

Catalytic conversions in water. Part 9. High activity of the Pd/dpppr-s/Brønsted acid system in the alternating copolymerization of ethene and carbon monoxide {dpppr-s = C₃H₆-1,3-[P(C₆H₄-*m*-SO₃Na)₂]₂}

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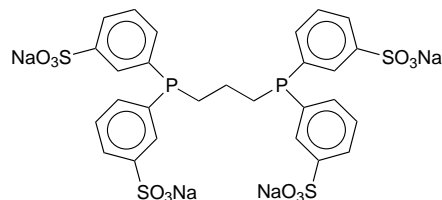
The formation of alternating copolymers of ethene and carbon monoxide proceeds rapidly in the aqueous phase in the presence of a water-soluble palladium catalyst and a Brønsted acid; activities of >4 kg of polymer per g palladium per hour were observed.

Currently there is a growing interest in organometallic catalysis in water.¹ The replacement of organic solvents by water is advantageous for environmental, safety and economical reasons and the use of biphasic systems facilitates catalyst recycling. Nevertheless, there are few examples of (biphasic) aqueous systems with acceptable catalytic activities.

The palladium catalyzed alternating copolymerization of α -olefins and carbon monoxide affords polyketones with commercially interesting properties.² The most active catalysts are palladium(II) complexes with bidentate phosphines, e.g. 1,3-bis(diphenylphosphino)propane (dpppr).³ Jiang and Sen⁴ attempted to perform the alternating copolymerization in pure water but, unfortunately, their system suffered from low catalytic activity (470 g polymer per gram Pd in 22 h).

We recently found high activities for the water-soluble palladium catalyst [Pd(tppts)]₃ [tppts = P(C₆H₄-*m*-SO₃Na)₃] in the biphasic hydrocarboxylation of propene.⁵ We now report on the facile formation of alternating copolymers of ethene and carbon monoxide in the presence of the bidentate water-soluble phosphine C₃H₆-1,3-[P(C₆H₄-*m*-SO₃Na)₂]₂ (dpppr-s) and a Brønsted acid cocatalyst (*vide infra*). Indeed, under mild and only partly optimized reaction conditions, the catalyst exhibits activities (ca. 4 kg polymer per gram Pd per hour, \pm 7600 mol ethene per mol Pd per hour) comparable to those observed with Pd/dpppr systems in organic solvents, e.g. MeOH which is quite extraordinary for a water-soluble catalyst.

We applied a recently developed sulfonation procedure for the synthesis of the water-soluble analogue of dpppr;⁶ dpppr-s[‡] was obtained in high yield (90%) and purity (98%) and its structure was confirmed by ¹H, ¹³C and ³¹P NMR and elemental analysis.



The catalyst was prepared *in situ* by addition of dpppr-s dissolved in water to an aqueous solution of [Pd{OTs}₂{NCMe}₂]. Analogous to non-aqueous systems, the use of a bidentate ligand has a dramatic effect on the outcome of the reaction (Scheme 1). Whereas tppts affords predominantly propionic acid, the water-soluble bidentate dpppr-s results in the formation of the alternating copolymer. The reaction conditions§ are rather mild and only extremely low concentrations of

palladium (<0.14 mmol l⁻¹) are needed for a rapid conversion. Under these conditions no low molecular weight compounds (*n* = 1–6) are formed, as determined by HPLC analysis.

The optimum dpppr-s : Pd ratio is 1 : 1 (see Table 1). Without ligand metallic palladium is formed, while an excess of ligand (dpppr-s : Pd = 2 : 1) inhibits the reaction. The addition of a Brønsted acid is important for the stability of the catalyst. At low Brønsted acid concentration a lower catalyst activity is observed and large amounts of metallic palladium are formed during the reaction. The optimum results were obtained with 50 equiv. of Brønsted acid per palladium (1.0 mmol, run 7).

