

Supporting Information

Oscillatory carbonylation using alkyne-functionalised poly(ethylene glycol)

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Experimental Section

Materials

Palladium(II) iodide (>99.99+%), potassium iodide, HPLC grade methanol, phenylacetylene (PhAc), poly(ethylene glycol) monomethyl ether 2000, poly(ethylene glycol) monomethyl ether 5000, 4-pentynoic acid (95%), anhydrous dichloromethane, 4-dimethylaminopyridine (DMAP), and *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDCI), were purchased from Sigma-Aldrich and used as received. Methyl 4-pentynoate (4MP)¹ and alkyne-terminated PEG derivatives (PEGA2000 and PEGA5000) were synthesised according to literature procedures.¹⁻³

Methods

Preparation of catalyst stock solution

A concentrated 'stock' solution of catalyst was prepared by dissolving palladium (II) iodide (401 mg, 1.1 mmol) and potassium iodide (24.93 g, 150 mmol) in HPLC grade methanol (300 mL). The mixture was stirred at ambient temperature for 48 h and the resulting solution filtered through a 0.2 µm Millipore membrane filter to remove residual PdI₂ (57 mg). The concentration of the resulting catalyst solution was then adjusted to 2.677 mM using additional methanol and stored until required.

Oscillatory runs

PEGA2000

Palladium catalyst solution (1.362 mL, 3.6×10^{-6} mol PdI₂) was diluted in methanol (85 mL) and the mixture equilibrated to 20 °C in a multiport jacketed glass reactor. The reactor was fitted with pH, temperature and turbidity probes connected to HEL WinISO software. pH was monitored for 5 min to establish a baseline value and the solution purged with CO and air (15 mL min⁻¹) for 15 min. The reactor was then treated with a solution of PEGA2000 (379 mg, 1.8×10^{-4} mol) in MeOH (2 mL) and the PEGA vial washed with additional MeOH (1.638 mL) to ensure complete transfer of the substrate and give a total reaction volume of 90 mL. CO/air flow was maintained throughout the course of the reaction and pH continually monitored.

PEGA5000

PEGA5000 runs were carried out in a similar manner to PEGA2000. However due to the slightly lower solubility of PEGA5000 in MeOH the substrate (925 mg, 1.81×10^{-4} mol) was dissolved in 20 mL MeOH with sonication (10 min) in order to ensure complete dissolution. The initial reaction mixture consisted of palladium catalyst solution (1.362 mL, 3.6×10^{-6} mol PdI₂) diluted in MeOH (60.638 mL); a further 8 mL of MeOH was used to rinse the PEGA vial giving a total reaction volume of 90 mL.

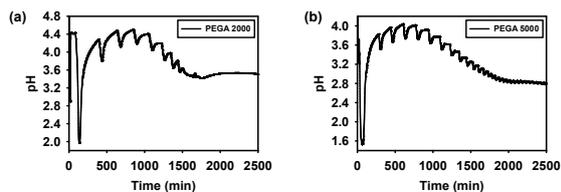


Fig. S1. Oscillatory pH behaviour recorded during repeat runs using PEGA substrates. (a) PEGA2000; (b) PEGA5000. Initial conditions: $[PdI_2] = 4.05 \times 10^{-5} \text{ M}$; $[KI] = 2.28 \times 10^{-3} \text{ M}$; $[PEGA] = 2.03 \times 10^{-3} \text{ M}$; CO flow = 15 mLmin^{-1} ; Air flow = 15 mLmin^{-1} .

