FACULTY OF SCIENCES

PBM-UGent
Polymer Chemistry & Biomaterials Group

# Transparent Poly(ε-Caprolactone-co-δ-Valerolactone) Networks Towards Multi-Material Volumetric 3D Printing

**Bart Bijleveld***, Fátima Trejo Arroyo*, Edward Vermeersch*, Antonio Jaén Ortega*, Bo Li±, Quinten Thijssen*, Sandra Van Vlierberghe*

* Ghent University, Polymer Chemistry and Biomaterials Group (PBM), Centre of Macromolecular Chemistry, Department of Organic and Macromolecular Chemistry, Krijgslaan 281 S4, 9000, Ghent, Belgium
± Department of Chemistry, RCSI, University of Medicine and Health Sciences, Dublin, D02 YN77, Ireland

## Introduction

The demand for complex materials in the biomedical sector is increasing, often exceeding the capabilities of traditional 3D printing. Multi-material printing offers a solution by combining different materials with varying (sometimes opposing) properties. However current 3D printing techniques fails to incorporate these materials with high design flexibility due to the layer by layer printing approach.

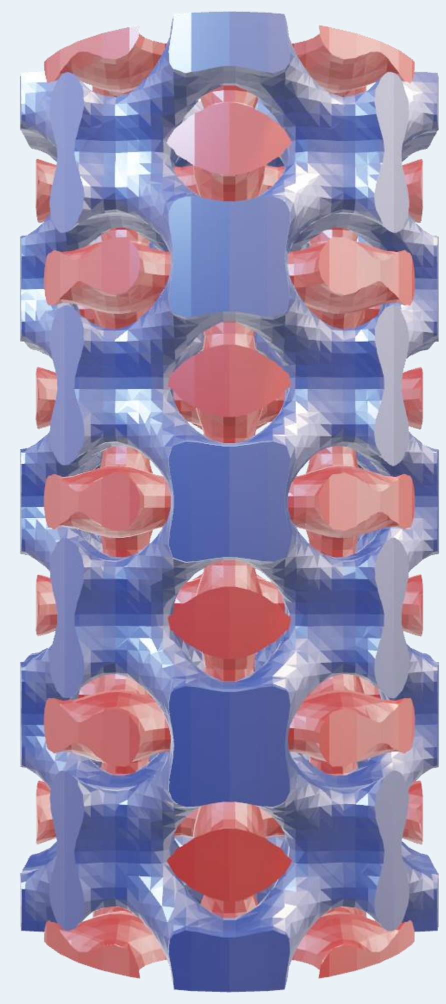
Volumetric 3D printing has emerged as an innovative method that can create intricate structures in less than a minute, achieving resolutions down to to 20 µm.[1,2] Unlike traditional techniques, it builds entire objects in one single step, allowing greater design flexibility and significantly reducing production time.

However, a key challenge in multi-material objects is ensuring the initial structure's light transparency. Crystalline microstructures can scatter light, resulting in resolution loss in subsequent print layers. For optimal results, the first material must have over 90% transparency at 405 nm.

### Co-Polyester

Function as long-term structural support scaffold

- Slow degradation (months-years)
- Lacks cell-adhesive motifs
- Hydrophobic
- Minimal swelling
- Mechanically strong and elastic

