating again to 85 °C gives the same picture (Figure 3c−d). Between 85 and 20 °C, the signal simply broadens without changing the chemical shift (Figure 3e). The heating/cooling process was repeated several times with no apparent degradation of the catalytic system. After 2 h, the tube was cooled to room temperature, and the contents were analyzed by multinuclear NMR spectroscopy (Figure 3f). The tube was then removed from the spectrometer, and the solid copolymer was separated by filtration and analyzed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy (vide infra). Water was removed from the liquid phase under reduced pressure, and the oily residue, extracted with $CHCl_3$, was analyzed by GC/MS. In line with the chemoselectivity of the copolymerization reaction, no trace of C_2H_4/CO oligomers or other carbonylation products was detected.

In an attempt to identify the palladium−diphosphine complex responsible for the sharp singlet observed at 85 °C, a D_2O solution **1** was heated at this temperature in an NMR tube. A black precipitate began to form in a few minutes together with phosphine oxide. The experiment was then repeated in the presence of 20 equiv of TsOH. As a result, no decomposition of the palladium precursor was observed, and the $^{31}P\{^1H\}$ NMR spectrum was coincident with that acquired at the same temperature under catalytic conditions (Figure 3b). The only palladium complex visible on the NMR time scale under catalytic conditions is thus a Pd(II) species containing diphosphine and TsO^- ligands[19] which acts as a reservoir of "(diphosphine)Pd" moieties. From this resting state, a very small aliquot of catalytically active species is apparently delivered into the catalysis cycle from which it is withdrawn when the experimental conditions for the copolymerization are not fulfilled.

Characterization of the E−CO Copolymers. The copolymers, which are insoluble in water, separated during the reactions as snow-white solids with a fluffy appearance.[8,9,20] They are insoluble in most common organic solvents, while they dissolve appreciably in highly polar solvents such as HFIP, *m*-cresol, or trichlorobenzene and in strong acids such as trifluoroacetic acid. The copolymers exhibit a relatively high degree of crystallinity (30−50% as determined by X-ray diffraction). The copolymers analyzed present limiting viscosity numbers (LVN, dL g^{-1}) and average molecular weights (M_n, kg mol^{-1}) in the ranges from 0.5 to 1.0 and from 10 to 30, respectively. A polydispersity (M_w/M_n) of 2.4 ± 0.1 was found for all of the samples. It is noteworthy that the highest values of both LVN and M_n were showed by the samples produced under higher pressures.

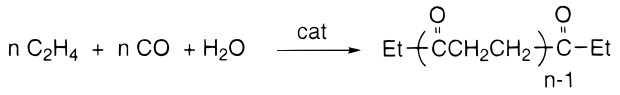
DSC curves showed T_m values between 256 and 259 °C with ΔH_f of 138 ± 2 J g^{-1}. After cooling to ambient temperature, a second scan produced a lowered melting transition in the temperature range from 213 and 226 °C with ΔH_f of 74 ± 10 J g^{-1}. The decreasing enthalpy associated with melting is a consequence of partial degradation of the samples. Indeed, the thermal degradation of the E−CO copolymers has already been widely investigated.[9c,20]

The alternating structure of the E−CO copolymers obtained in water was confirmed by elemental analysis as well as IR and NMR spectroscopies. The elemental analysis values are in agreement with an ethene/CO ratio of 1.

The IR spectra show a carbonyl stretching band centered at 1694 cm^{-1} instead of ca. 1720 cm^{-1} as in low molecular weight aliphatic ketones or in random E−CO copolymers.[9c] This feature was attributed to the presence of both dipolar interactions between carbonyl groups and electrostatic interactions among the carbonyls and the hydrogens of the methylenes in the α-position to carbonyl groups belonging to parallel chains.[9c]

The $^{13}C\{^1H\}$ NMR spectra in HFIP-d_2 contain two resonances in an approximate 2:1 intensity ratio at

Scheme 3



215.1 and 37.5 ppm, corresponding to the backbone carbonyl and α-methylene carbons, respectively. The remaining two carbon resonances at δ 219.0 and 8.3 are assigned to the carbonyl and the methyl of the ketonic end groups $-C(O)CH_2CH_3$, respectively.

