

Tunable Nonlinear Optical Pattern Formation and Microstructure in Crosslinking Acrylate Systems during Free-Radical Polymerization

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Supporting Information:

Figure S1. Spatial intensity profile of the transmitted optical field during an HDDMA photopolymerization for (a) 25, (b), 50, and (c) 75 min. Exposure intensity: 12 mW/cm². Scale bars = 160 μ m.

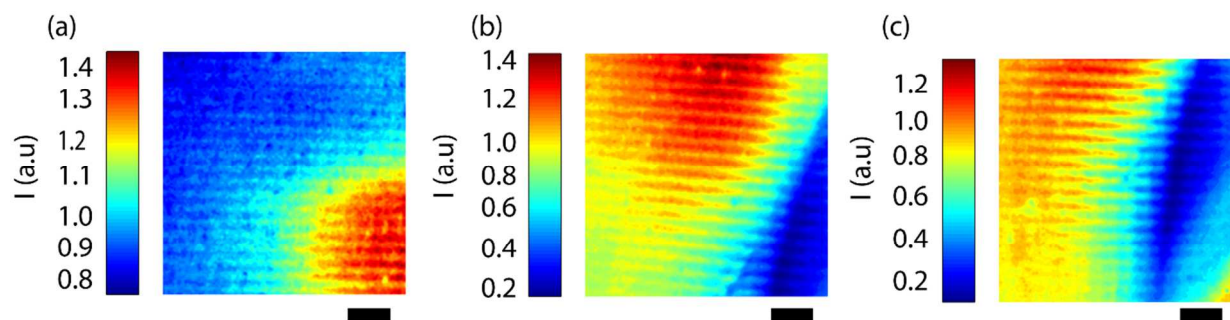


Figure S2. Pattern formation in TMPTA. (a) Modulation instability of a broad, uniform beam with no mask employed. (b) Filamentation of a beam spatially modulated using a 1D mask (line width = 40 μ m, line spacing = 80 μ m). Exposure intensity: 12 mW/cm². Exposure time: 25 min. Scale bars = 160 μ m.

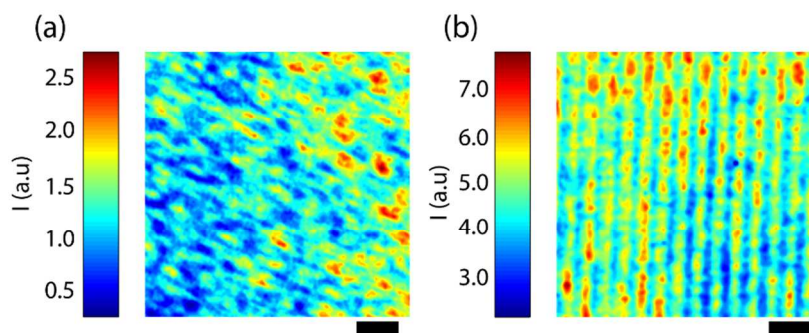


Figure S3. Optical intensity profiles at the exit face of the sample (path length = 3 mm) at the beginning of the photopolymerization ($t = 0$ s) for different modulations of the input beam. (a) A broad, uniform beam propagating through the medium (no mask employed). (b) A 1D mask modulates the beam into the form of an array of uniform intensity bright stripes, within which filamentation occurs over time. (c) A 2D mask modulates the beam into the form of two perpendicular arrays of bright stripes. After 3 mm of propagation, divergence results in the intensity being moderately higher at the points of intersection of the bright stripes. These locations are where the self-trapped beams form. Scale bars = 160 μm .

