# Versatile Biodegradable Polymer Platform – From 3D-Printing towards Biomedical Application

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BNN

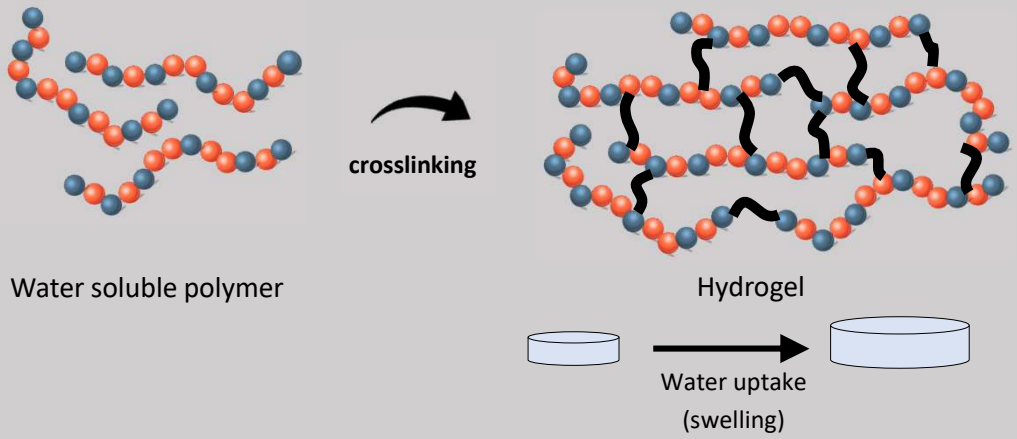
# Introduction



**POLYMER**

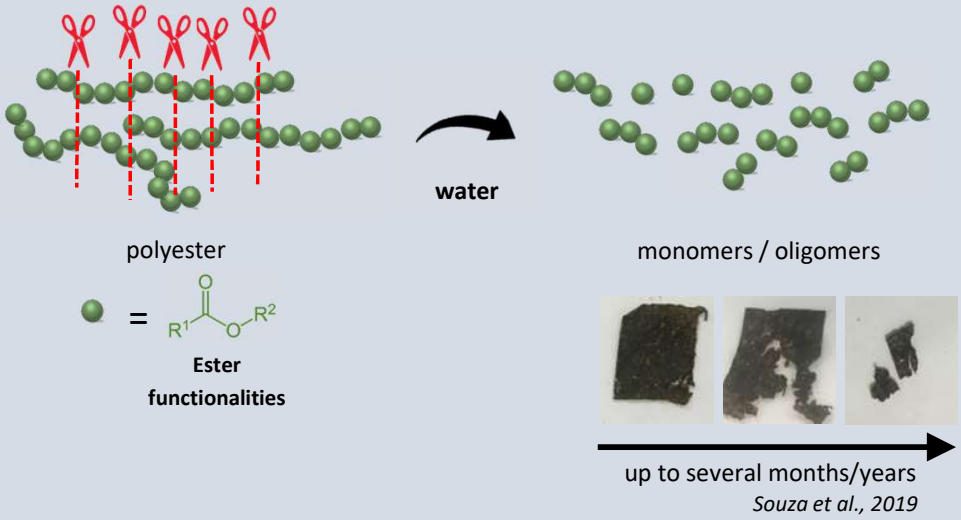
- Biocompatible
- Controlled physical properties

## HYDROGELS




- Mimic the physical properties of soft tissues
- Difficult to process
- Not biodegradable (synthetic hydrogels)

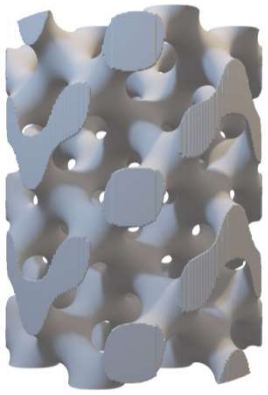
## ALIPHATIC POLYESTERS

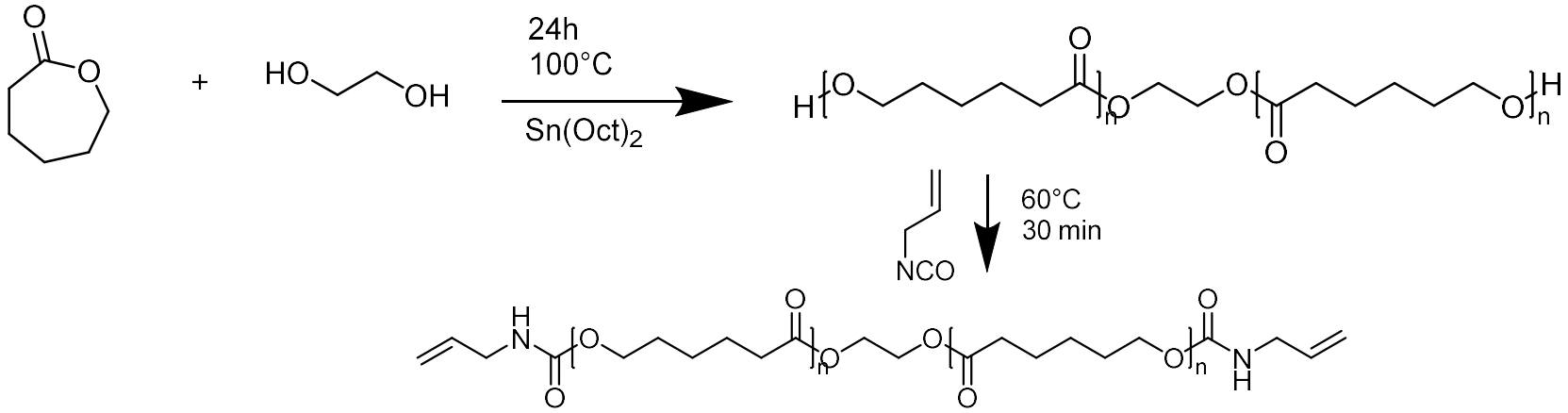



*Souza et al., 2019*

- Biodegradable: complete elimination from the body
- Require the use of organic solvents

