Supporting Information

Delayed Crosslinking Enables Ultra-High-Resolution Melt Electrowriting of Responsive Liquid Crystal Elastomers

*Mehrzad Javadzadeh1, María Fernández-Melero[1], Jesús del Barrio[2] and Carlos Sánchez-Somolinos[1,3]**

[1] Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, Departamento de Física de la Materia Condensada, Zaragoza, 50009, Spain.

[2] Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, Departamento de Química Orgánica, Zaragoza, 50009, Spain.

[3] Centro de Investigación Biomédica en Red de Bioingeniería, Biomateriales y Nanomedicina (CIBER-BBN), Instituto de Salud Carlos III, Madrid 28029, Spain.

*Corresponding author: carlos.s@csic.es

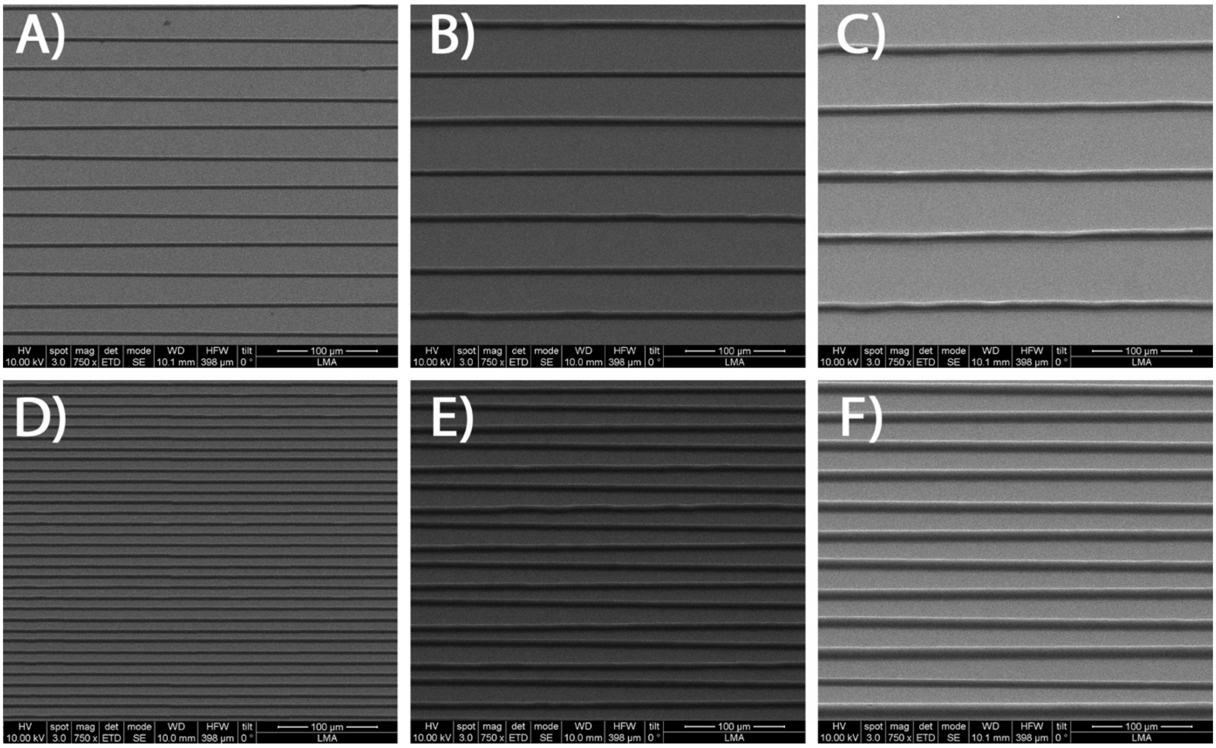

Figure SI1. Raw SEM images corresponding to Figure 2. Illustrating the effect of UV light intensity and number of printed layers on the minimum inter-fiber distance (IFD) without fiber bridging for 5 µm-diameter fibers. A-C) Samples printed under high UV intensity (15 mW/cm^2), showing the minimum IFD without fiber bridging for A) 1 layer (1L), B) 5 layers (5L), and C) 10 layers (10L). D-F) Samples printed under low UV intensity (9 mW/cm^2), showing the corresponding minimum IFD for D) 1 layer (1L), E) 5 layers (5L), and F) 10 layers (10L).