The anion of the Brønsted acid should be weakly- or non-coordinating, e.g. CF₃CO₂⁻ or TsO⁻. With the strongly coordinating iodide anion no catalytic activity was observed (run 6). These results are consistent with those observed in the Pd/tppts-catalyzed hydrocarboxylation of α -olefins.⁵

The copolymers are white solids that precipitate during the reaction, which implies that the reaction can proceed heterogeneously in aqueous media. The average molecular weights (Table 1) are lower than for copolymers obtained in the Pd/dpppr system in MeOH (6.6 vs. 8.5 kg mol⁻¹).^{3a}

We assume that the aqueous phase copolymerization proceeds *via* a similar reaction pathway to that proposed by Drent *et al.*^{3a} for the organic soluble system (Scheme 2). Initiation takes place by ethene insertion in a palladium-hydride bond. The palladium hydride [PdH{dpppr-s} {L}]⁺ (L = H₂O,

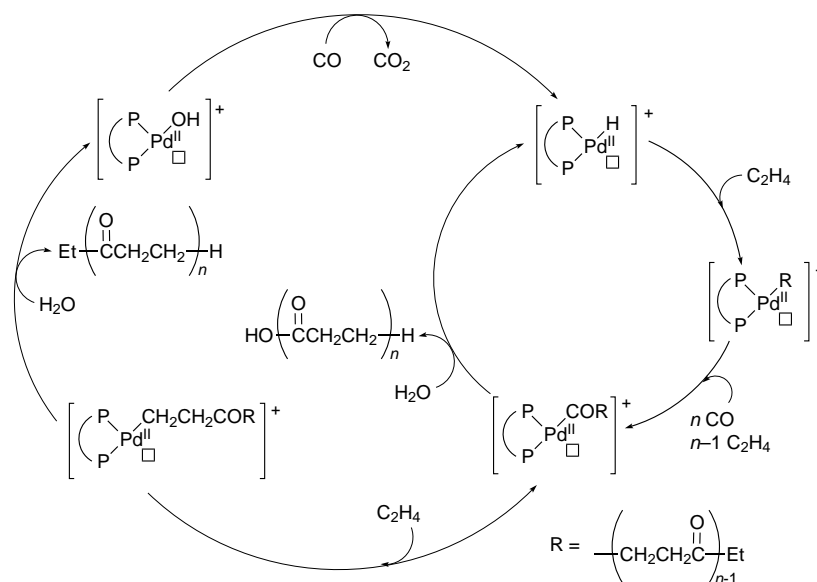


Scheme 1

Table 1 The alternating copolymerization of ethene and carbon monoxide catalyzed by the aqueous Pd/dpppr-s system^a

Run	Ligand	Ligand : Pd	Brønsted acid	(mmol)	Activity ^b	Molecular weight/kg mol ^{-1c}
1 ^{d,e}	—	0.0	TsOH	(30.0)	0	—
2	dpppr-s	1.0	TsOH	(10.0)	3.58	6.1
3	dpppr-s	1.5	TsOH	(10.0)	1.56	6.5
4	dpppr-s	2.0	TsOH	(10.0)	0.56	6.1
5	dpppr-s	1.0	TFA	(10.0)	3.87	6.9
6	dpppr-s	1.0	HI	(10.0)	0	—
7	dpppr-s	1.0	TsOH	(1.0)	4.03	6.6
8 ^d	dpppr-s	1.0	TsOH	(0.2)	3.44	7.7
9 ^d	dpppr-s	1.0	—	(0.0)	2.83	6.5
10 ^f	dpppr-s	1.0	TsOH	(10.0)	2.04	10.9

^a Reaction conditions: 0.020 mmol [Pd{OTs}₂{NCMe}₂], ligand and Brønsted acid in water, 141.9 g of total reaction mixture, 0.20 mol ethene, 40 bar constant total pressure, 90 °C, 60 min, stirring speed: 1000 rpm. ^b In kg polymer per gram Pd per hour. ^c Determined by quantitative ¹³C NMR analysis. ^d Formation of metallic palladium during reaction. ^e Reaction time: 120 min. ^f Reaction temperature: 70 °C, reaction time: 65 min.