Alternative substrates

Experiments were carried out in which PEGA2000 was replaced with $1.81 \times 10^{-4} \text{ mol}$ of alternative substrates to explore the effect of the macromolecular nature of PEGA on oscillatory behaviour under the conditions reported. Four substrates were selected: PhAc (18.6 mg, $20 \mu\text{L}$), 4MP (20.4 mg, $20.9 \mu\text{L}$), poly(ethylene glycol methyl ether) 2000 (PEG 2000, 365 mg) and a 1:1 molar mixture of PEG 2000 (365 mg) and 4MP (20.4 mg, $20.9 \mu\text{L}$). In all cases the reaction conditions and procedures were identical to those described for PEGA2000. Although fluctuations in pH were noted in all cases, no oscillations were observed, Fig. S2.

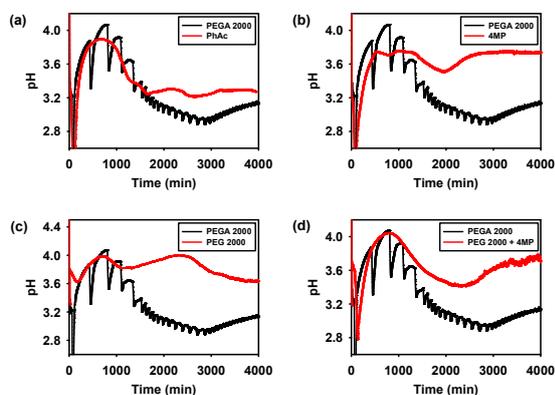


Fig. S2. pH behaviour of various substrates under identical reaction conditions to those used for oscillatory PEGA2000 runs. (a) Phenylacetylene (PhAc); (b) methyl 4-pentynoate (4MP); (c) poly(ethylene glycol) mono methyl ether 2000 (PEG 2000); (d) 1:1 molar ratio of 4MP and PEG 2000. Initial conditions: $[PdI_2] = 4.05 \times 10^{-5} \text{ M}$; $[KI] = 2.28 \times 10^{-3} \text{ M}$; $[PEGA]$ or $[\text{substrate}] = 2.03 \times 10^{-3} \text{ M}$; CO flow = 15 mLmin^{-1} ; Air flow = 15 mLmin^{-1} .

pH monitoring

pH values were measured using an aqueous pH electrode connected to HEL WinISO software. Calibration was carried out using aqueous buffers at pH 2, 7 and 10. Due to the non-aqueous nature of the reaction media (MeOH) absolute values of hydrogen ion activities are not calculated. Instead an approximation for use in modelling studies can be obtained using adjusted pH values (pH_{adj}). In MeOH pH_{adj} is approximated by adding 2.3 pH units to pH values measured using an all aqueous pH electrode set up (pH_{app}). Hydrogen ion concentrations can then be estimated using $10^{-(pH_{app} + 2.3)}$. Detailed discussion of pH measurement in methanol, including during oscillatory PCPOC runs have been published previously.⁴⁻⁵

GC-MS

Analysis of the reaction products for oscillatory runs using PEGA2000 was carried out using GC-MS. A sample of 4MP was also analysed for comparison. A Varian Saturn 2000 GC-MS instrument fitted with a Varian VF-5ms column was used in both cases. The GC method used was as follows: injector temperature $150 \text{ }^\circ\text{C}$, initial oven temperature $100 \text{ }^\circ\text{C}$, 5 successive ramps ($1 \text{ min at } 20 \text{ }^\circ\text{C min}^{-1}$ then hold for 5 min) up to $195 \text{ }^\circ\text{C}$, which was held for 8 min. 4MP shows a retention time of 2.02 min; no evidence for either 4MP or expected carbonylation products was noted in the GC-MS of samples taken from oscillatory PEGA2000 runs.⁶⁻⁷

Modelling

A modelling and simulation study was performed using BatchCAD kinetic fitting and simulation software. Experimentally obtained pH values were adjusted due to the non-aqueous nature of the reaction medium (MeOH), as discussed in the pH monitoring section. Approximate values of hydrogen ion concentrations were then obtained and used in simulations to estimate reaction rate constants. Finally, modelled values of hydrogen ion concentration were converted back to apparent pH values to allow direct comparison with experimental data.

References

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