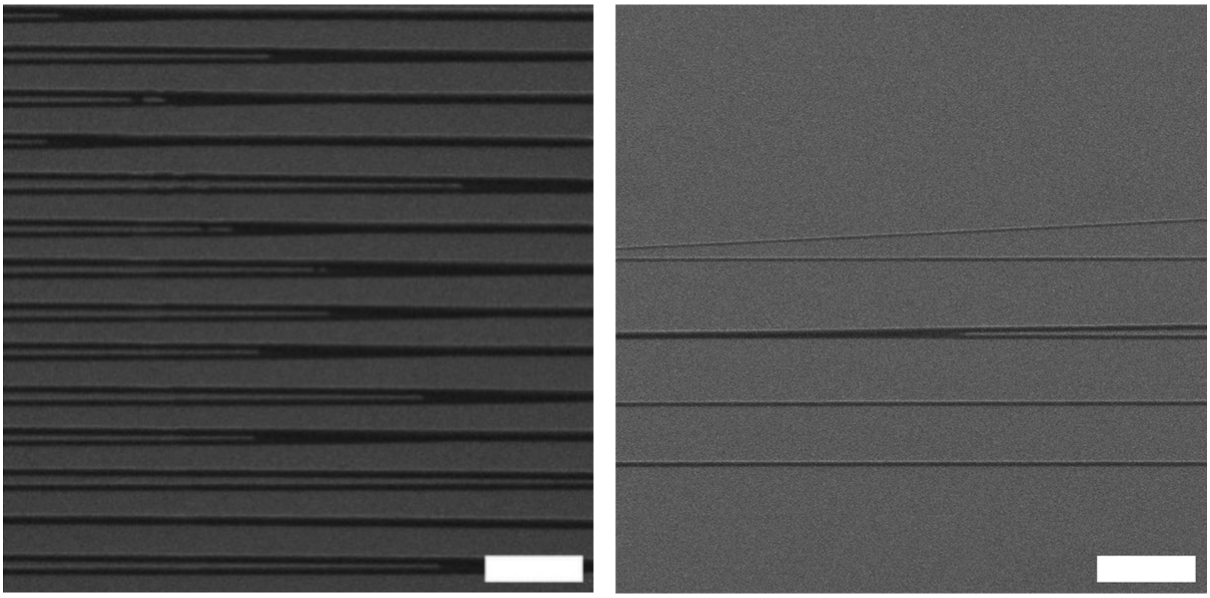

Figure SI2. Fiber Bridging at Low IFD under High UV Light Intensity. SEM image of melt electrowritten (MEW) 5 µm diameter fibers (one layer) deposited under high UV light intensity (15 mW/cm^2). Fibers were printed with an interfiber distance (IFD) of 25 µm. Scale bar: 50 µm.

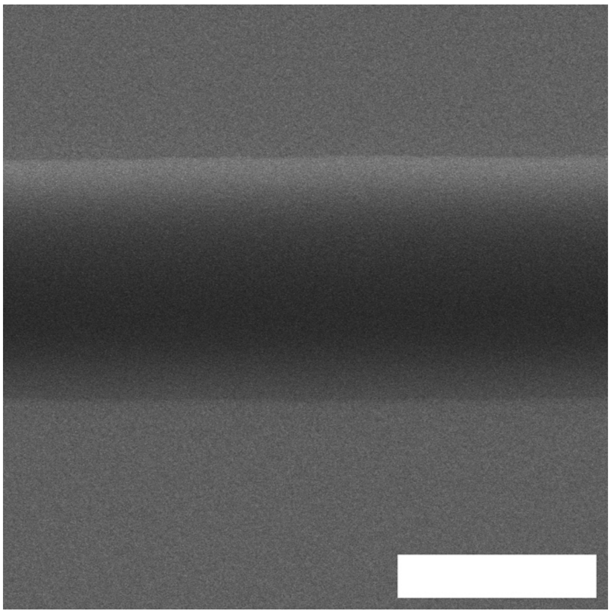

Figure SI3. Fiber Fusing due to Insufficient UV Light Intensity. Four printed stacked fibers (5 µm diameter) that fuse due to insufficient crosslinking during deposition. Scale bar: 5 µm.