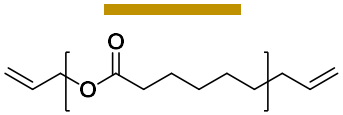
# Design of biodegradable networks



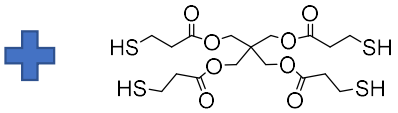


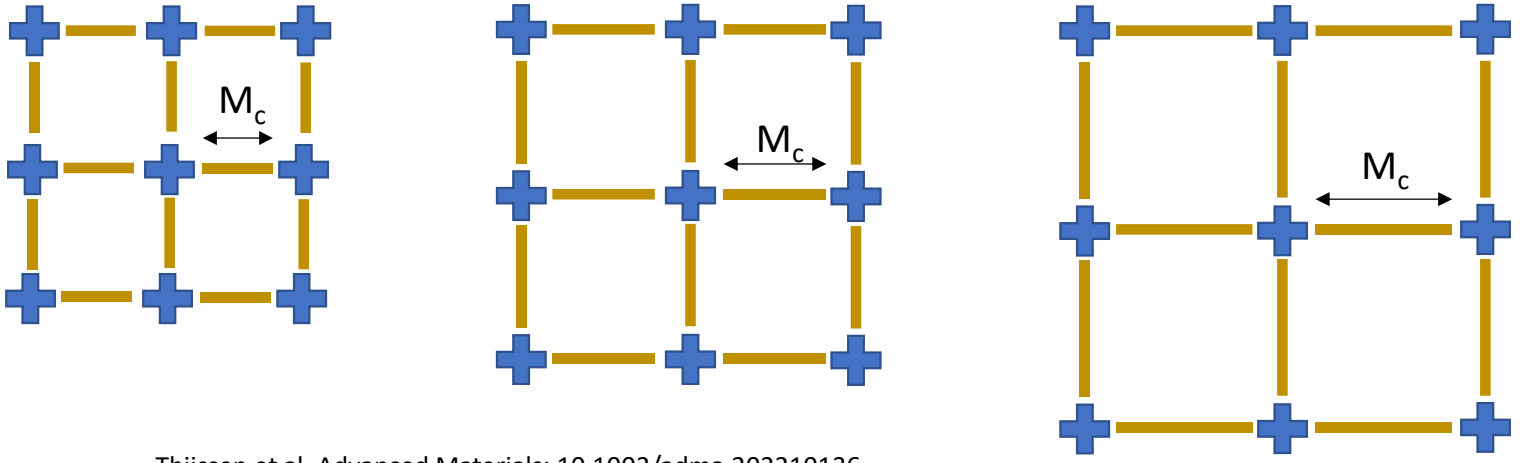

**↑ Molar mass ($M_c$)**

**Ene-functional PCL**



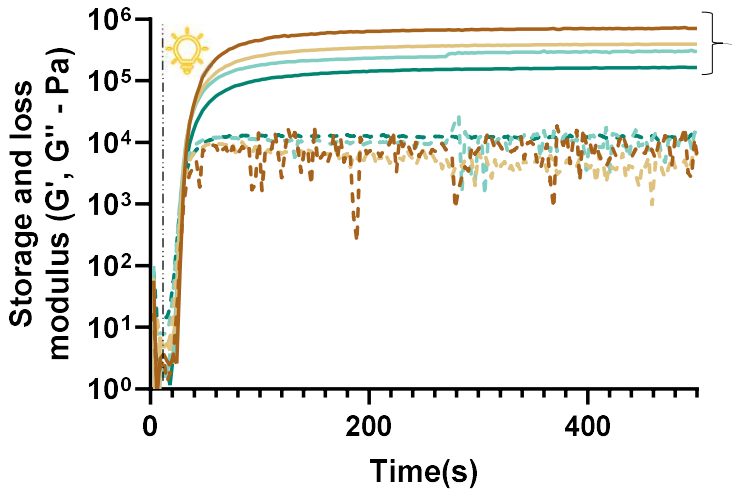
**Thiol crosslinker**



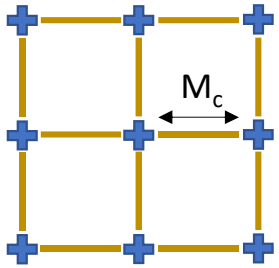




Thijssen et al. Advanced Materials: 10.1002/adma.202210136

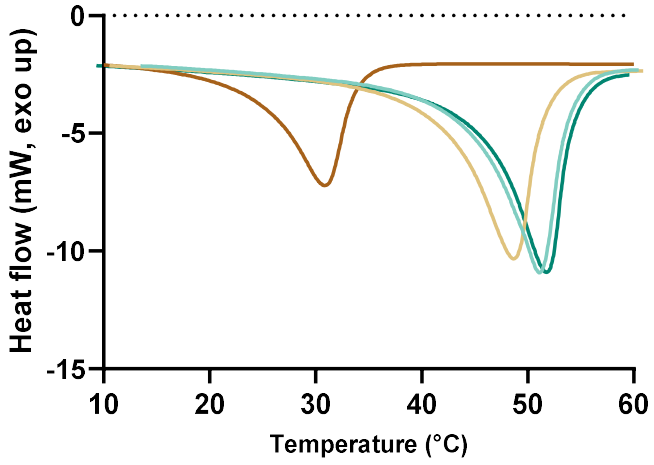
# Predictability and tunability

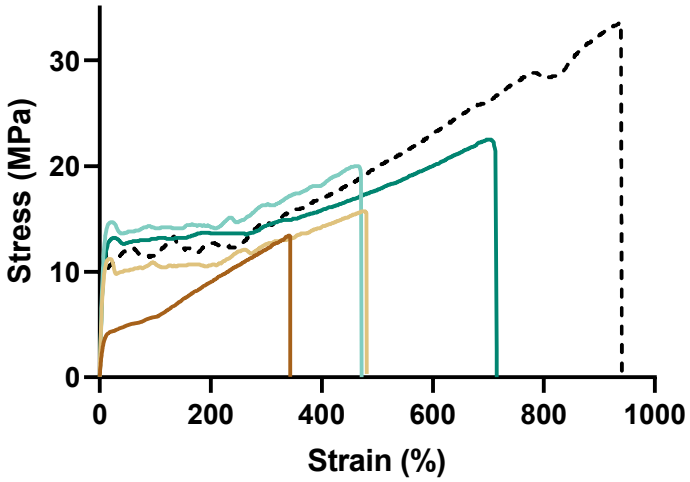


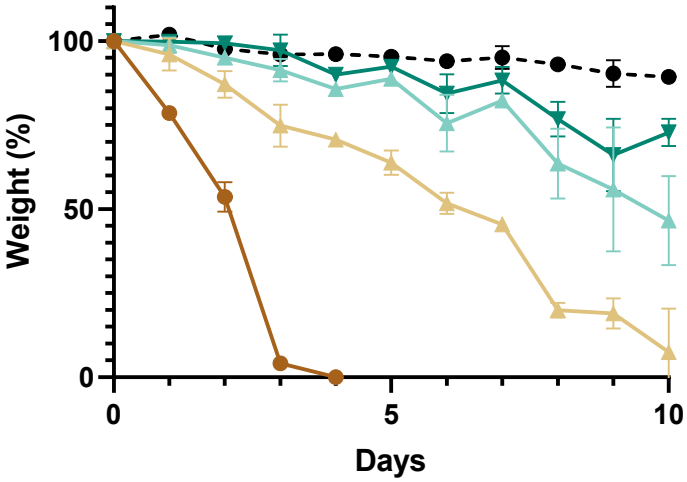

$$G' = \frac{\rho\, RT}{M_c}\left(1 - \frac{2}{f}\right)$$




| $M_c$ | Theor. G' (MPa) | Exp. G' (MPa) |
|---|---|---|
| E-PCL 2300 | 0.70 | 0.77 ± 0.11 |
| E-PCL 4700 | 0.34 | 0.47 ± 0.12 |
| E-PCL 6400 | 0.25 | 0.26 ± 0.04 |
| E-PCL 8700 | 0.18 | 0.17 ± 0.01 |
| PCL 80 000 | N.A. | N.A. |



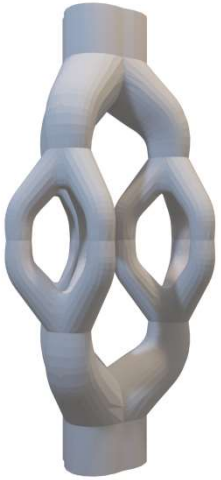



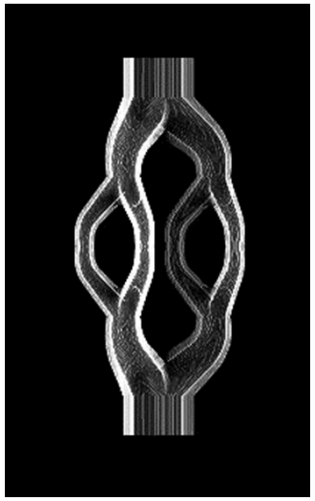
# Volumetric 3D-Printing

| $M_c$ | Theor. G' (MPa) | Exp. G' (MPa) |
|---|---|---|
| E-PCL 2300 | 0.70 | 0.77 ± 0.11 |