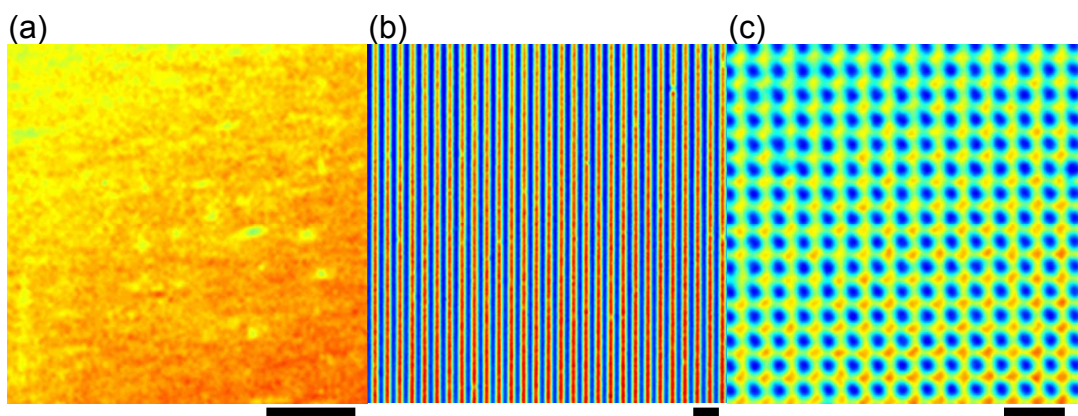


Figure S4. DSC crosslinking degree for (a) TMPTA photopolymerized at different exposure intensities for 75 min. (b) HDDMA formulated with varied weight fractions of TMPTA (●), PETA (■), DPEPA (▲). Respective red, green, and blue lines are to guide the eye. Exposure intensity: 12 mW/cm^2 . Exposure time: 75 min.

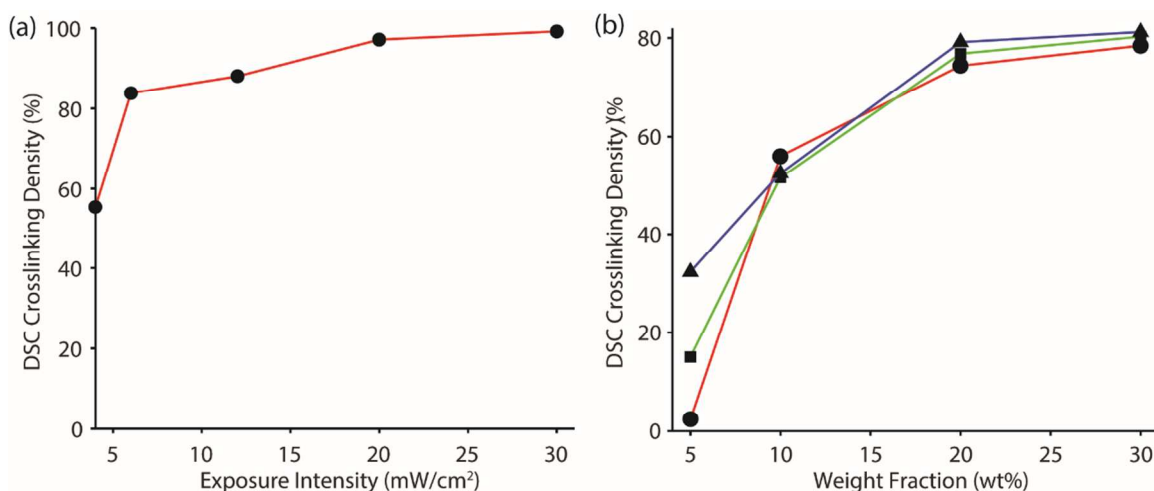


Figure S5. Modulation instability emerging (a-c) spontaneously in a broad uniform beam and (d-f) using a 1D mask to seed filamentation, in formulations of HDDMA and 5 wt%, TMPTA (a, d) , PETA (b, e), and DPEPA (c,f). Exposure intensity: 12 mW/cm². Exposure time: 25 min. Scale bars = 160 μ m.