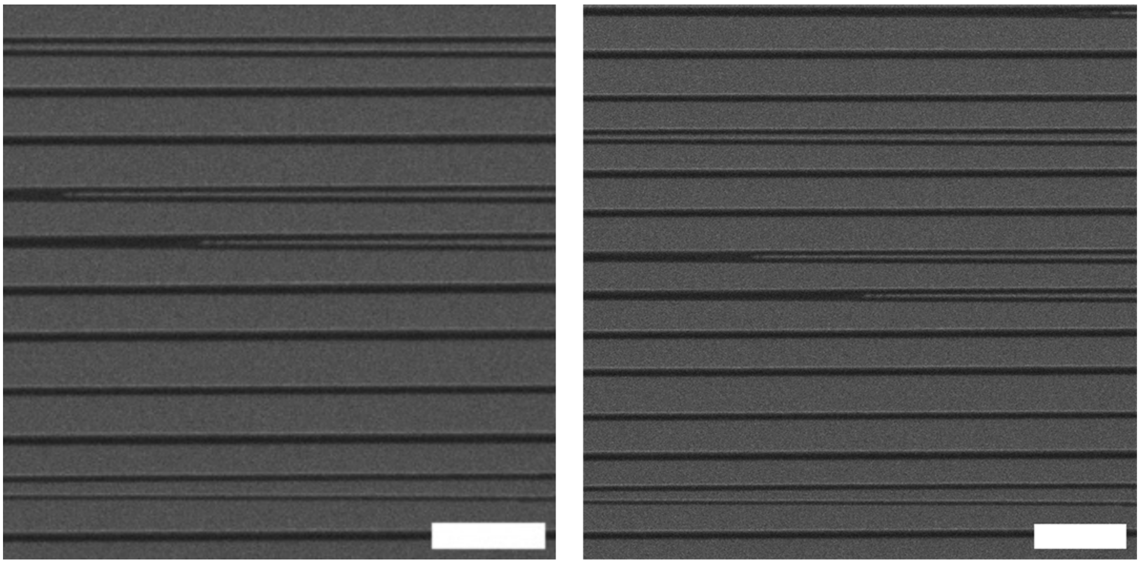

Figure SI4. Fiber Bridging at 10 µm IFD under Low UV Light Intensity. SEM image showing 5 µm-diameter fibers printed with a 10 µm inter-fiber distance (IFD) under low UV light intensity (9 mW/cm^2). Fiber bridging is observed. Scale bar: 50 µm.