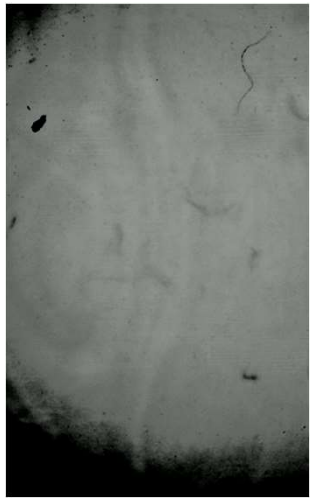
**CAD Model**



**Projections**



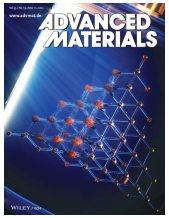
**3D-printing**



**Final print**

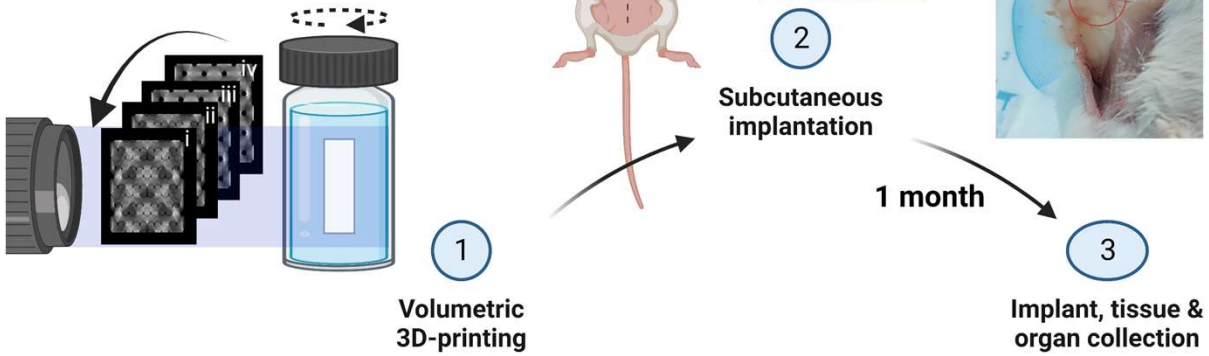


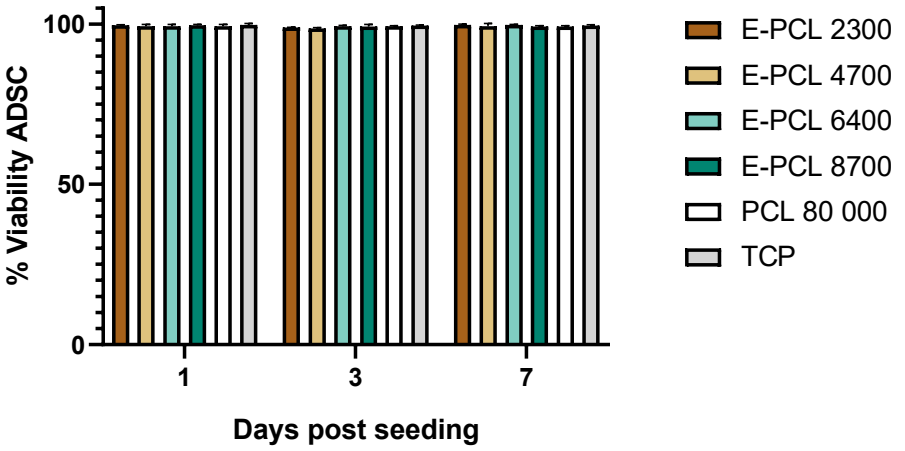


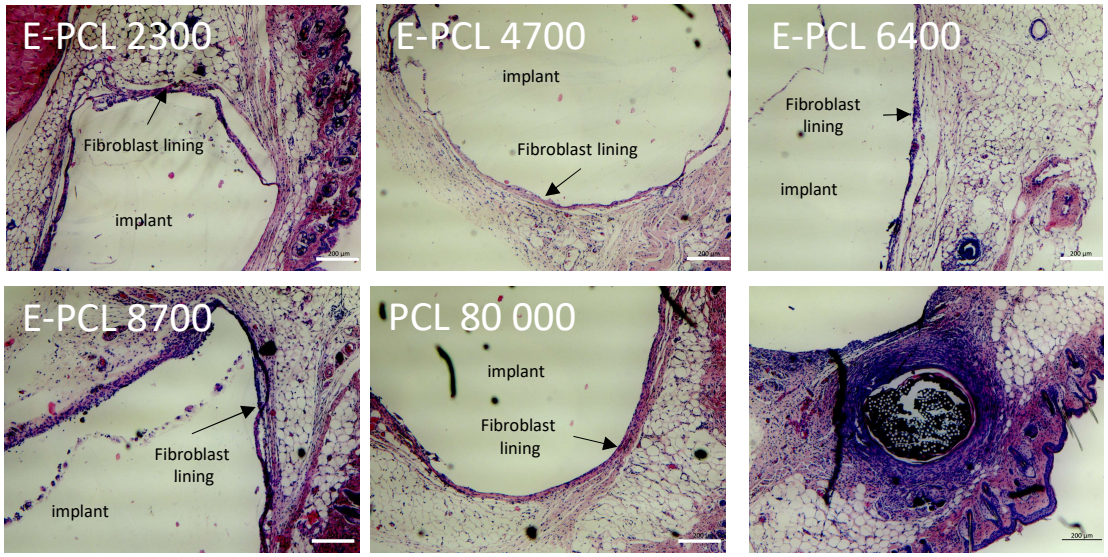



Thijssen et al. Advanced Materials: 10.1002/adma.202210136

# In-vitro and in-vivo biocompatibility

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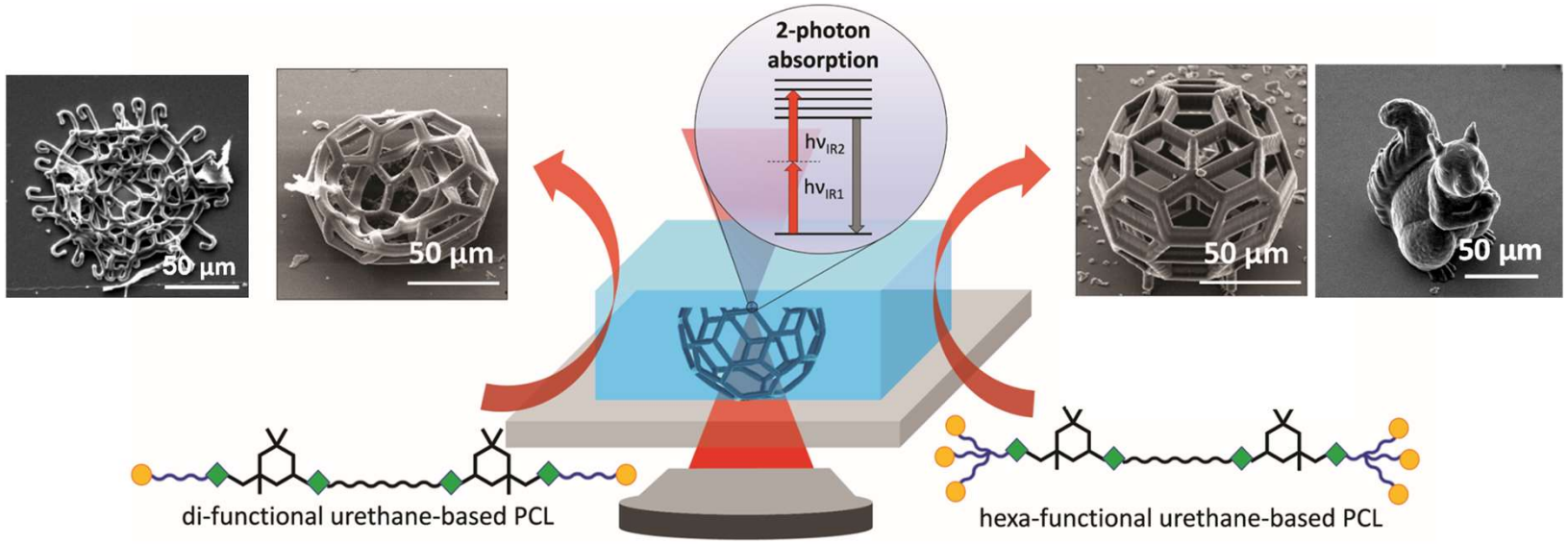
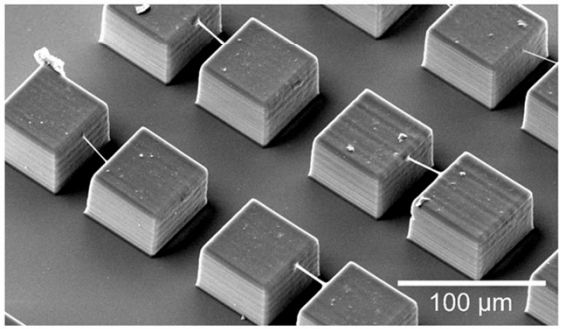
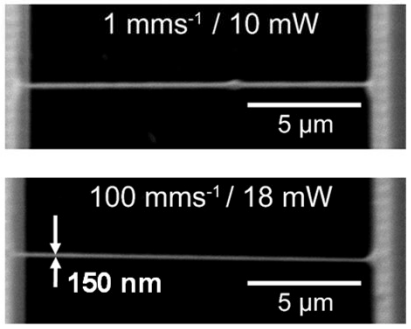
# Two-photon polymerization



A. Ovsianikov



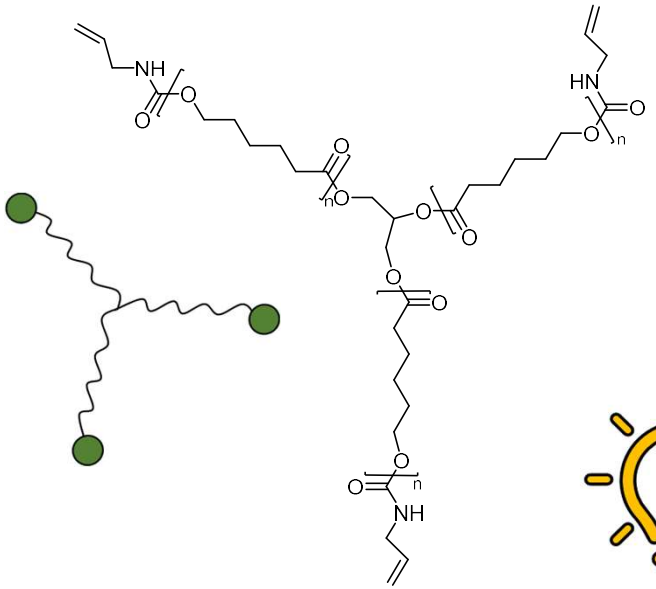



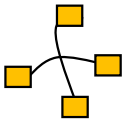



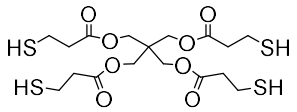

- No stable structures using di-functional AUPs
- Excellent CAD-CAM mimicry using multi-functional AUPs
- Multi-functional AUPs: high spatial resolution (±150 nm)
  high speed (up to at least 100 mm $s^{-1}$)

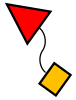
Arslan et al. Materials Today (2021), 44, 25-39