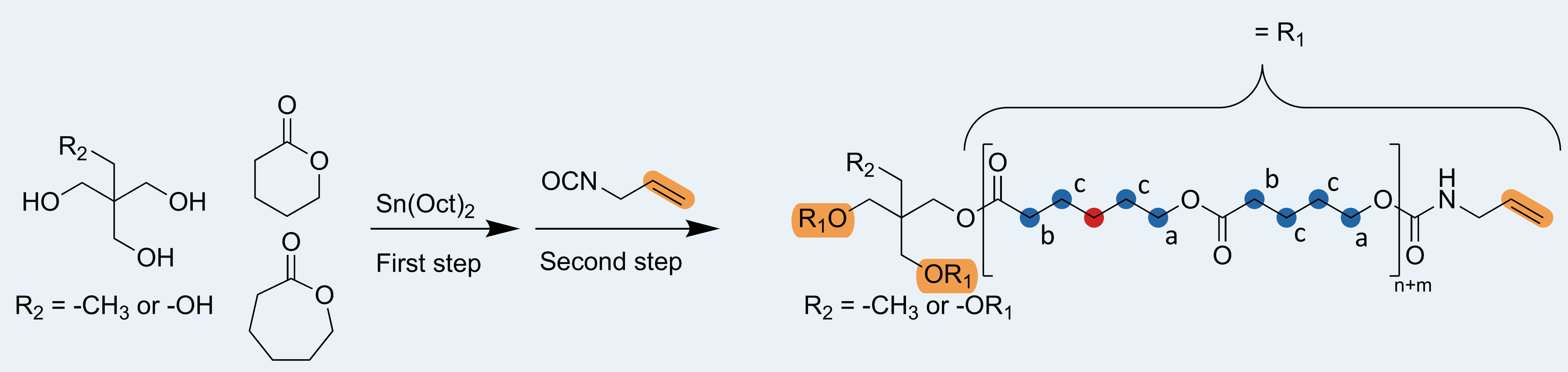


### GelMa

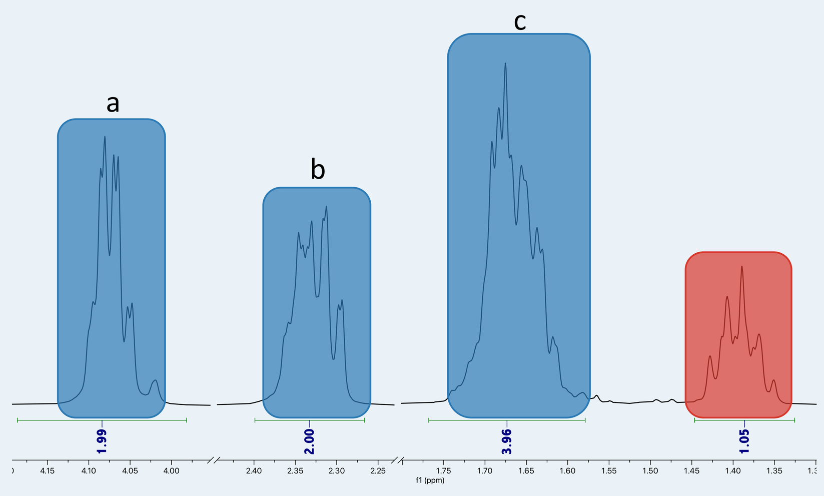
Mimics soft tissue to ensure bioactivity

- Rapid enzymatic degradation (days to months)
- Bioactive
  - Cell adhesion
  - Cell proliferation
- Hydrophilic
- Significant swelling in aqueous environments
- Soft but with tunable stiffness

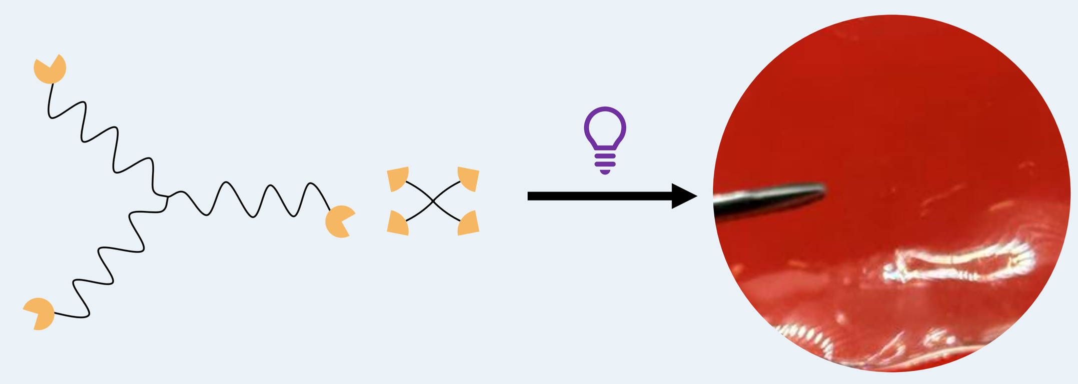
## Synthesis of Amorphous Poly(ε-Caprolactone-co-δ-Valerolactone)