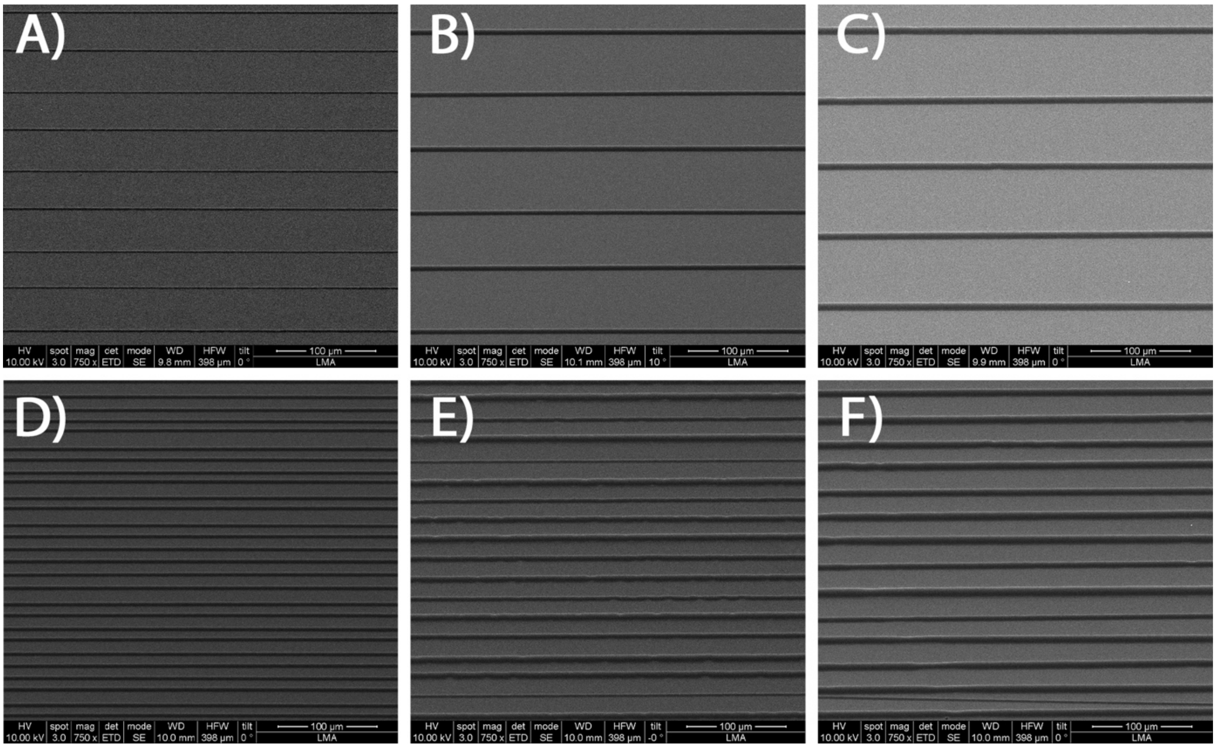

Figure SI5. Raw SEM images corresponding to Figure 3. Illustrating the effect of UV light intensity and number of printed layers on the minimum inter-fiber distance (IFD) without fiber bridging for 2 µm-diameter fibers. A-C) Samples printed under high UV intensity (15 mW/cm^2), showing the minimum IFD without fiber bridging for A) 1 layer (1L), B) 5 layers (5L), and C) 10 layers (10L). D-F) Samples printed under low UV intensity (9 mW/cm^2), showing the corresponding minimum IFD for D) 1 layer (1L), E) 5 layers (5L), and F) 10 layers (10L).

