4D – Printing of reversible stress-free semicrystalline shape-memory polymers

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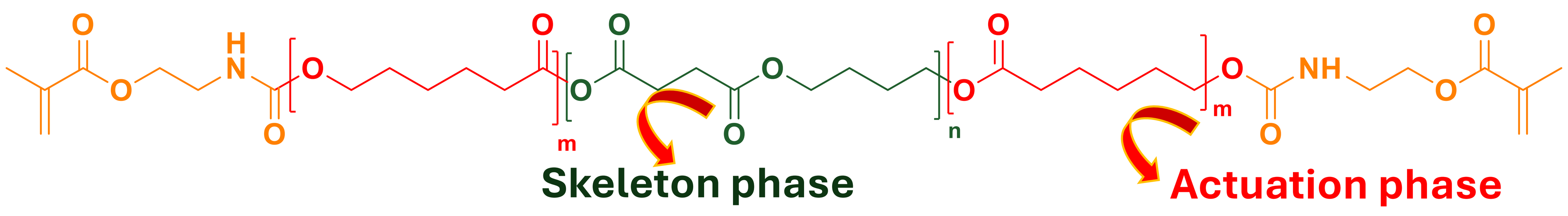
Reversible stress-free shape-memory polymers

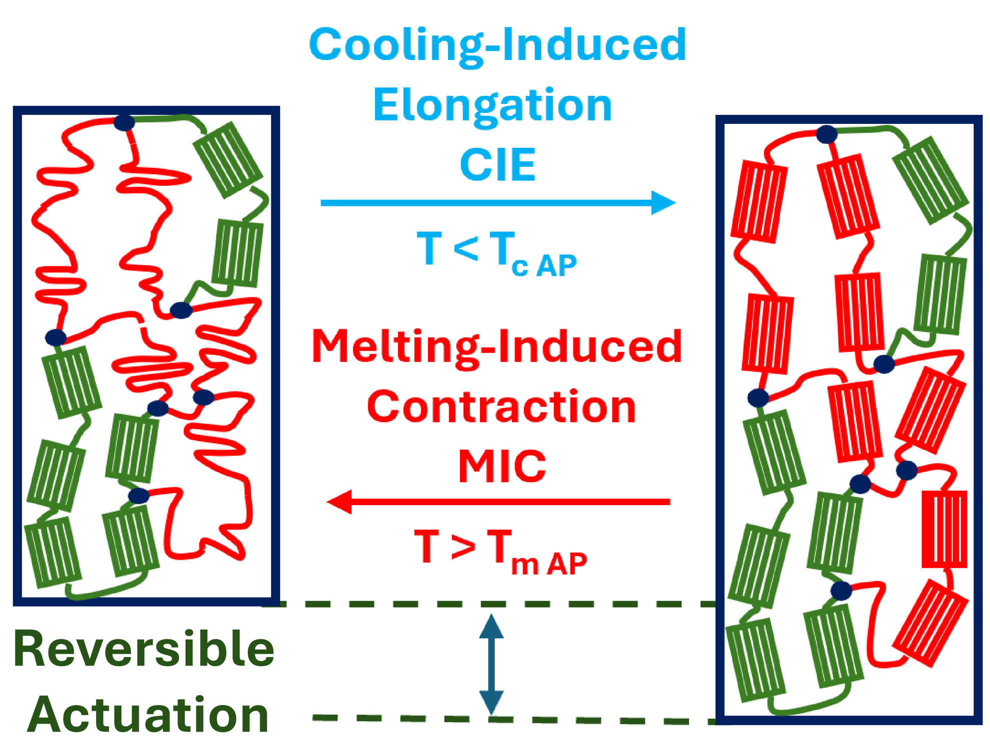


Skeleton phase
Polybutylene succinate - PBS

Actuation phase
Poly-(ε-caprolactone) - PCL

Crosslinkable triblock PCL-PBS-PCL copolymers were synthesized varying molecular weights and films were produced by photo-polymerization.

The multicrystalline network can be programmed to change shape by reversibly *melting* and *re-crystallizing* the *actuation phase (AP)* through a mechanism of elongation and contraction known as *CIE* (crystallization-induced elongation) and *MIC* (melt-induced contraction)[1].