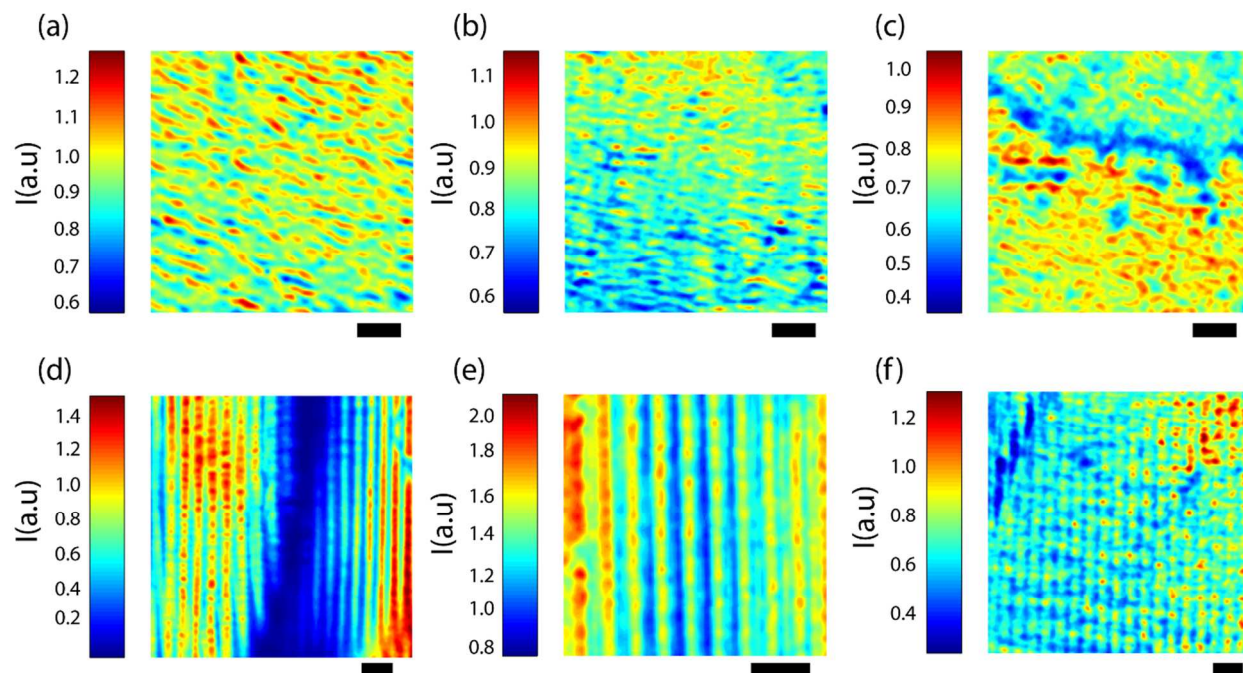


Figure S6. Pattern evolution over time in a photopolymerization of HDDMA with 5wt% TMPTA for (a) 25, (b), 50, and (c) 75 min. Exposure intensity: 12 mW/cm². Scale bars = 160 μ m.