The ^{1}H NMR spectra of the copolymers in HFIP-d_2 exhibit a main resonance at δ 2.80 due to the methylene protons. The small resonances at 2.55 (q, J(HH) = 7.5 Hz) and 1.07 (t, J(HH) = 7.5 Hz) are assigned to the methylene and the methyl of the ketonic end groups, respectively.

On the basis of the NMR characterization, one may thus conclude that the copolymer obtained in water with the catalyst precursor **1** contains exclusively ketone end groups as illustrated in Scheme 3.

Although the degradability of the present polyketones has not yet been studied, the presence of ketone end groups only anticipates an improved stability as compared to copolymers bearing esters or acid terminal groups as they are more susceptible to hydrolysis. The E−CO copolymers are indeed hygroscopic, and water can irreversibly modify their chemical structure so as to increase the copolymer degradability.[20]

Characterization of the E−P−CO Terpolymers. The terpolymers exhibit the same features as the E−CO copolymers in terms of solubility and crystallinity.[7−9] They present limiting viscosity number (LVN, dL g^{-1}) and average molecular weight (M_n, kg mol^{-1}) in the ranges from 0.7 to 1.1 and from 14 to 28, respectively. A polydispersity (M_w/M_n) of 2.4 ± 0.1 was found for all of the samples.

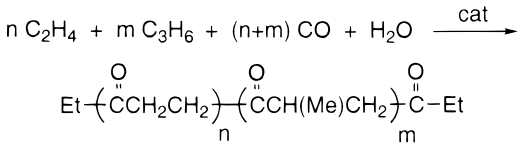
The terpolymers exhibit melting endotherms at temperatures a little lower than those of the E−CO counterparts (T_m of 240 ± 5 °C with ΔH_f of 123 ± 5 J g^{-1}) which indicates a relatively low propene content. Indeed, the amount of propene incorporated in the polymeric chains ranges from 2 to 5% as calculated by ^{1}H NMR integration. Analogously to the E−CO copolymers, lowered values of both melting point and enthalpy were observed in the second scan (T_m of 205 ± 5 °C with ΔH_f of 62 ± 4 J g^{-1}).

Elemental analysis as well as IR and NMR spectroscopies confirmed also the alternating structure of the E−P−CO terpolymers. The IR spectra show a carbonyl stretching band centered at 1694 cm^{-1} slightly broader than that found in E−CO copolymers. This is consistent with the presence of the distinct carbonyl units $CH_2C(O)CH_2CH_2$, $CH_2C(O)CH(Me)CH_2$, and $CH_2C(O)CH_2CH(Me)$.

The ^{13}C{^{1}H} NMR spectra in HFIP/C_6D_6 (9:1, v:v) are consistent with the insertion of propene into the polyketone backbone.[8e,9c] As a matter of fact, besides the signals found for the pure copolymers [δ 216.9 (C(O)CH_2CH_3), 212.7 (CH_2C(O)CH_2), 35.5 (CH_2C(O)CH_2), 6.6 (C(O)CH_2CH_3)], there are new resonances at δ 214.2, 44.9, 41.2, 34.3, and 15.5 which were assigned to the following carbon atoms: CH_2C(O)CH(Me), (C(O)CH_2-CH(Me), (C(O)CH_2CH(Me), CH_2C(O)CH(Me), and (C(O)CH_2CH(*Me*), respectively.

The ^{1}H NMR spectra of the terpolymers in HFIP-d_2 show, in addition to the resonances due to the E−CO copolymers [δ 2.80 (s, CH_2C(O)CH_2), 2.55 (q, J(HH) = 7.5 Hz, C(O)CH_2CH_3), 1.07 (t, J(HH) = 7.5 Hz, C(O)-CH_2CH_3)], resonances at δ 3.05 (m) and 1.15 (d, J(HH) = 6.5 Hz) which are assigned to the methyne and the methyl hydrogen atoms of a CH_2CH(Me) unit, respectively.