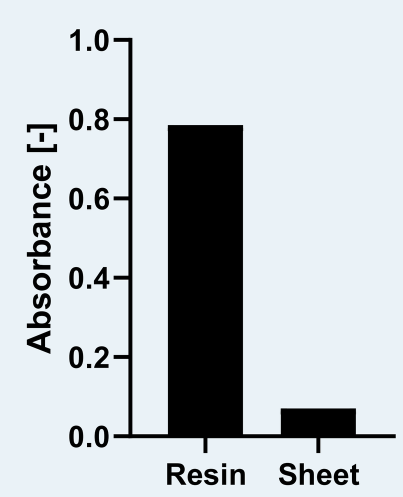

| Material | $M_N^{theor.}$ (Da) | $M_N^{exp.}$ (Da, H-NMR) | Conv. (%, $^1$H-NMR) | ε-CL: δ-VL | Alkene content$^{theor.}$ (mmol/g) | Alkene content$^{exp.}$ (mmol/g) |
|---|---|---|---|---|---|---|
| PCL:VL-8k-3A | 8000 | 7827 | 95.5 | 1:0.94 | 0.36 | 0.40 |
| PCL:VL-8k-3A | 8000 | 7904 | 97.7 | 1:1.1 | 0.36 | 0.37 |
| PCL:VL-8k-3A | 8000 | 8149 | 99.8 | 1:0.92 | 0.36 | 0.34 |
| PCL:VL-8k-4A | 8000 | 8320 | 99.5 | 1:0.89 | 0.47 | 0.48 |