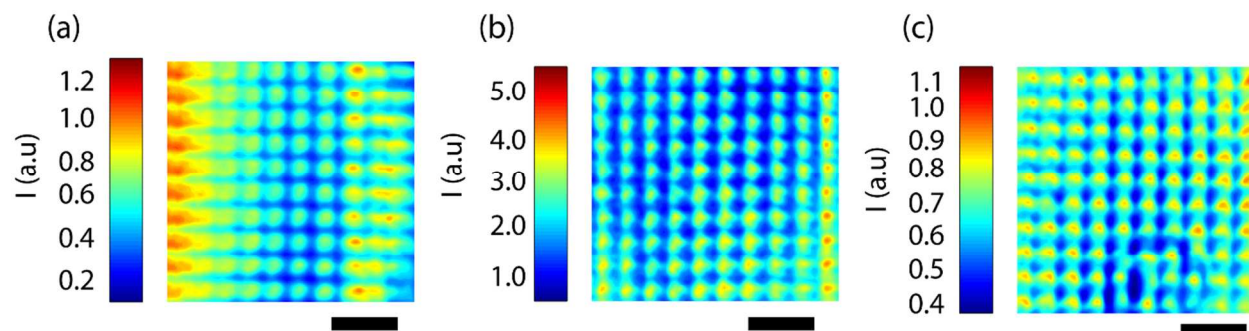


Figure S7. Pattern formation in formulations of methyl methacrylate with 5 wt% TMPTA. Exposure intensity: 12 mW/cm². Exposure time: 25 min. (a) Filamentation occurs; however, due to shrinkage, although significantly reduced from pure methyl methacrylate, the filaments appear compressed in the vertical direction and their positions were not commensurate with the mask pattern. The sample remained in a low viscosity state. (b) With a 10 minute preheating at 80 °C, the filaments retain with their circular cross-section, but the arrangement is still not commensurate with the mask, and the sample remains in a low viscosity state. Scale bars = 320 μ m.

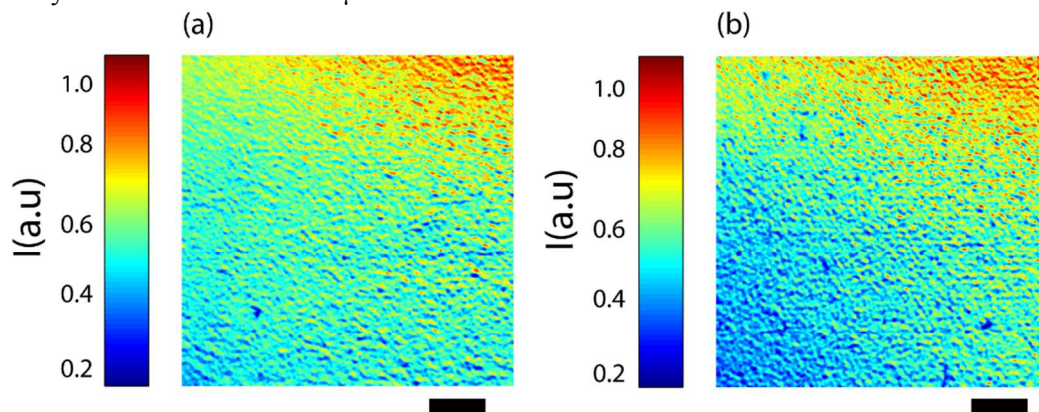


Figure S8. Optical micrograph of the transverse cross section of a TMPTA medium, showing the permanent inscription of a periodic arrangement of channels, as shown by their cross sections. Exposure intensity: 12 mW/cm². Exposure time: 75 min.

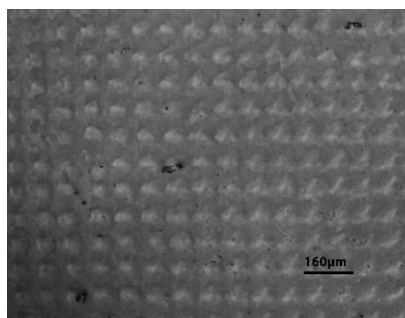


Figure S9. Raman maps for the 1636 cm^{-1} and 1720 cm^{-1} peaks acquired (a-b) at the sample surface and (c-d) $5\text{ }\mu\text{m}$ below the sample surface of a TMPTA sample. Exposure intensity: 12 mW/cm^2 . Exposure time: 25 minutes. Images map the integrated peak intensity. Congruent profiles of the maps (a) and (c) as well as (b) and (d) confirm that acquiring compositional information at the surface accurately represents the bulk, and with no observable surface artifacts.