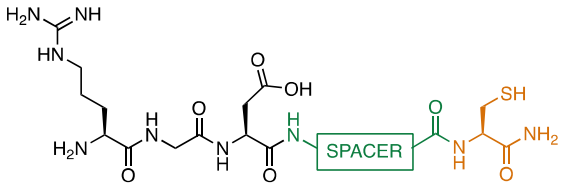
# Cell-adhesive networks







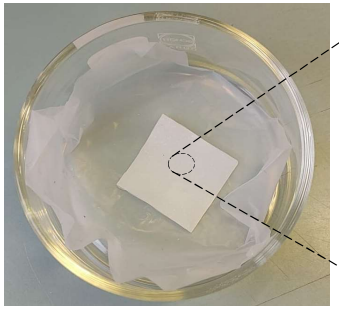


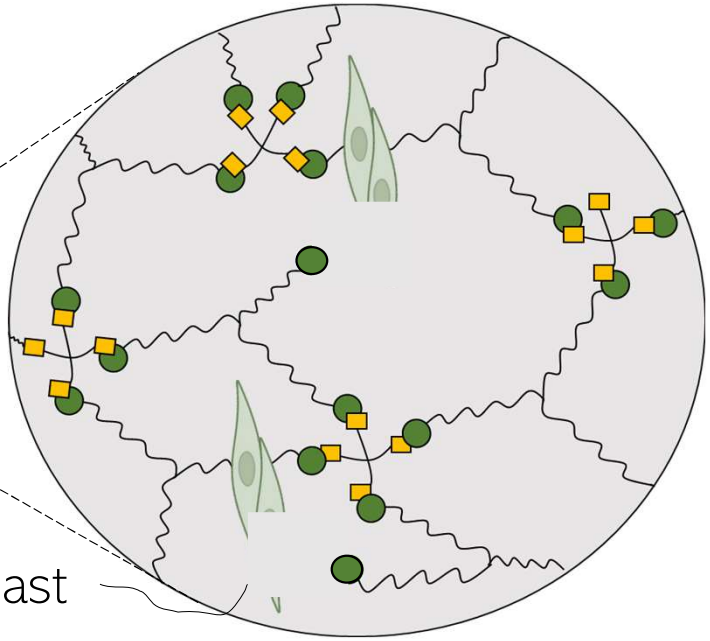






TPO-L



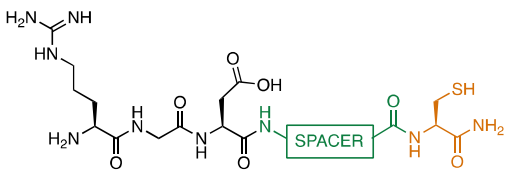


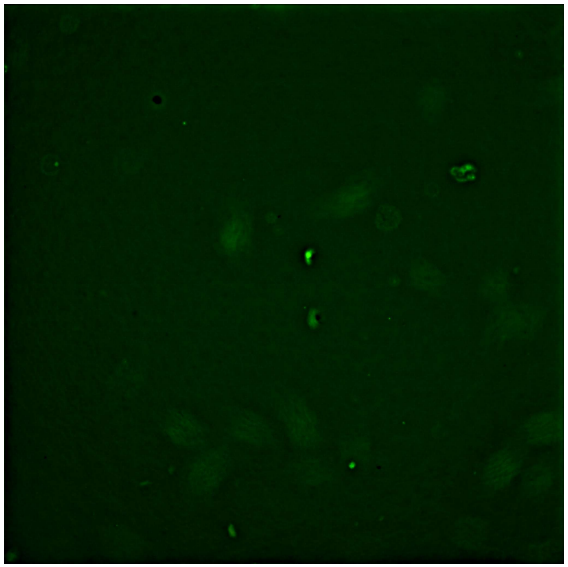
Fibroblast

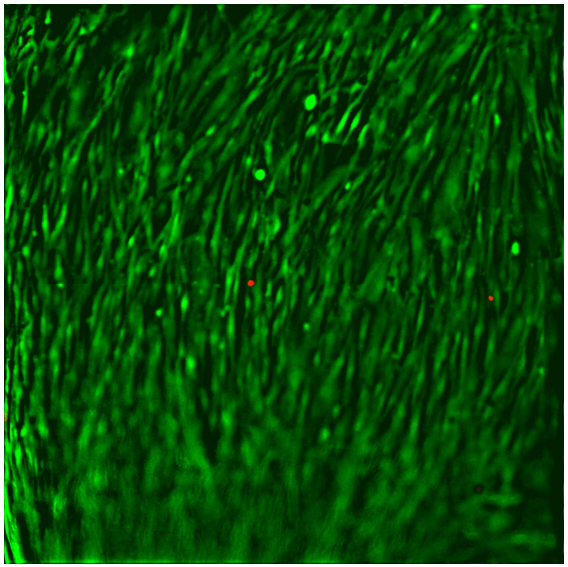
Thijssen et al. Biomacromolecules: 10.1021/acs.biomac.2c01389