Scheme 2

NCMe, anion or monomer) can for instance be formed *in situ* by successive reduction of $[\text{Pd}\{\text{dpppr-s}\}\{\text{L}\}]_2^{2+}$ by CO and water to a Pd^0 complex⁷ and oxidative addition of the Brønsted acid. The initiation is followed by alternating insertion of carbon monoxide into a palladium-alkyl bond and ethene insertion in a palladium-acyl bond. The strictly alternating fashion of chain growth is terminated by hydrolysis of either a palladium-acyl or a palladium-alkyl bond, resulting in the formation of a carboxylic or a keto end group, respectively. In the latter case a palladium(II) hydroxo species is formed which can be reduced by carbon monoxide to regenerate the original hydride.

The much higher activity of our system compared to that previously reported⁴ can be explained by the addition of a Brønsted acid cocatalyst and the high purity of the ligand. The addition of a Brønsted acid prevents decomposition of the catalyst and thus enhances its productivity. Moreover, impurities, such as partly oxidized ligand $[\text{Ar}_2\text{PO}-(\text{CH}_2)_3-\text{PAR}_2]$ and inorganic salts can inhibit the reaction by occupying free coordination sites on the palladium.

We conclude that the alternating copolymerization of olefins and carbon monoxide in water constitute an alternative, environmentally friendly method for the preparation of new low-cost polymers with interesting properties. Studies are underway aimed at further optimization of this system and confirming the molecular weights of the polymers by alternative techniques.

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Notes and References

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‡ *Ligand synthesis*: 4.95 g of dpppr (12.0 mmol) was dissolved in a solution of 4.00 g of orthoboric acid (64.7 mmol) in 37.5 ml of H_2SO_4 (98%). After ca. 90 min 67.5 ml oleum (65%) was added at 0–5 °C under vigorous stirring. After the addition the solution was stirred at room temperature for 48 h. The mixture was hydrolyzed at 0–5 °C with 800 ml of H_2O . The product was extracted from the water phase with tri-isooctylamine in toluene. The organic layer was washed repeatedly with water. By addition of 5% aq. NaOH, the pH was increased and the fraction of pH 4.6–12.5 was collected, washed with pentane and evaporated to dryness. Yield: 90%, purity: 98% (based on ^{31}P -NMR analysis). *Selected data*: δ_{H} (300.2 MHz,

25 °C, D_2O) δ : 7.70 (m, 4 H), 7.65 (m, 4 H), 7.35 (m, 8 H), 2.19 (t, J 8 Hz, 4 H), 1.39 (m, 2 H); δ_{C} (100.6 MHz, 25 °C, D_2O) 144.4 (d, J 6 Hz), 140.0 (d, J 12 Hz), 136.8 (d, J 17 Hz), 131.0 (s), 130.8 (d, J 15 Hz), 121.6 (s), 29.1 and 29.0 (dd, J 9 Hz), 22.7 (t, J 16 Hz); δ_{P} (121.5 MHz, 25 °C, D_2O) –16.3 (s). Calc. for $\text{C}_{27}\text{H}_{22}\text{O}_{12}\text{P}_2\text{S}_4\text{Na}_4\cdot 4\text{H}_2\text{O}$: P, 6.67, S, 13.81. Found: P, 6.52, S, 13.6% (S/P = 2.0).

§ *Copolymerization reactions*. Under an argon atmosphere an aqueous solution of $[\text{Pd}\{\text{OTs}\}_2\{\text{NCMe}\}_2]$ (0.020 mmol), dpppr-s and Brønsted acid was transferred to a 300 ml Hastelloy C autoclave and diluted to give 141.9 g of reaction mixture ($[\text{Pd}] = 0.14 \text{ mmol l}^{-1}$). The argon was replaced by carbon monoxide after five pressurizing–depressurizing cycles. The reaction mixture was stirred (1000 rpm) and the autoclave was pressurized with carbon monoxide *via* a stainless steel cylinder that contained 0.20 mol of ethene and heated to the reaction temperature. The pressure was kept constant by addition of carbon monoxide. After the reaction the autoclave was cooled to room temperature immediately. The reactant gasses were vented and the product was filtered, washed with water (50 ml) and EtOH ($2 \times 50 \text{ ml}$) and dried *in vacuo*. The average molecular weights of the copolymer samples were determined by quantitative ^{13}C NMR analysis in a mixture of 1,1,1,3,3,3-hexafluoropropan-2-ol and CDCl_3 (9 : 1).

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