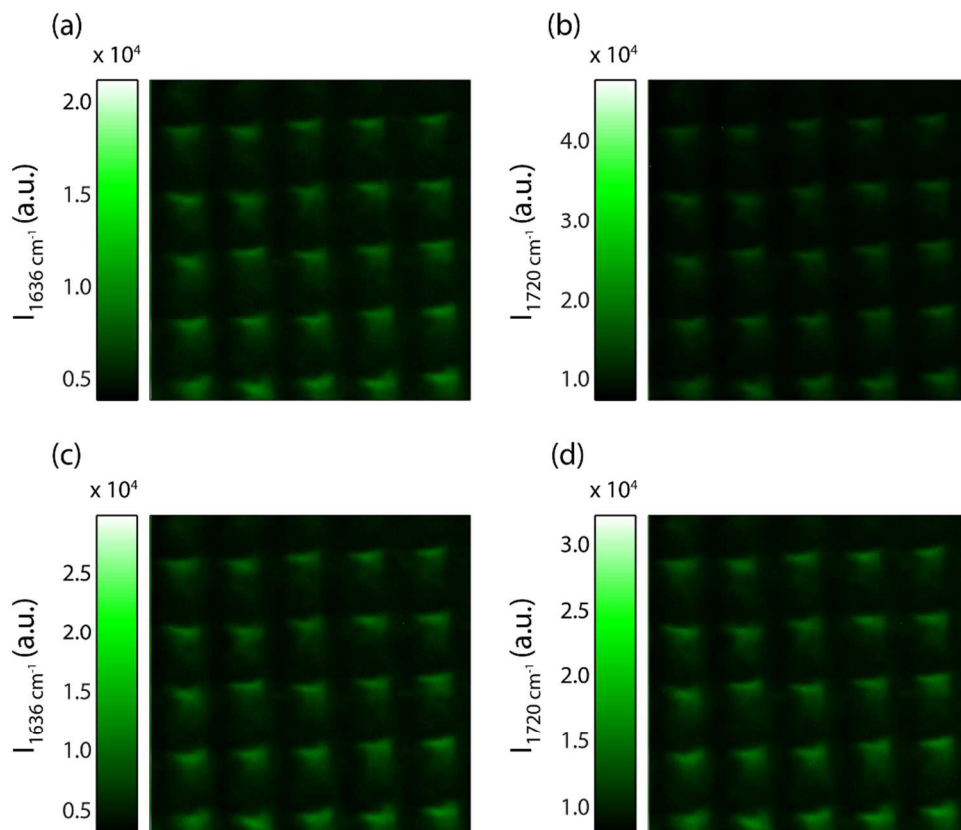


Figure S10. Raman images of a close up of an array of channels (5×5 shown) produced from a formulation of HDDMA and 5 wt %, TMPTA (a, d), PETA (b, e), and DPEPA (c, f) for exposure durations of (a-c) 25 min. and (d-f) 75 min. Images map the integrated peak intensity for the C=C bond of the acrylate group (1636 cm^{-1}). Exposure intensity: 12 mW/cm^2 .