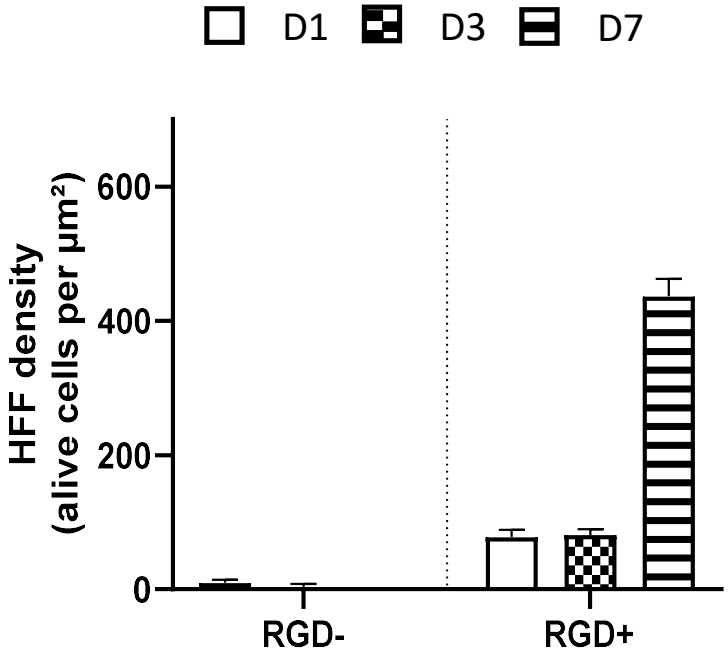
# Cell-adhesive networks



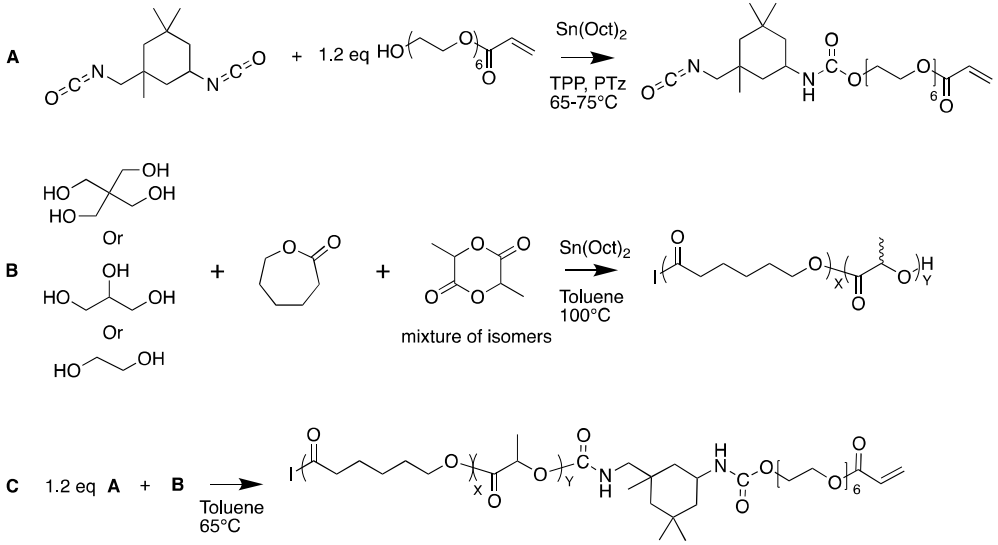



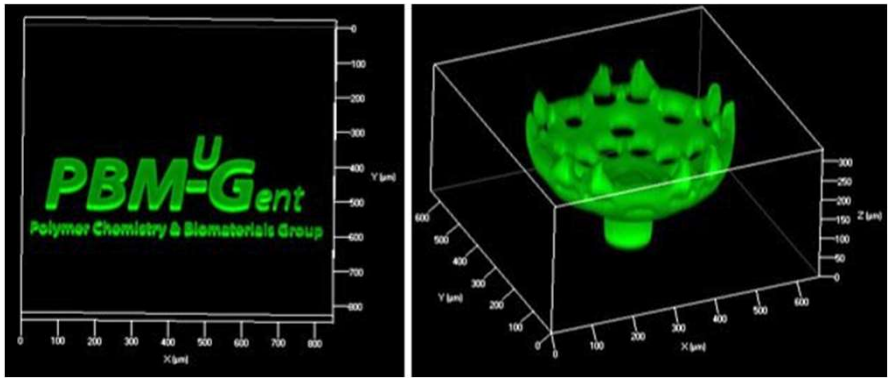


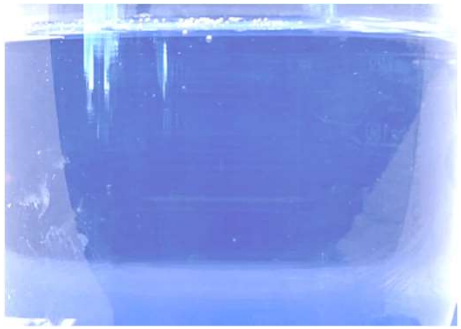


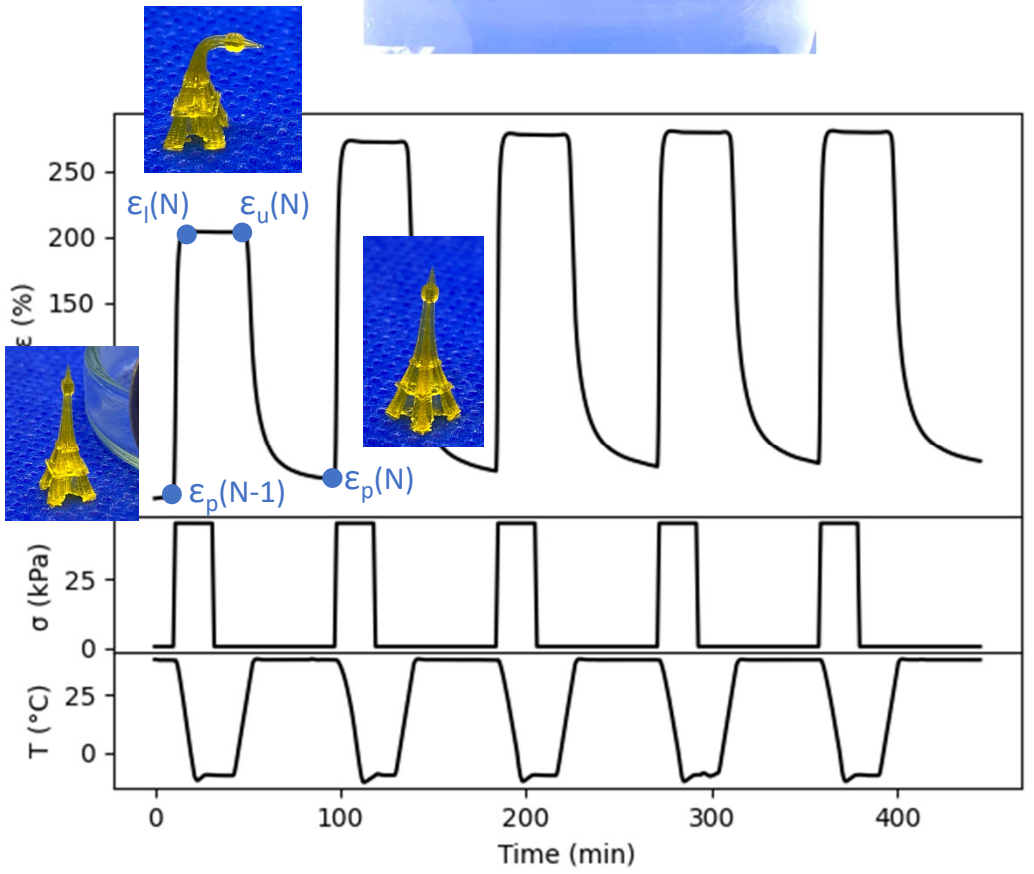

Thijssen et al. Biomacromolecules: 10.1021/acs.biomac.2c01389

# Shape memory polymers



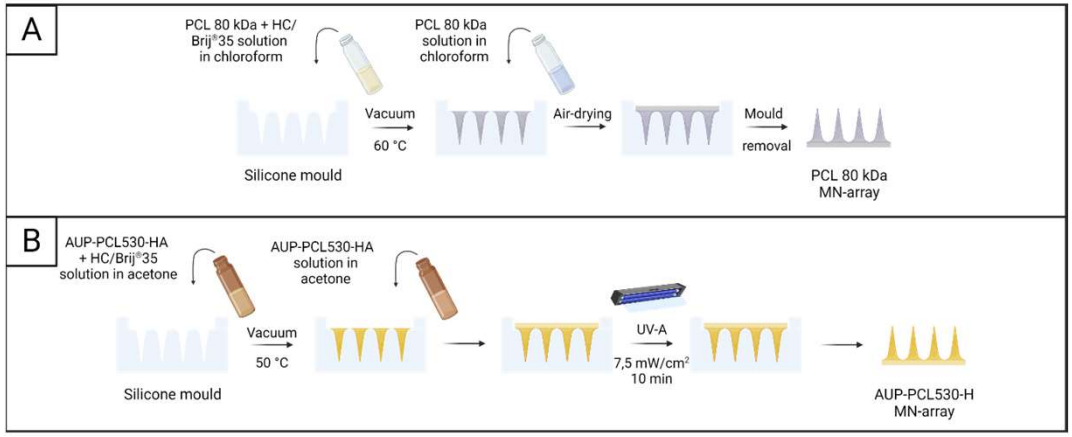



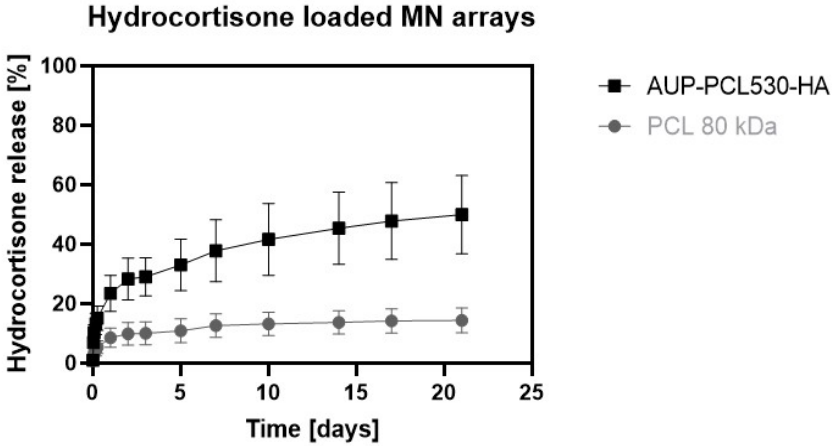



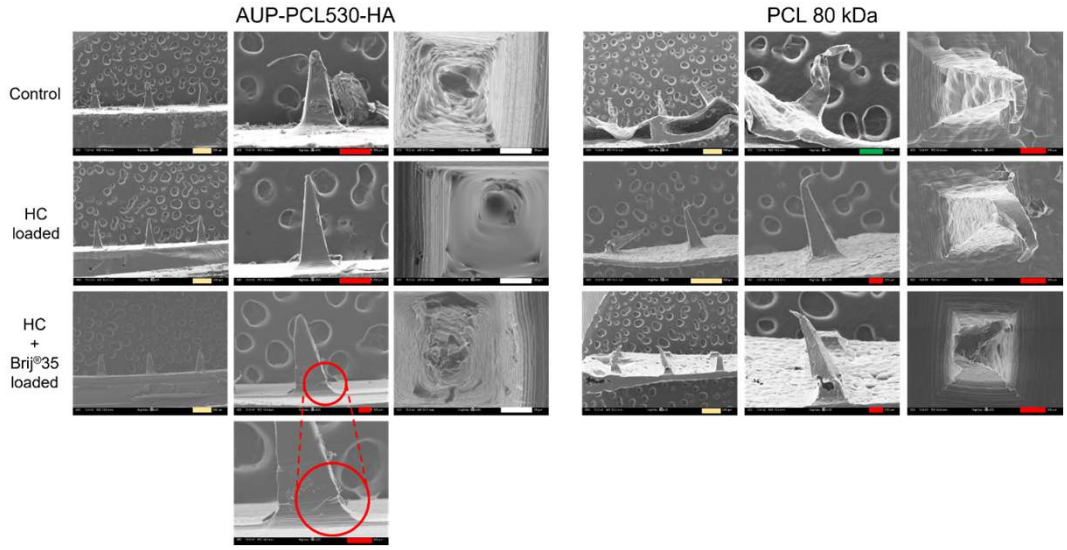


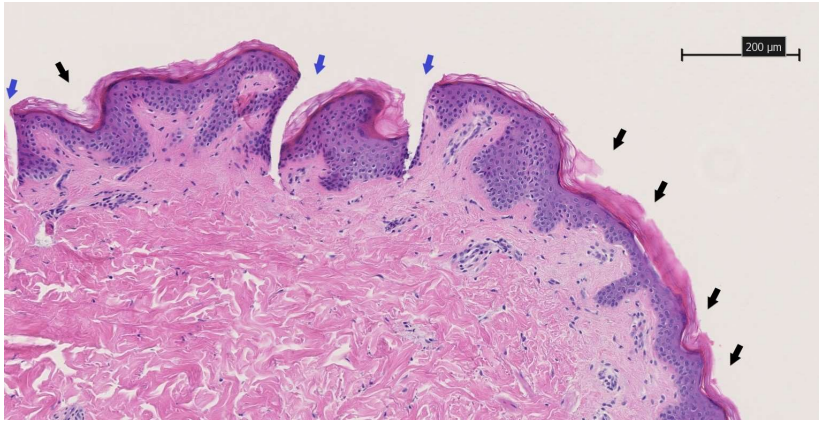

Delaey et al. Macromolecular Rapid Communications, 2023, 2200955

