Pulsatile release from a flat self-oscillating chitosan macrogel

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Electronic Supporting Information

Contents

1. Characterisation of Chi-IM-PdCl$_2$

Chi-IM polymer formation was confirmed by Fourier-Transform Infrared (FTIR) spectroscopy. In the FTIR spectra (Figure S1), the intensity of the band at 1648 cm^{-1}, typically attributed to the amide and imine groups, increased, whereas the intensity of the amino group bands (1537 and 1556 cm^{-1}) decreased, in line with consumption of the amine groups to form imines.[1,2] The additional peak observed at 773 cm^{-1} (weak sharp band) is attributed to the alkene bending vibrations (=C-H).

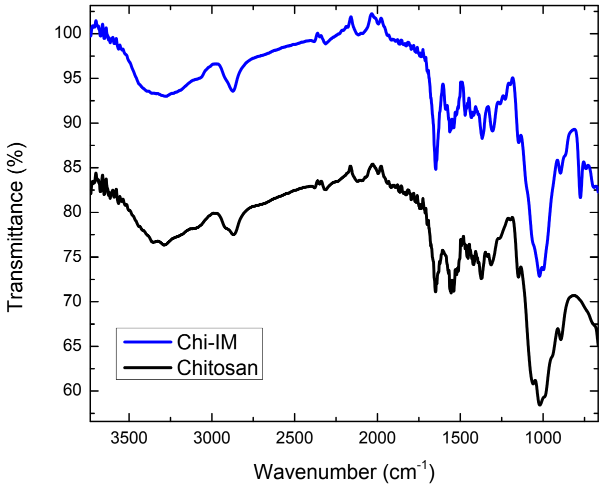

Figure S1. FTIR spectra of chitosan and Chi-IM polymer.

2. Gas Chromatography with Mass Spectrometry detector (GC-MS)

The method was as follows: injector temperature 150 ˚C; helium flow rate 1 mL min^{-1}; oven temperature 100-195 ˚C over 35 min in 5 steps. All samples were taken at their indicated time intervals of the experimental runs (unless otherwise stated within the main text) and filtered over silica prior to being diluted 1:2 with methanol.

3. Photoluminescence intensity (PL)

PL intensity was measured by FLUOstar® Omega UV-Vis filter-based multi-mode microplate reader, using 480 nm filter for absorbance and 530 nm filter for fluorescence collection. For measurements, 200 µl of sample solution were deposited per well and three scans taken.

4. Scanning electronic spectroscopy (SEM)

Samples of the dried gels were mounted in an aluminium stub, using adhesive carbon discs. Samples were examined using a TESCAN VEGA LMU scanning electron microscope at 8 kV supplied voltage, and images were collected using TESCAN supplied software.

5. pH-associated release of reaction products in methanol

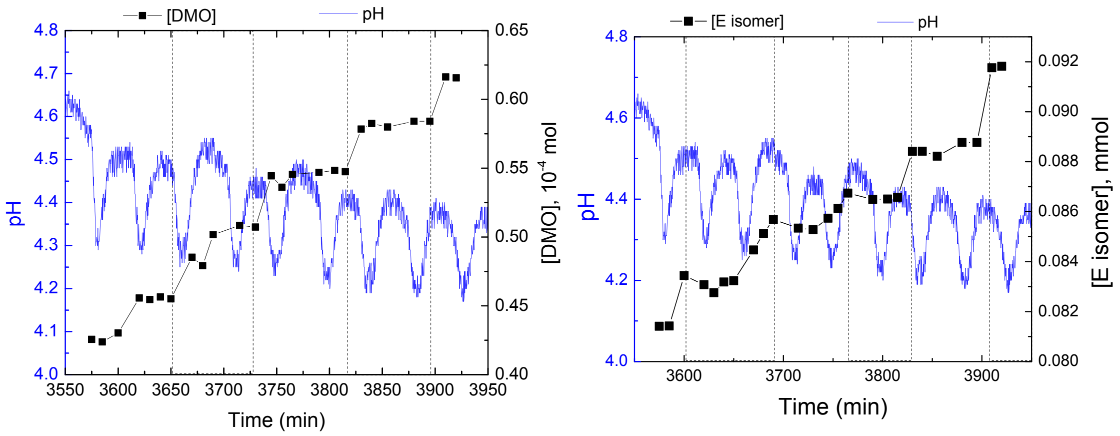

Figure S2. (left) pH-associated pulsed release of DMO as a function of time in methanol. (right) pH-associated pulsed release of E-isomer as a function of time in methanol. Concentrations of DMO and

E-isomer are shown with closed symbols, the connecting lines are only as a guide for the eye and do not represent actual data.