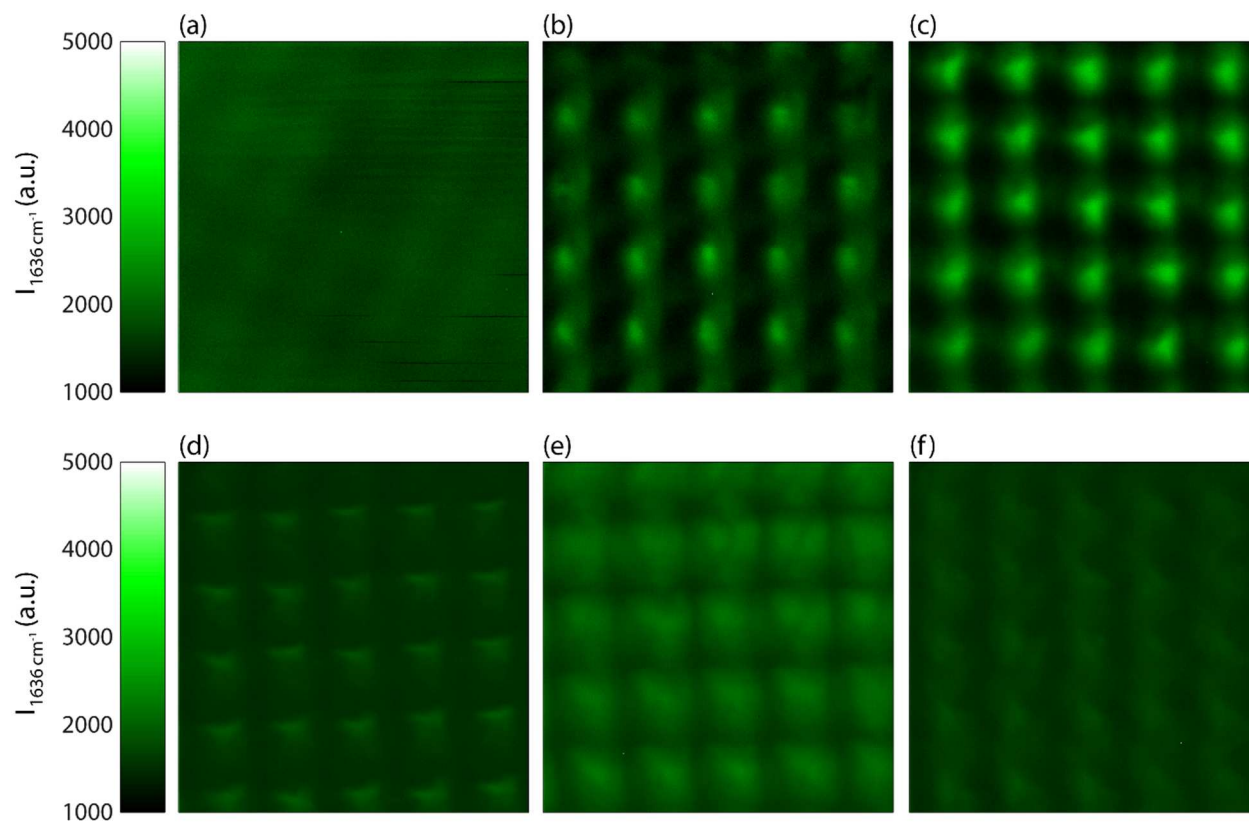


Figure S11. Pattern formation in formulations of HDDMA and 5 wt%, TMPTA (a) , PETA (b), and DPEPA (c). Exposure intensity: 12 mW/cm². Exposure time: 75 min. Scale bars = 160 μ m.

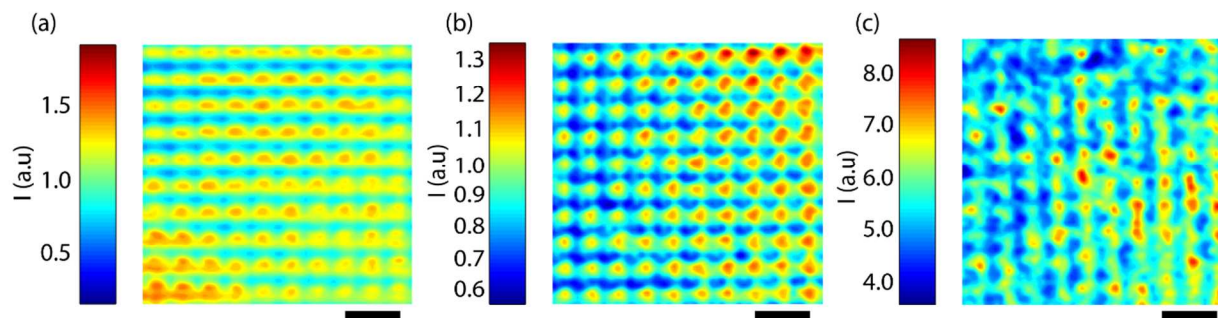


Figure S12. Spatial map of the ratio of the integrated peak intensity for the C=C bond (1636 cm⁻¹) to that for the C=O group, for media consisting of HDDMA formulated with 5 wt% (a) TMPTA, (b) PETA, and (c) DPEPA. Exposure intensity: 12 mW/cm². Exposure time: 75 min. Scale bars = 80 μ m. (d-f) Frequency distributions of the calculated ratio values for their maps (a) to (c), respectively.