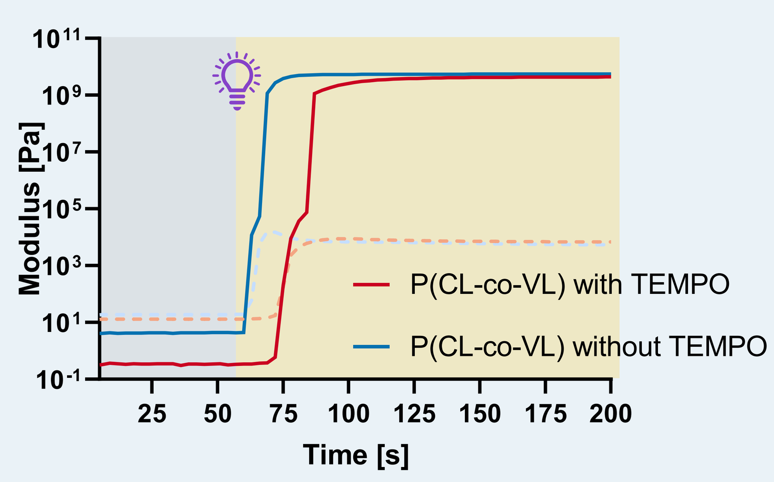



## Transparent Poly(ε-Caprolactone-co-δ-Valerolactone) Network

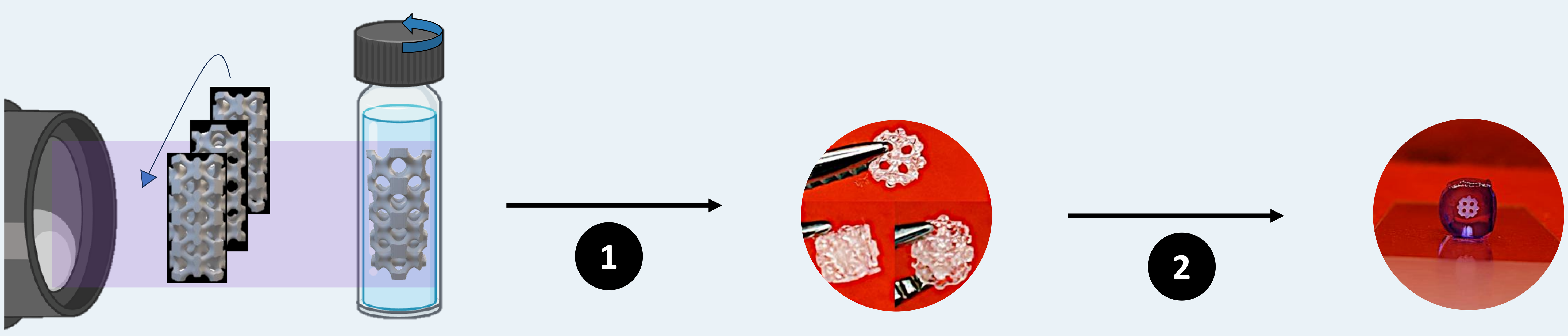


*Transparent sheet*

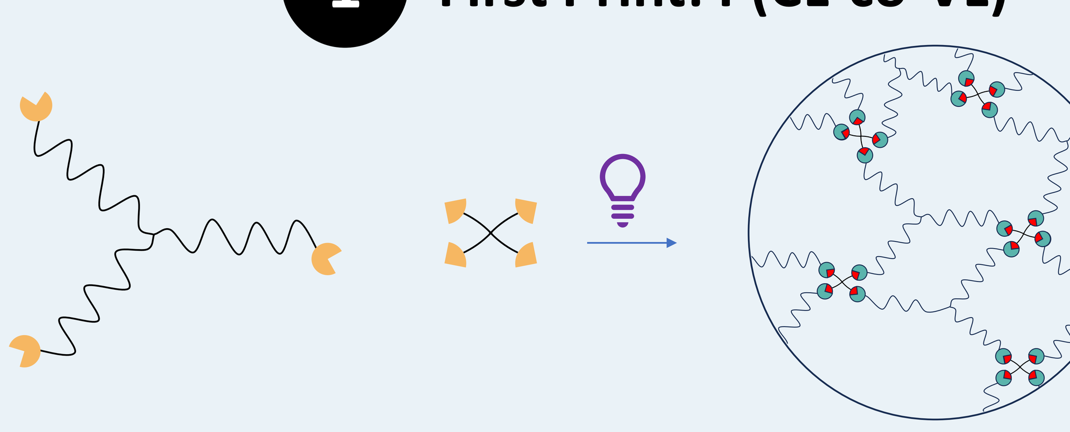



## Sequential Volumetric 3D printing of Amorphous Polyester Network (1) Followed by GelMA (2)

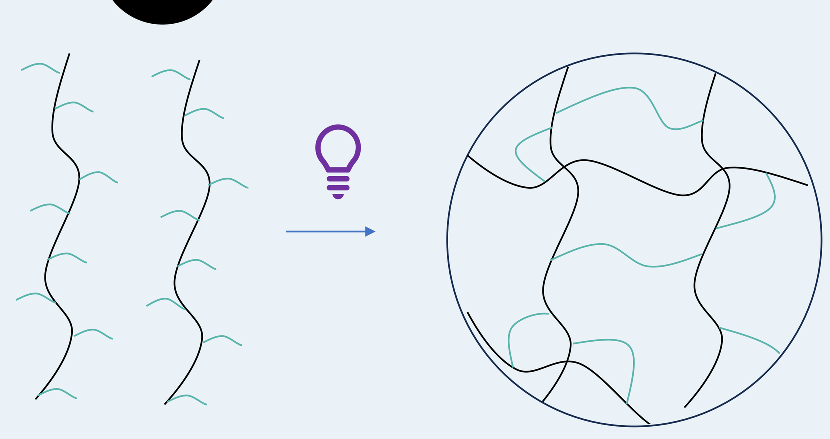



### 1 First Print: P(CL-co-VL)



- Extraction of delicate structure
- Post UV curing after extraction

### 2 Second Print: GelMA



- Transparency of structure decreased in GelMA resin
- Solution needs time to settle

## Conclusion and Future Perspectives

A highly transparent three-arm polyester, synthesized from ε-CL and d-VL, achieved over 90% transmittance at 405 nm through the amorphous polyester pre-polymer.

Following the polyester synthesis, multi-material printing was conducted using sequential VAM printing. After photo-induced polymerization, the polyester was extracted, washed, and placed inside a GelMA resin.

Initial findings indicate that crosslinking occurs in the scaffold's pores. For more complex designs, precise alignment of the scaffold in the secondary resin is essential, and considerations regarding light diffusion and refraction are necessary to avoid artifact creation due to the high internal surface area affecting light dosage received.

+ »

Biomedical Applications
Incorporation of varying materials
More complex design
Higher resolution

VAM multi-material printing enables the integration of incompatible properties within a single structure, such as combining flexible and rigid elements. The technique meets the increasing complexity requirements of biomedical applications, especially in the replication of natural environments and cellular layered structures. By sequentially printing materials through an initial transparent framework, this approach facilitates a level of complexity that traditional 3D printing methods cannot achieve.

## Contact

E: Bart.Bijleveld@ugent.be

PBM UGent
@PBMUGENT
PBM UGent

**References**
(1) Thijssen, Q.; Toombs, J.; Li, C. C.; Taylor, H.; Van Vlierberghe, S. From Pixels to Voxels: A Mechanistic Perspective on Volumetric 3D-Printing. *Prog. Polym. Sci.* **2023**, *147*, 101755. https://doi.org/10.1016/j.progpolymsci.2023.101755.
(2) Thijssen, Q.; Quaak, A.; Toombs, J.; De Vlieghere, E.; Parmentier, L.; Taylor, H.; Van Vlierberghe, S. Volumetric Printing of Thiol-Ene Photo-Cross-Linkable Poly(ε-Caprolactone): A Tunable Material Platform Serving Biomedical Applications. Adv. Mater. 2023, 35 (19), 2210136. https://doi.org/10.1002/adma.202210136.

GHENT UNIVERSITY