# PCL-based microneedles



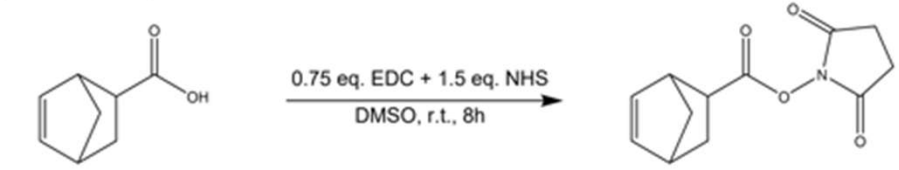



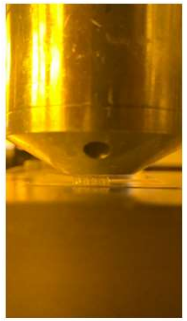



# Bioprinting of gelatin derivatives

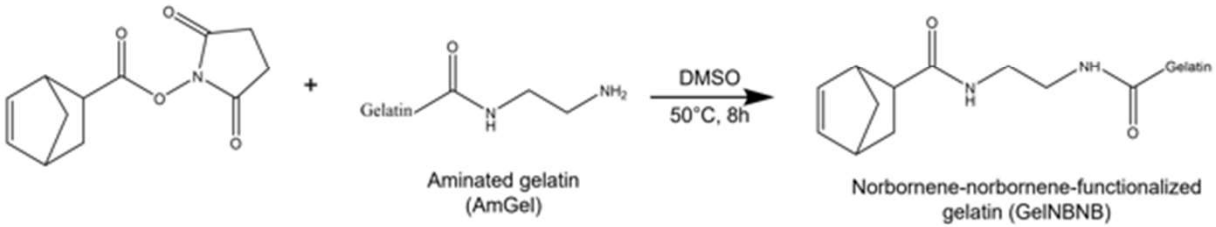
**1) Activation step**




5-norbornene-2-carboxylic acid

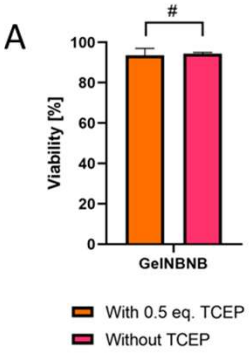


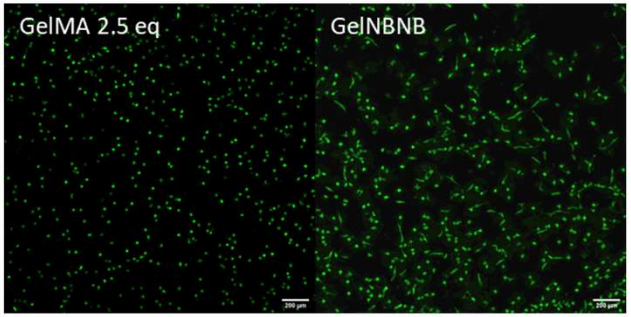
**2) Reaction**

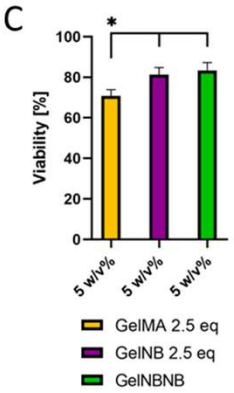


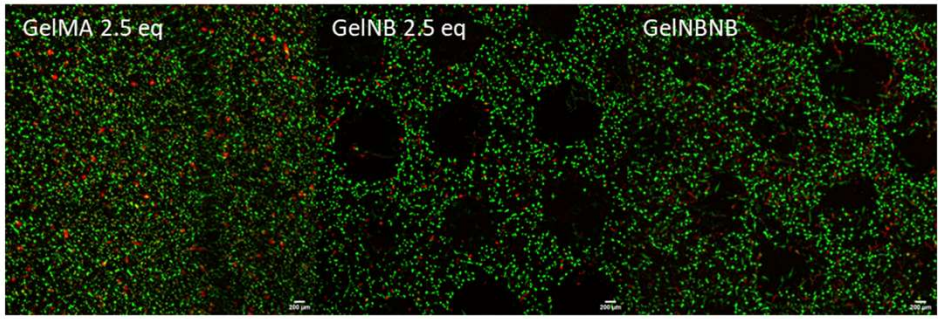

Aminated gelatin (AmGel)

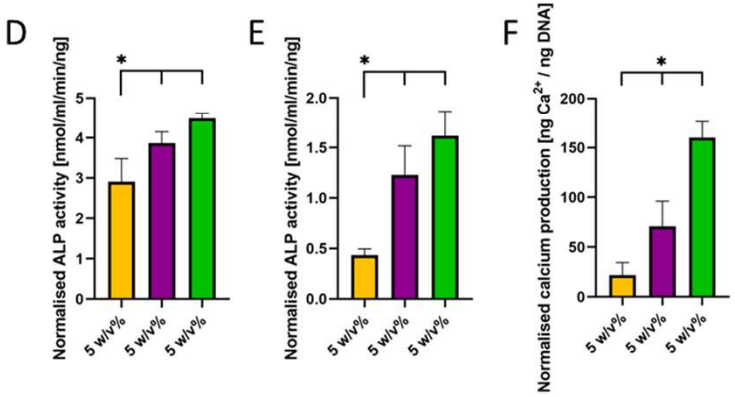
Norbornene-norbornene-functionalized gelatin (GelNBNB)