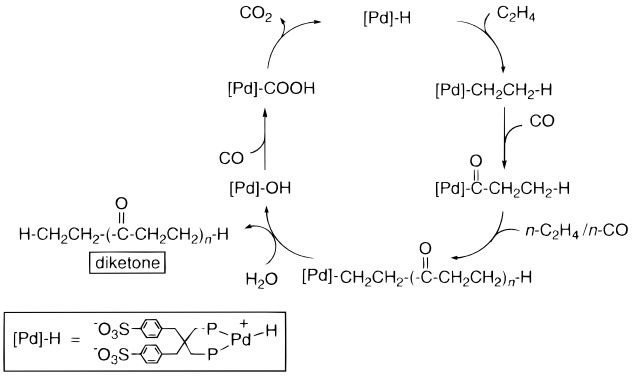
Scheme 4



Like the copolymer, the terpolymer contains exclusively ketone end groups (Scheme 4).

Mechanistic Conclusions. A catalysis cycle that nicely fits the experimental observables reported in the previous sections is the one shown in Scheme 5.

Scheme 5



The overall mechanism is substantially similar to those proposed by Drent et al. for the C_2H_4/CO copolymerization catalyzed by Pd(II)−dppp catalysts in methanol[8e,9b] and by Sheldon et al. for the analogous reaction catalyzed by Pd(II)−(dppp-SO_3Na) catalysts in water.[12] A few important differences need to be stressed, however. First of all, the selective production of copolymers containing ketonic end groups rules out termination steps involving the hydrolysis of the Pd−C bonds in the propagation units Pd−$(C(O)CH_2CH_2)_n$H.[9,12] Second, the production of free CO_2 suggests that the insertion of CO into Pd−OH bonds to give Pd−COOH indeed takes place. The deinsertion of the oxidized product CO_2 to generate the Pd−H initiating species, however, must be much faster than the insertion of C_2H_4 given the absence of COOH end groups in the copolymer. On the basis of these experimental observables, the catalysis mechanism previously reported for the Pd(II)-assisted copolymerization reactions can greatly be simplified as shown in Scheme 5. The catalytic cycle contains the usual steps of insertion of ethene into the Pd−H bond to give Pd−ethyl (initiation), CO insertion to give Pd−acyl, nC_2H_4/nCO insertions (propagation), and hydrolysis to give Pd−OH (termination).[9,12,21]

Besides the contribution of the WGS reaction, the catalytically active Pd−H moieties may be produced via oxidative addition of H^+ to Pd(0) species.[22] The reduction of Pd(II) to Pd(0) by tertiary phosphine ligands is quite common for Pd(II) complexes, especially in water,[23] and indeed we have found that, although slowly, both Pd metal and phosphine oxides are formed by heating water solutions of **1** (particularly in the presence of CO/C_2H_4). In the presence of an excess of H^+, BQ, or Na_2-DPPPDS, the catalyst degradation is apparently minimized as much higher productivities were obtained.

Enhanced productivity was also observed by either addition of H_2 to the catalytic mixtures or use of a 1:1 water/1,4-dioxane mixture as reaction medium. The positive effect of H_2 has previously been observed for CO/C_2H_4 copolymerization reactions in MeOH and was interpreted in terms of an accelerated production of Pd−H species by hydrogenolysis of the Pd−C bond in the propagation moieties.[13] Besides increasing the solubility of the gaseous reactants and BQ in the reaction medium, 1,4-dioxane also seems to stabilize the Pd(II) resting state most likely via coordination (see Figure 1). Enhancement of catalytst lifetime by simply changing the solvent has already been reported for Pd-assisted CO/olefin copolymerizations.[24]

Conclusions

With the use of the water-soluble diphosphine ligand Na_2DPPPDS, new Pd(II) catalysts for the co- and terpolymerization of CO and olefins in aqueous media have been designed. Under partly optimized conditions, the catalyst systems with Na_2DPPPDS are the most efficient ever reported in water and comparable to the well-known dppp-based catalysts in MeOH. Most importantly, the copolymers and terpolymers produced with the Na_2DPPPDS-based catalysts have exclusively ketonic end groups, while diketone, keto-acid, and diacid terminal groups characterize the structure of the polymers obtained with the dppp-SO_3K(Na)-based catalysts.

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Supporting Information Available: Detailed description of the synthesis and characterization of the Na_2DPPPDS ligand and cyclic voltammogram of **1** in water (Figure 1S). This material is available free of charge via the Internet at http://pubs.acs.org.

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