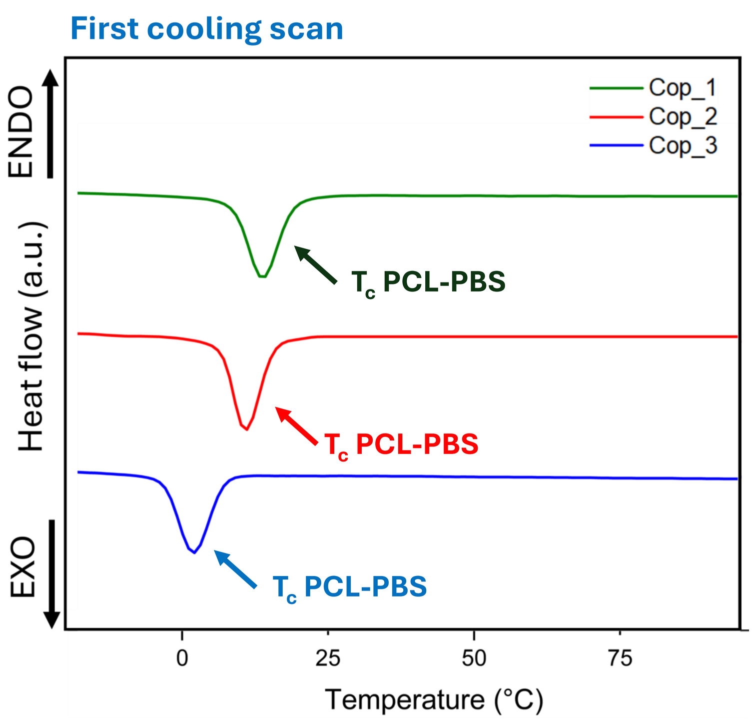


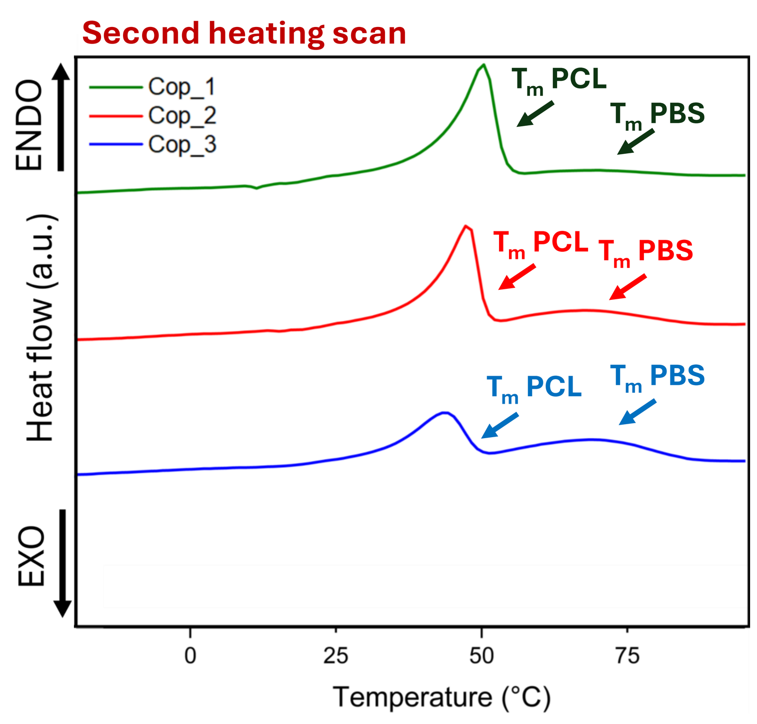
Shape-memory properties of copolymers mixture were evaluated under stress-free conditions, by monitoring the evolution of the strain upon heating-cooling cycles without any external load applied. The magnitude of the *actuation* represents the amount of elongation registered during the crystallization.