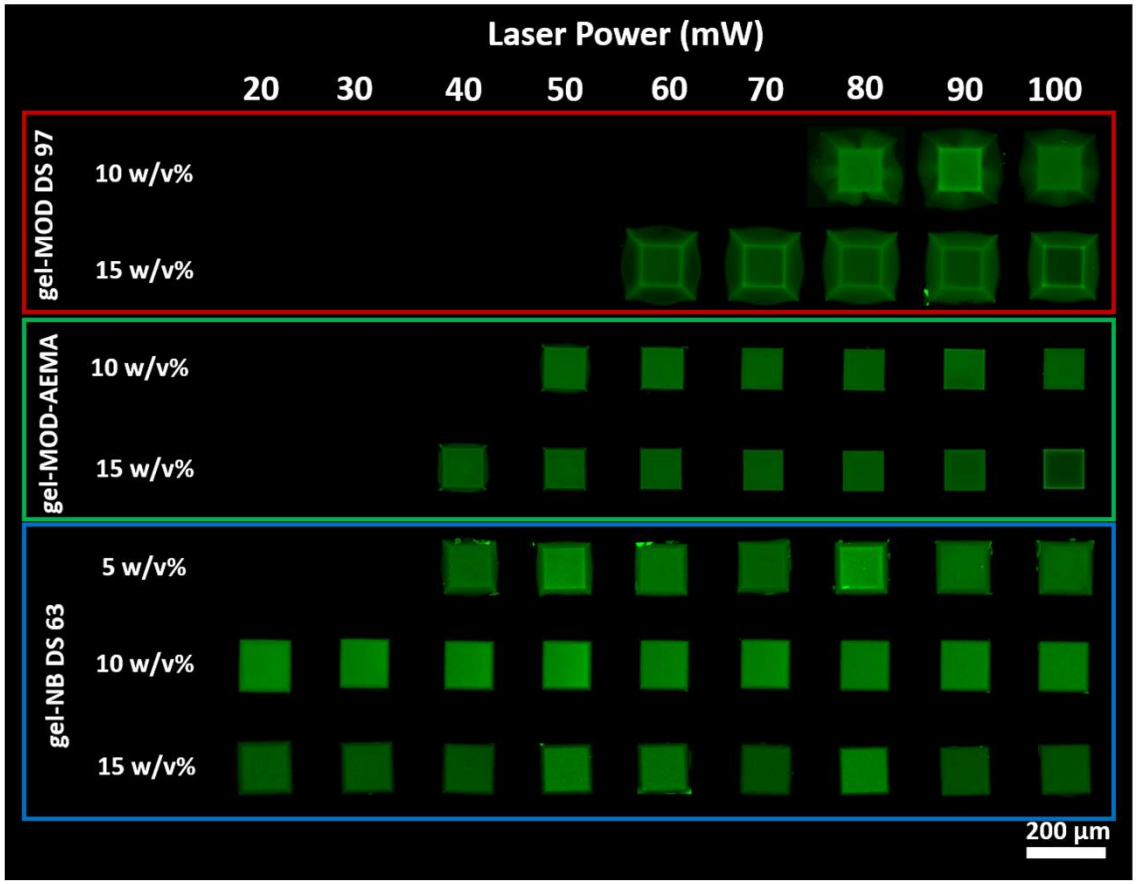



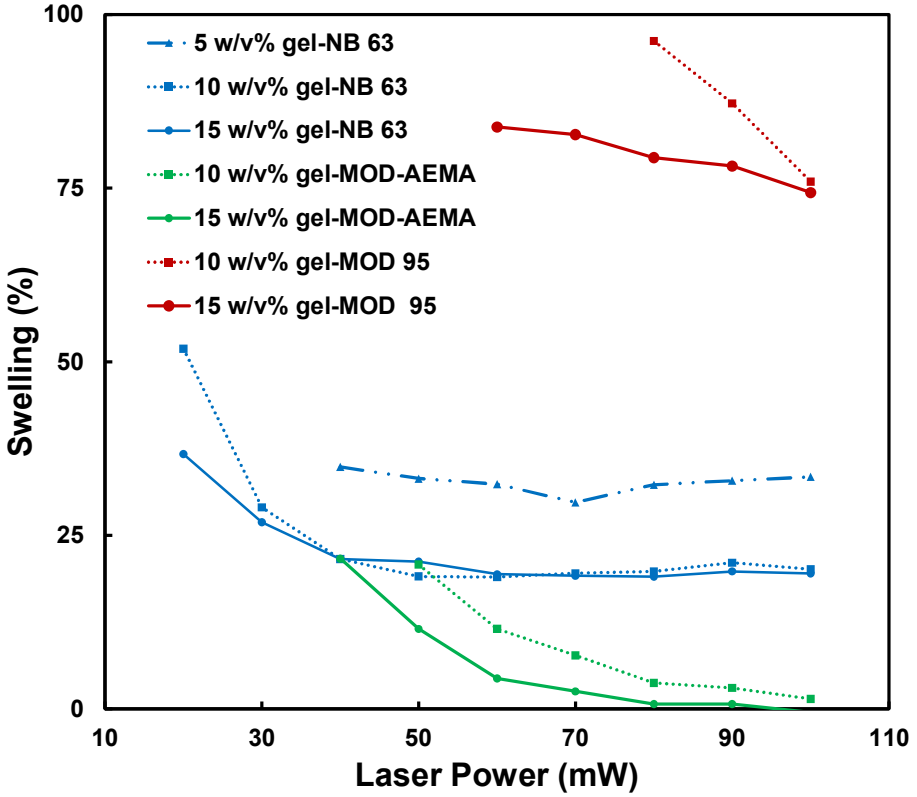



# Two-photon polymerization





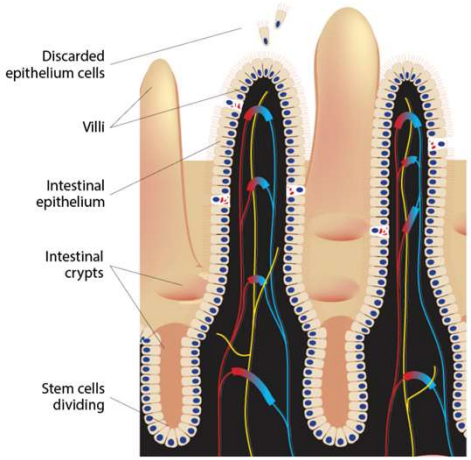

A. Ovsianikov

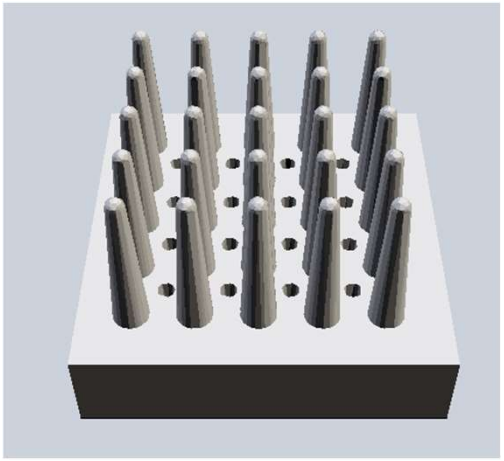


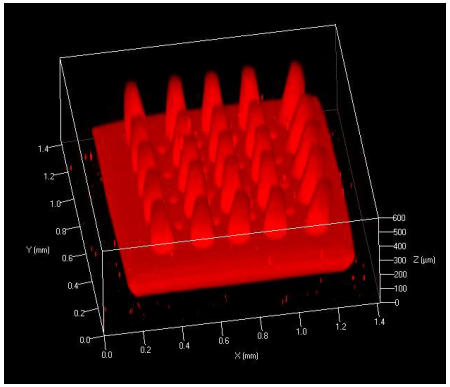


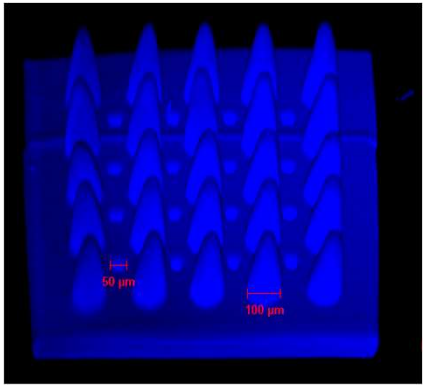
Van Den Bulcke, A. I. *et al. Biomacromolecules* 1, 31–38 (2000);
Ovsianikov, A. *et al. Biomacromolecules* 12, 851–858 (2011);
Van Hoorick, J. *et al. Biomacromolecules (2017)*
Van Hoorick, J. *et al. Macromolecular Rapid Communications (2018)*

# Intestinal TE



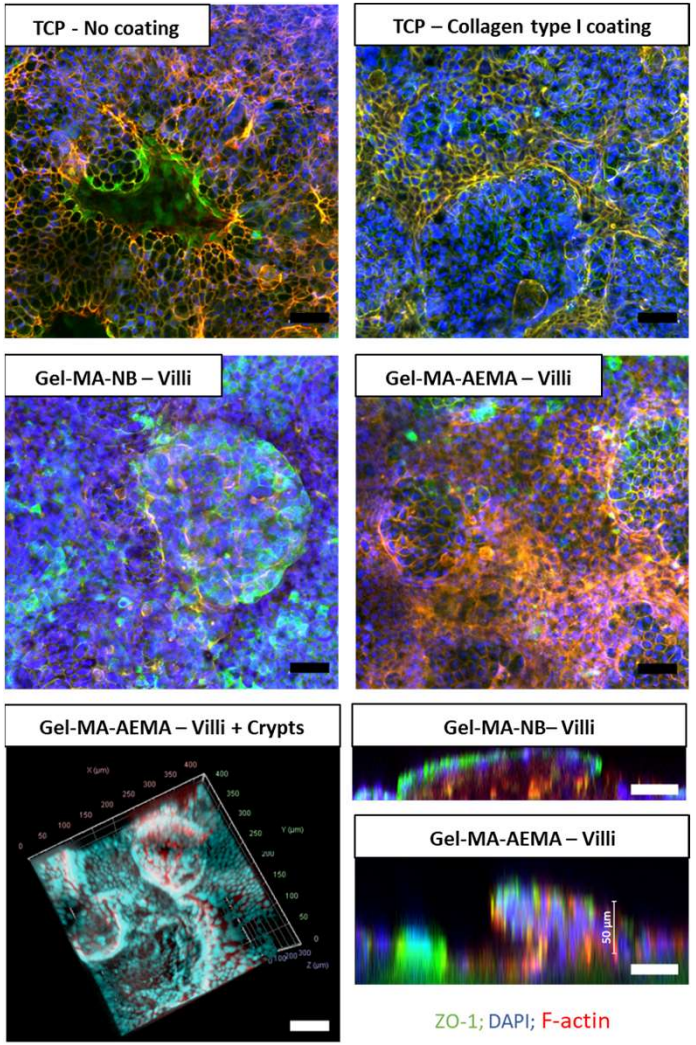



HYDROBIO INX© X400

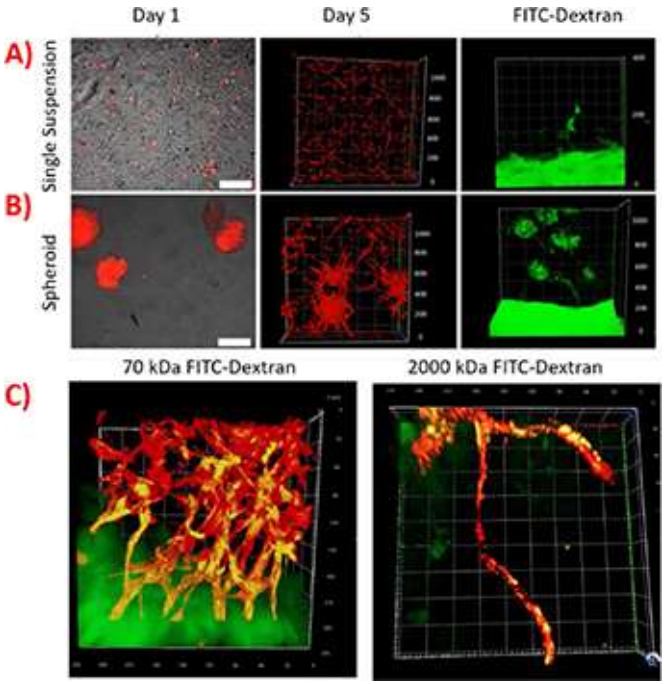
HYDROBIO INX© U200

***Overall dimensions:*** *1 mm x 1 mm x 0.680 mm*
***Villi:*** *100 µm bottom diameter, 50 µm top diameter, 425 µm height*
***Crypts:*** *50 µm diameter, 100 µm deep*




ZO-1; DAPI; F-actin

# Two-photon polymerization

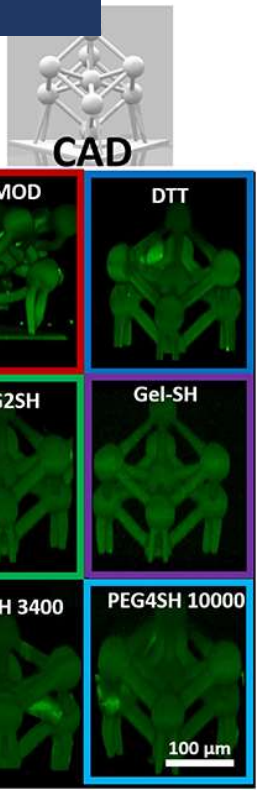



Dobos, *et al, Biofabrication*, (2021)

