Electronic Supplementary Material (ESI) for Materials Advances. This journal is © The Royal Society of Chemistry 2023

# Supporting Information

## 4D-printed hydrogels based on poly(oxazoline) and poly(acrylamide) copolymers by

## stereolithography

Thomas Brossier, Michel Habib, Belkacem, Tarek Benkhaled, Gael Volpi, Vincent Lapinte<sup>\*</sup>, Sebastien Blanquer<sup>\*</sup>

### Supplementary Table

Hydrogels	G' (Pa)	ξ (Å)
PMOx <sub>20</sub> - <i>net</i> -PNIPAM <sub>4</sub>	44	473
PMOx <sub>20</sub> - <i>net</i> -PNIPAM <sub>100</sub>	29	542
PiPrOx <sub>20</sub> - <i>net</i> -PAM <sub>4</sub>	173	299
PiPrOx <sub>20</sub> -net-PAM <sub>100</sub>	115	342

Table S1. Storage modulus in the linear viscoelastic domain and mesh size for the hydrogels at equilibrium at 20°C.

**Supplementary Figures** 



Figure S1. <sup>1</sup>H NMR spectrum of the synthesized 1,6-hexaneditosylate (HDOTs).



**Figure S2.** Size Exclusion Chromatography spectrum and <sup>1</sup>H NMR spectrum of the synthesized poly(2-isopropyl-2-oxazoline) (PiPrOx),  $DP_n = 20$ .



**Figure S3.** Size Exclusion Chromatography spectrum and <sup>1</sup>H NMR spectrum of the synthesized poly(2-methyl-2-oxazoline) (PMOx),  $DP_n = 20$ .



**Figure S4.** Picture of the swollen thermo-responsive hydrogels  $PiPrOx_{20}$ -*net*- $PAM_4$  (left) and  $PMOx_{20}$ -*net*- $PNIPAM_{100}$  (right) at the equilibrium at 20°C.



**Figure S5.** Diffusion mechanism of the thermo-responsive hydrogels  $PiPrOx_{20}$ -*net*- $PAM_4$  and  $PMOx_{20}$ -*net*- $PNIPAM_{100}$  using the Ritger-Peppas model.



**Figure S6.** Illustrative picture of the thermo-sensitivity of the PiPrOx<sub>20</sub>-*net*-PAM<sub>4</sub>, with the hydrogel in this swollen state at 20 °C (left), where the beads can fall down through the device, and the hydrogel in the collapsing state at 50 °C (right), where the beads cannot go through the device.

### **Supplementary Movies**

Movie S1. Mechanical performance of 4D printed device based on  $PMOx_{20}$ -net-PNIPAM<sub>100</sub> in swollen state.

**Movie S2.** Mechanical performance of 4D printed device based on PiPrOx<sub>20</sub>-*net*-PAM<sub>4</sub> in swollen state.

Movie S3. 4D printed device based on  $PiPrOx_{20}$ -net- $PAM_4$  with golden beads release.