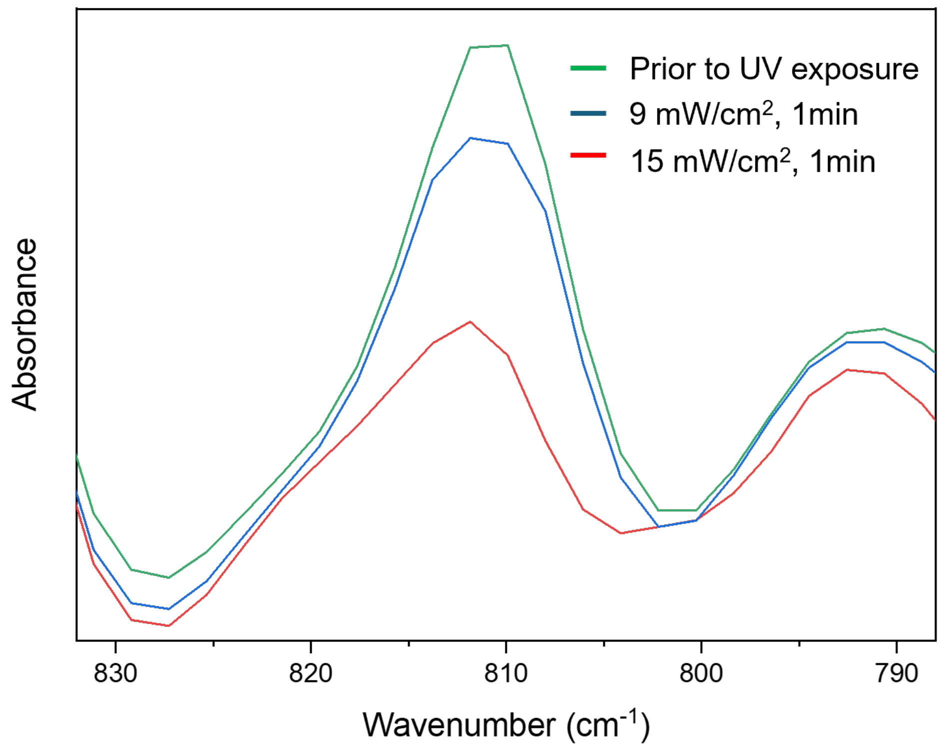

Figure SI6. Fourier transform infrared (FTIR) spectra of the reactive LCE ink before curing (uncured) and after UV irradiation for 60 s at 9 mW/cm^2 and 15 mW/cm^2. The progressive reduction of the acrylate band at approximately 810 cm^{-1} with increasing UV intensity indicates increased acrylate conversion at higher irradiation intensity.

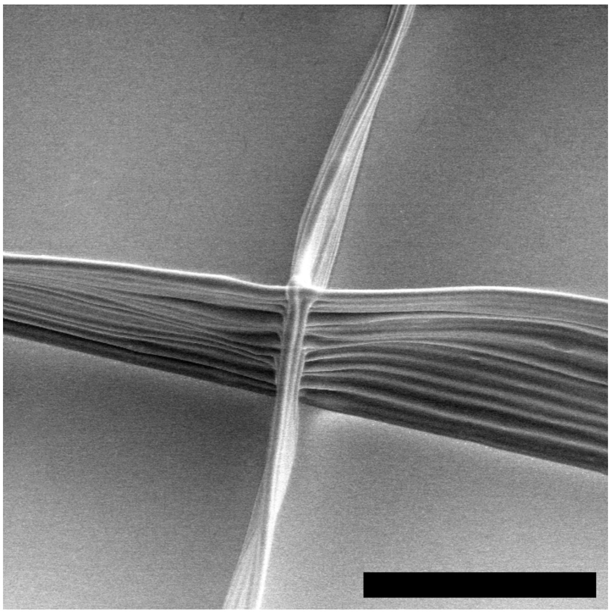

Figure SI7. MEW of Square Lattice LCE Structures using High UV Light Intensity. SEM image of a 50-layer scaffold, prepared under high UV light intensity of 15 mW/cm^2, showing well-defined, stacked fibers with minimal fusion, resulting from rapid curing. Scale bar: 100 µm.