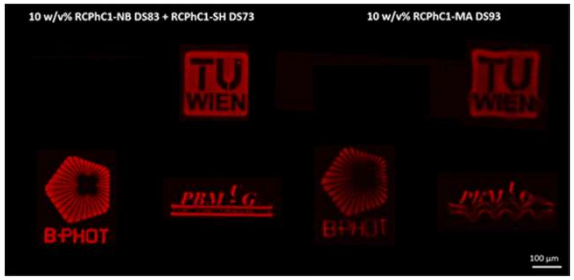




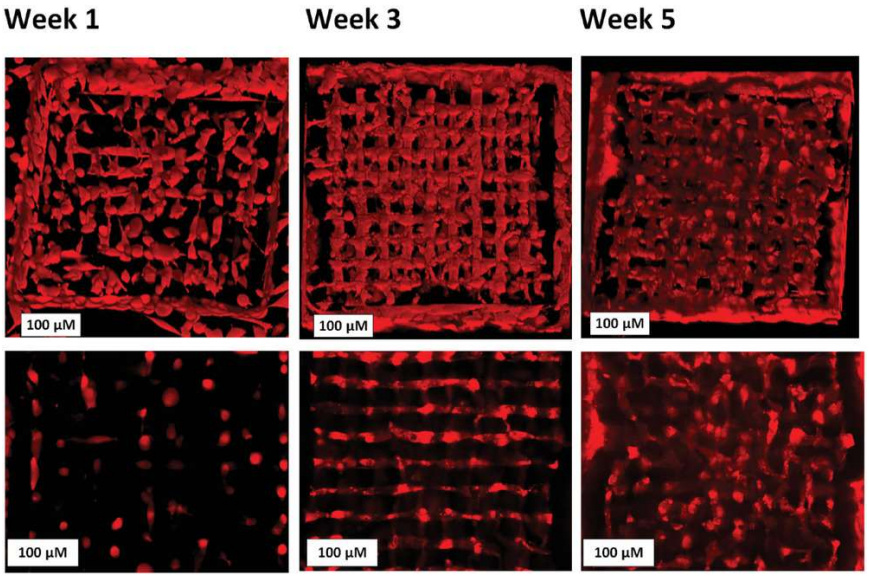

**A. Ovsianikov**



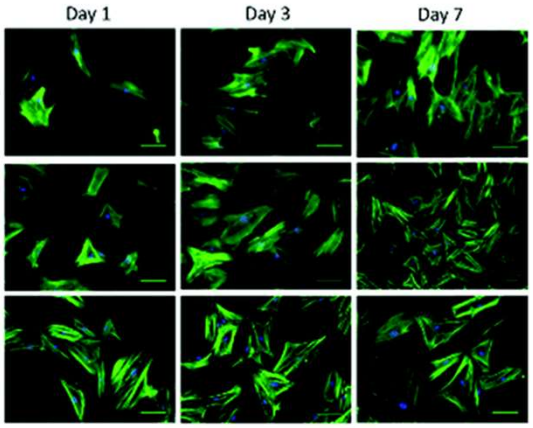

Van Hoorick, *et al, Biofabrication*, (2021)




Tygat, *et al, Biomacromolecules*, (2020)

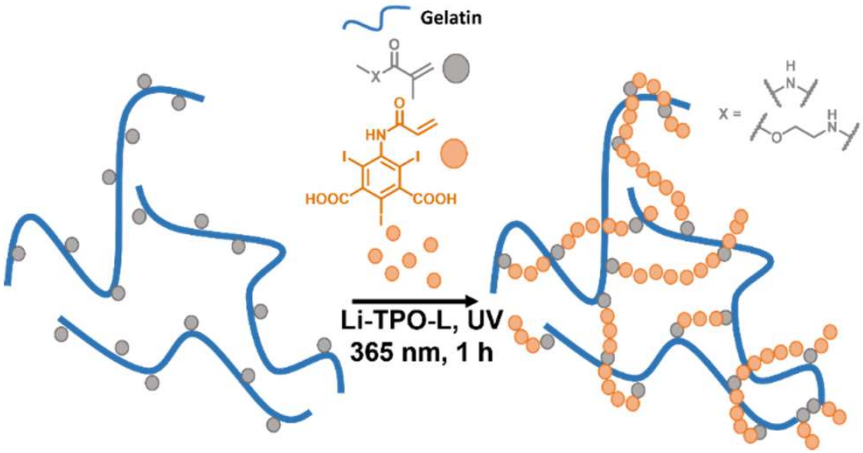


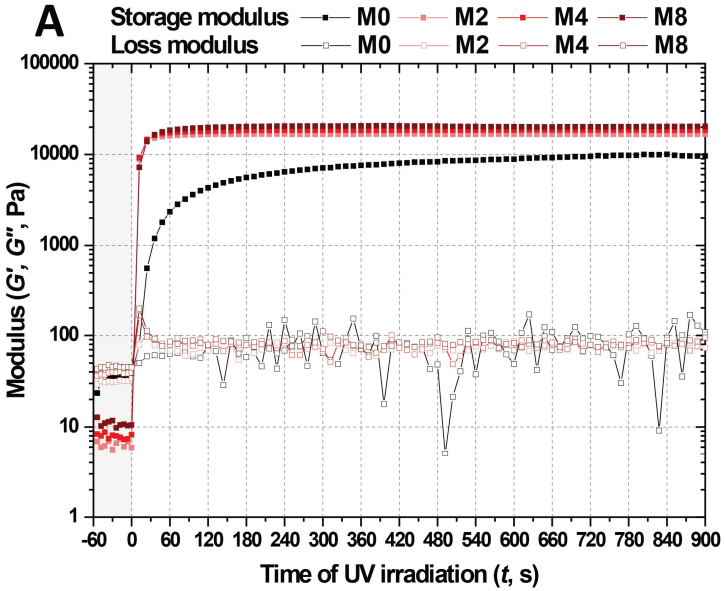

Dobos, *et al, Advanced Healthcare Materials*, (2019)

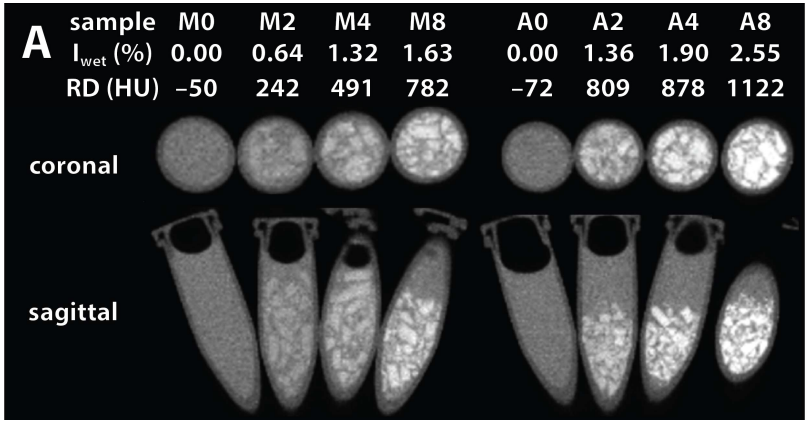


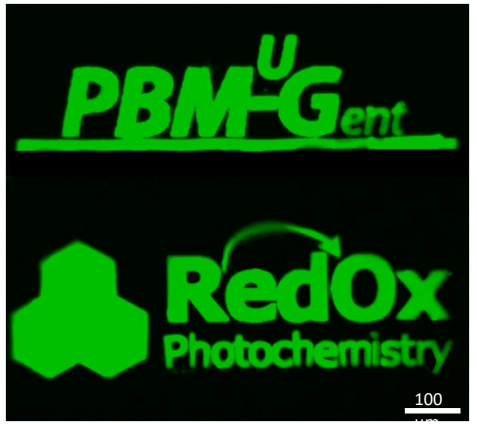

Tygat, *et al, Journal of Materials Chemistry B*, (2019)

# X-ray and CT detectable hydrogels




M = Gel-MA-100
A = Gel-MA-AEMA

***10 w/v% Gel-MA-AEMA + ATIPA, 1 mM P2CK*** *in PBS*
*(laser power = 150 mW, scanning speed = 100 mm* $s^{-1}$*)*

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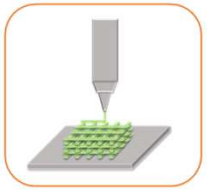
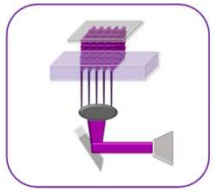
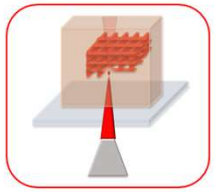


Deposition based 3D printing



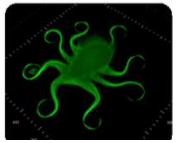
Digital light processing



Multiphoton lithography





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