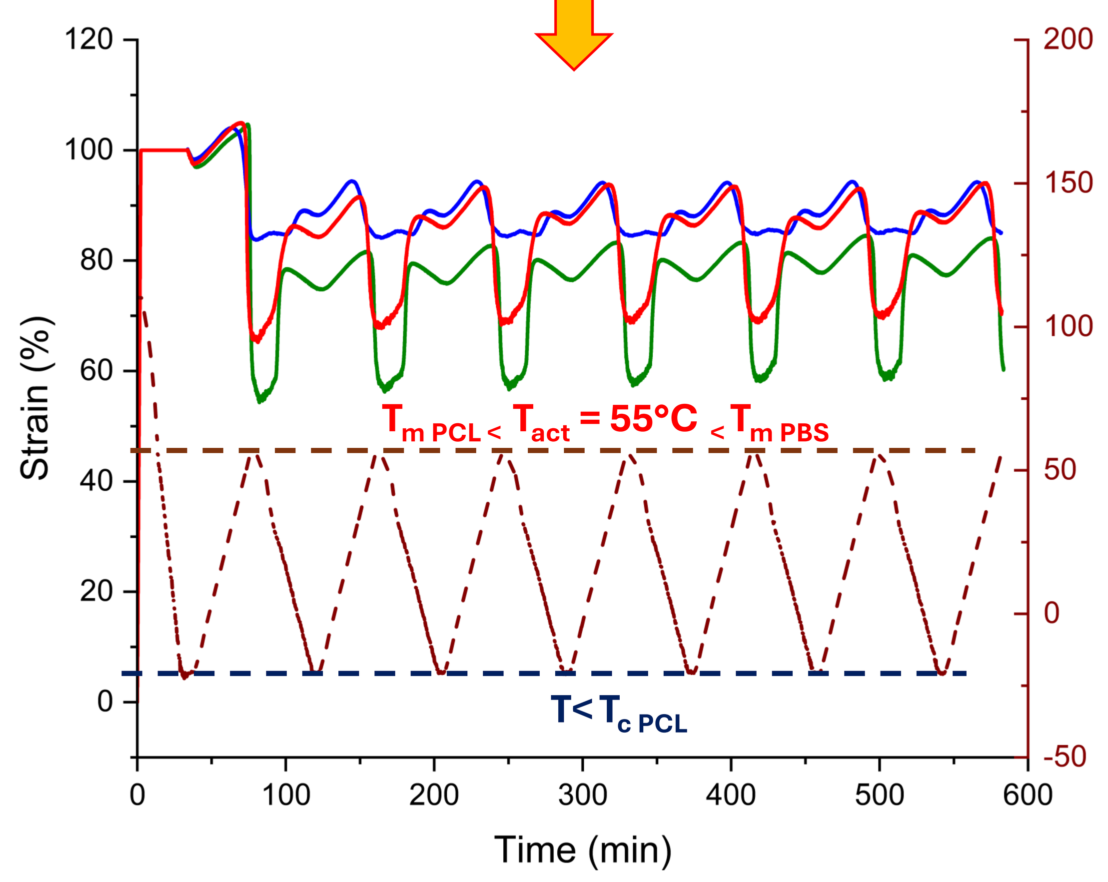
Code	M_n PCL block	M_n PBS block
S_1	9K	4 K
S_2	3K	

Sample	Composition
Cop_1	75% S_1 – 25% S_2
Cop_2	50% S_1 – 50% S_2
Cop_3	25% S_1 – 75% S_2