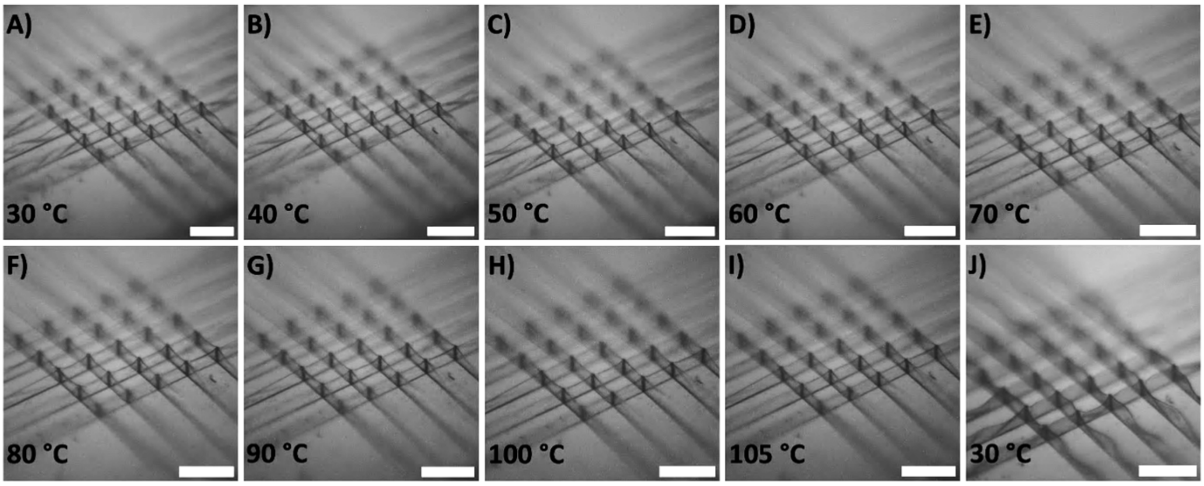

Figure SI8. **Thermal Actuation and Recovery of a Square Lattice LCE Structure (1:1.3 stoichiometry)**. A sequence of optical images showing the thermal response of a 300 µm period, 20+20 layered structure during heating from 30 °C to 105 °C (A-I) and shape recovery upon cooling back to 30 °C (J), demonstrating reversible actuation. Scale bars: 500 µm.

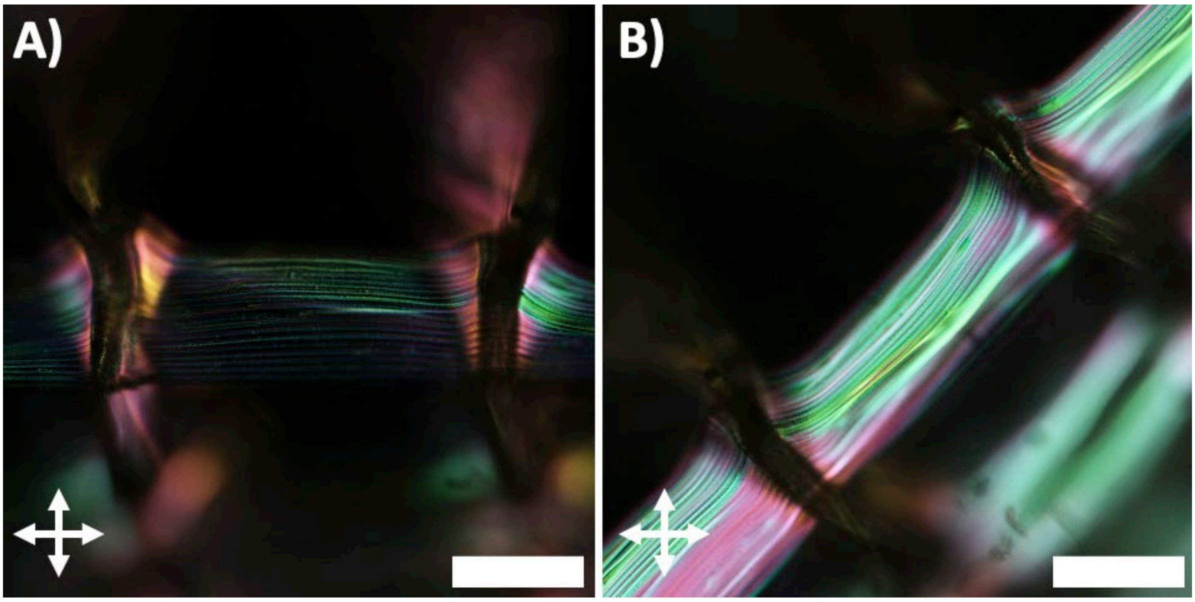

Figure SI9. **Birefringence of a Square Lattice LCE Structure.** Polarized optical microscopy (POM) images of a MEW fabricated 50-layer (25+25) structure. White arrows indicate polarizer transmission directions with the fiber direction oriented parallel (A) and at 45° (B) to the polarizer transmission directions. Scale bar: 100 µm.