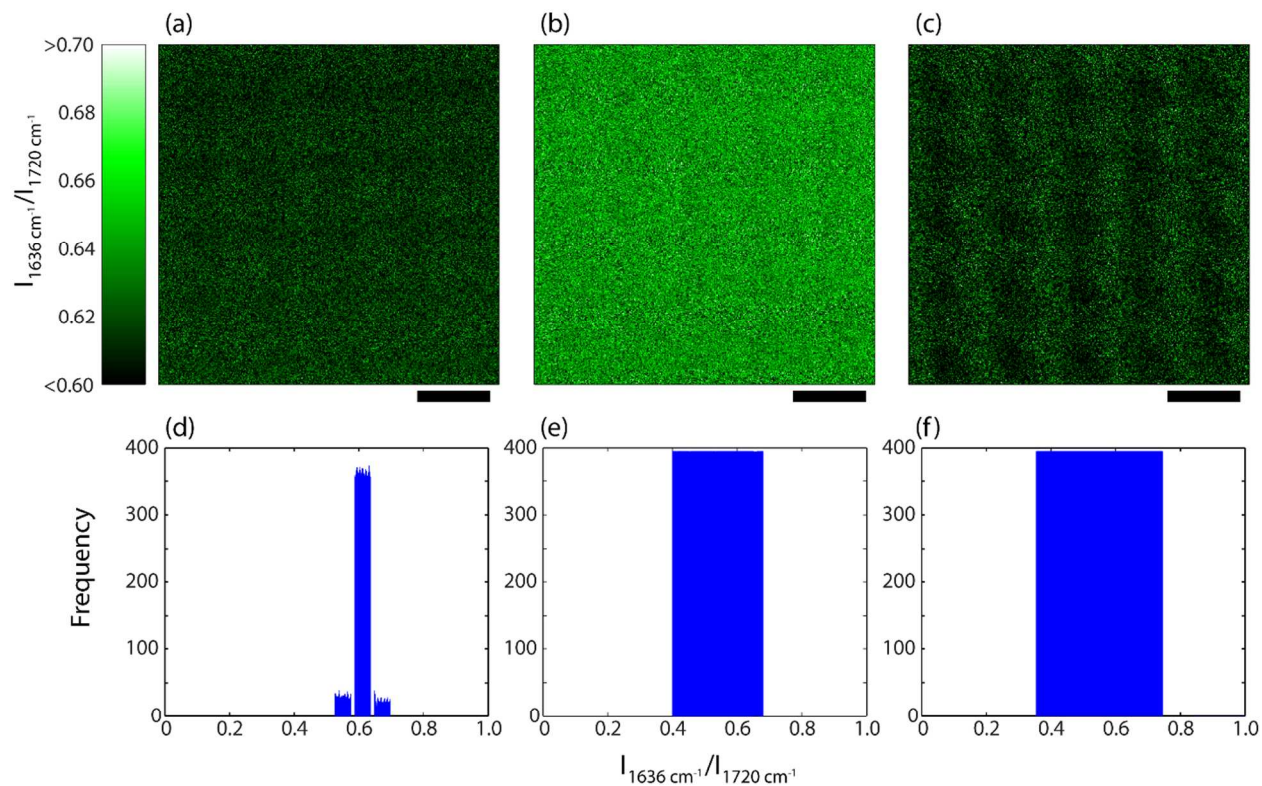


Table S1. Comparison of the filament FWHM for an HDDMA formulation with 20 wt% of TMPTA, PETA, and DPEPA for two different exposure times. Exposure intensity: 12 mW/cm².

Polyfunctional Acrylate	After 75 Min. Exposure (μm)	After 150 Min. Exposure (μm)
HDDMA + 20% TMPTA	39	36
HDDMA + 20% PETA	38	36
HDDMA + 20% DPEPA	46	45