Sample	Actuation
Cop_1	24 %
Cop_2	18 %
Cop_3	4 %





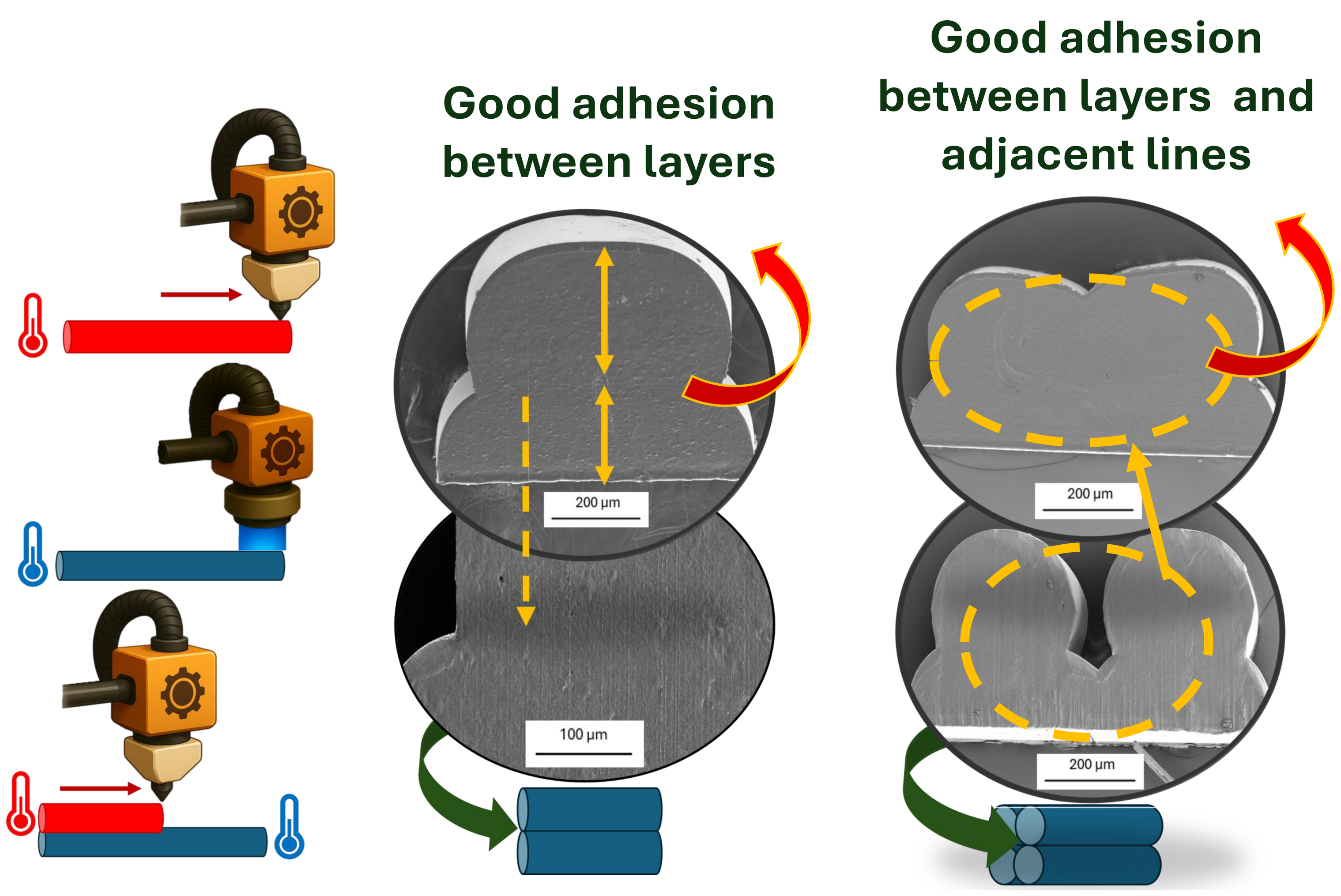


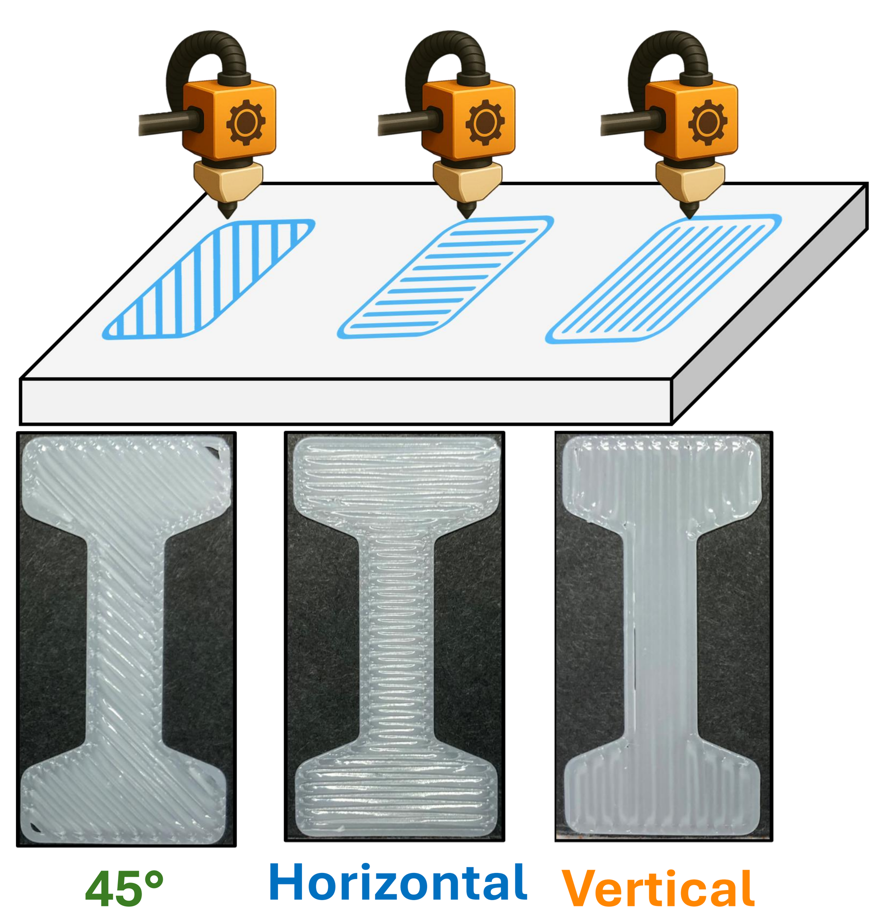
4D-Printing and shape-memory effects

Manufacturing of shape-memory polymers through 3D-printing[2-5].

Fused Particle Fabrication (FPF) extrusion-based 3D-printing technique.

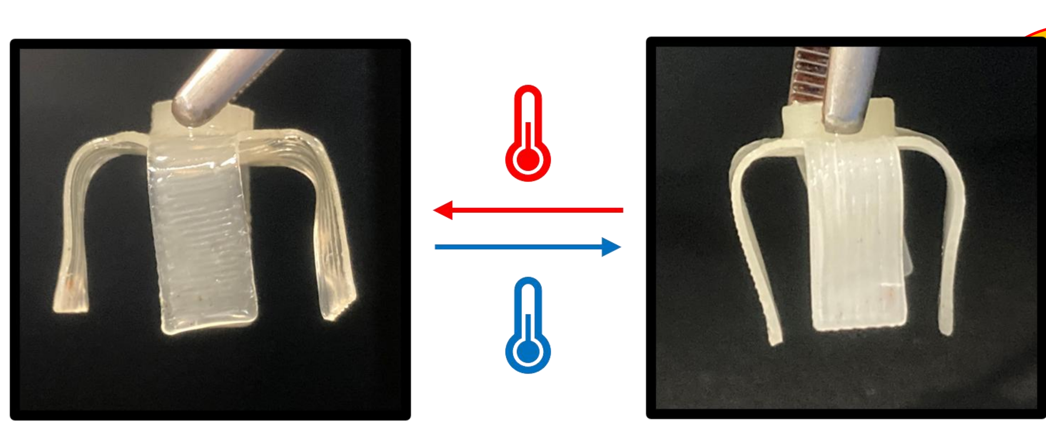
Optimized Printing conditions	
Temperature	100 °C
Pressure	3.5 bar
Speed	4 mm/s





Filling orientation	Average E (MPa)	Average Actuation
Vertical 1 Layer	168.0 ± 5,2	8.0 %
Vertical 2 Layers	151.1 ± 7,8	8.0 %
Vertical 3 Layers	153.7 ± 6,3	7.5 %
Horizontal 1 Layer	163.2 ± 5,8	8.5 %
45° 1 Layer	163.3 ± 4,8	8.5 %

Cross-linked samples	Gel Content (%)	Actuation
FIlms	88 ± 1	24.0 %
4D-Printed - Monolayer	82 ± 1	7.5 – 8.5 %