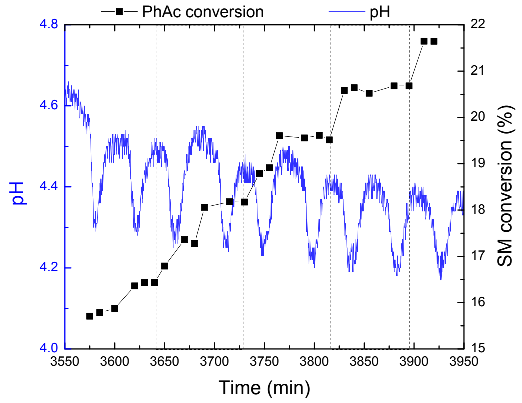

Figure S3. pH-associated pulsed increase of starting material (SM, PhAc) conversion as a function of time in methanol. PhAc conversion (in %) is shown with closed symbols, the connecting lines are only as a guide for the eye and do not represent actual data. The start of each pulse release is labelled with dashed vertical lines.

6. pH-associated release of reaction products in methanol:water system

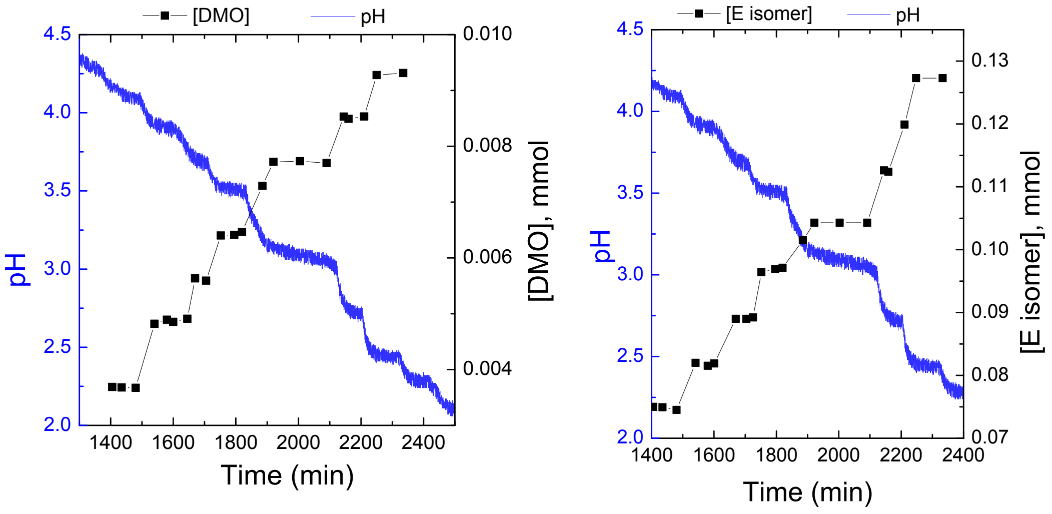

Figure S4. (left) pH-associated pulsed release of DMO as a function of time in methanol:water. (right) pH-associated pulsed release of E-isomer as a function of time in methanol:water. Concentrations of DMO and E-isomer are shown with closed symbols, the connecting lines are only as a guide for the eye and do not represent actual data.

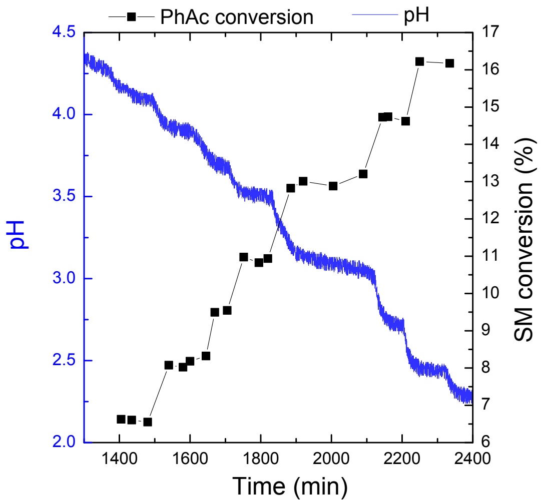

Figure S5. pH-associated pulsed increase of starting material (SM, PhAc) conversion as a function of time in methanol:water. PhAc conversion (in %) is shown with closed symbols, the connecting lines are only as a guide for the eye and do not represent actual data.

References

1 M.-M. Iftime, S. Morariu and L. Marin, *Carbohydr. Polym.*, 2017, **165**, 39–50.

2 V. B. Gavalyan, *Carbohydr. Polym.*, 2016, **145**, 37–47.