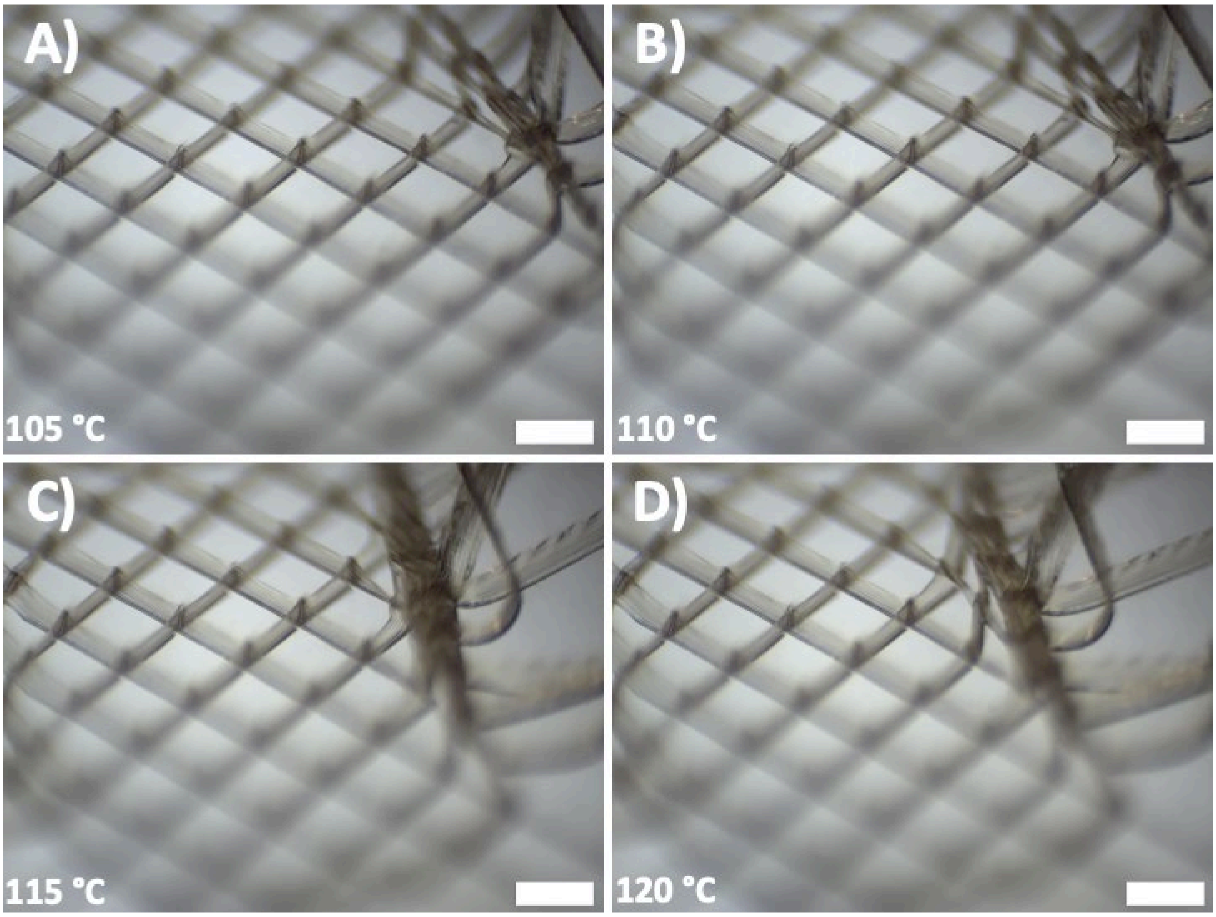

Figure SI10. Thermal Detachment of an LCE Structure from the Substrate. Optical images show the MEW LCE scaffold (1:1.01 stoichiometry) gradually detaching as temperature increases from 105 °C (A) to 120 °C (D), likely due to thermal expansion and internal stress buildup. Scale bar: 500 µm.