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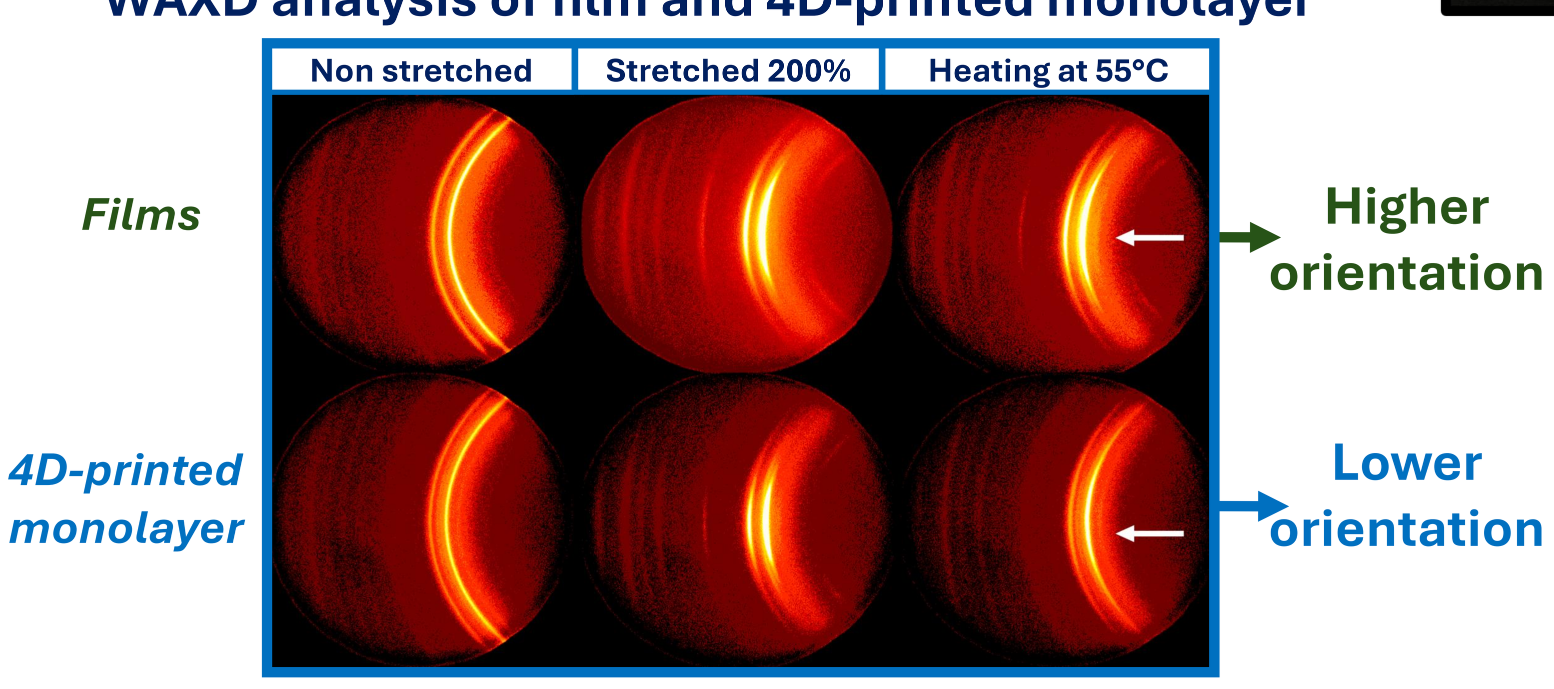
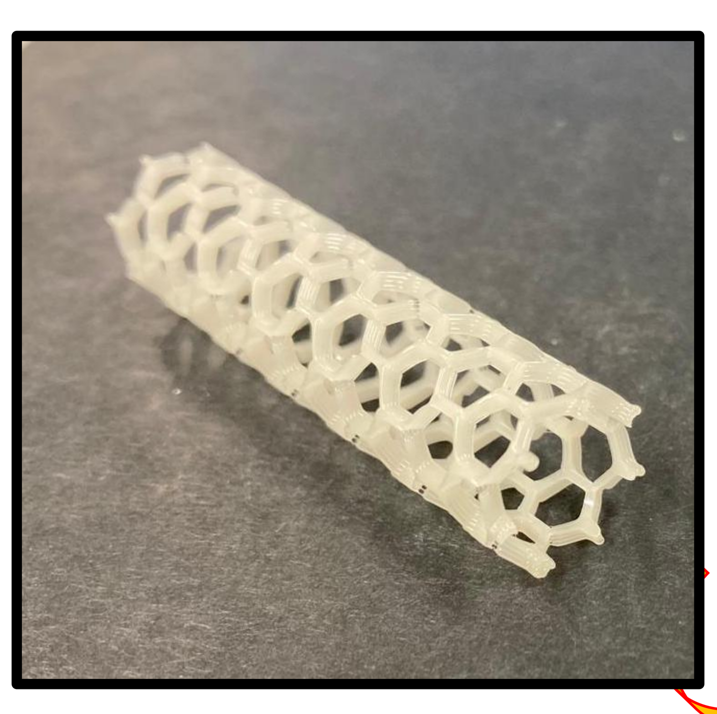
WAXD analysis of film and 4D-printed monolayer





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(1) Wang, K.; Jia, Y. G.; Zhao, C.; Zhu, X. X. *Progress in Materials Science*. Elsevier Ltd August 1, 2019.
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