

Supplementary Information

Evolution of chemical and mechanical properties in two-photon polymerized materials during pyrolysis

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This Supporting Information document includes:

The calculation for DoC based on the Raman spectrum.

The calculation for I_D/I_G based on the Raman spectra.

M/Z peaks observed in direct insertion probe quadrupole mass spectroscopy.

Proposed chain scission mechanism.

XPS spectra of the pyrolyzed products.

SEM images of the pyrolyzed foam and structures

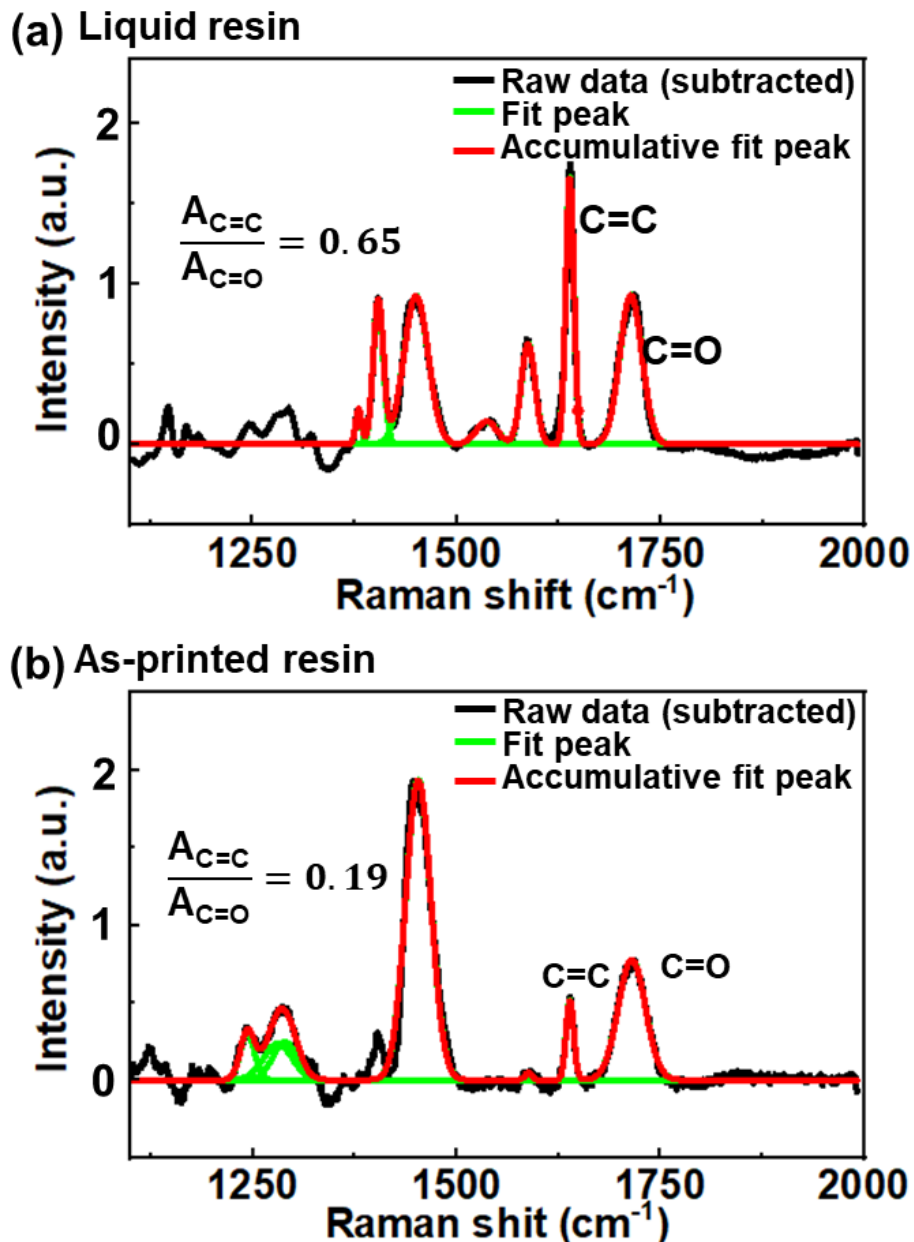


Figure S1. Raman spectra of (a) unpolymerized IP-Q resin (b) and as-printed IP-Q structures. The printing parameters for this measurement were: laser power 50 mW ,scan speed of 1 mm/s.

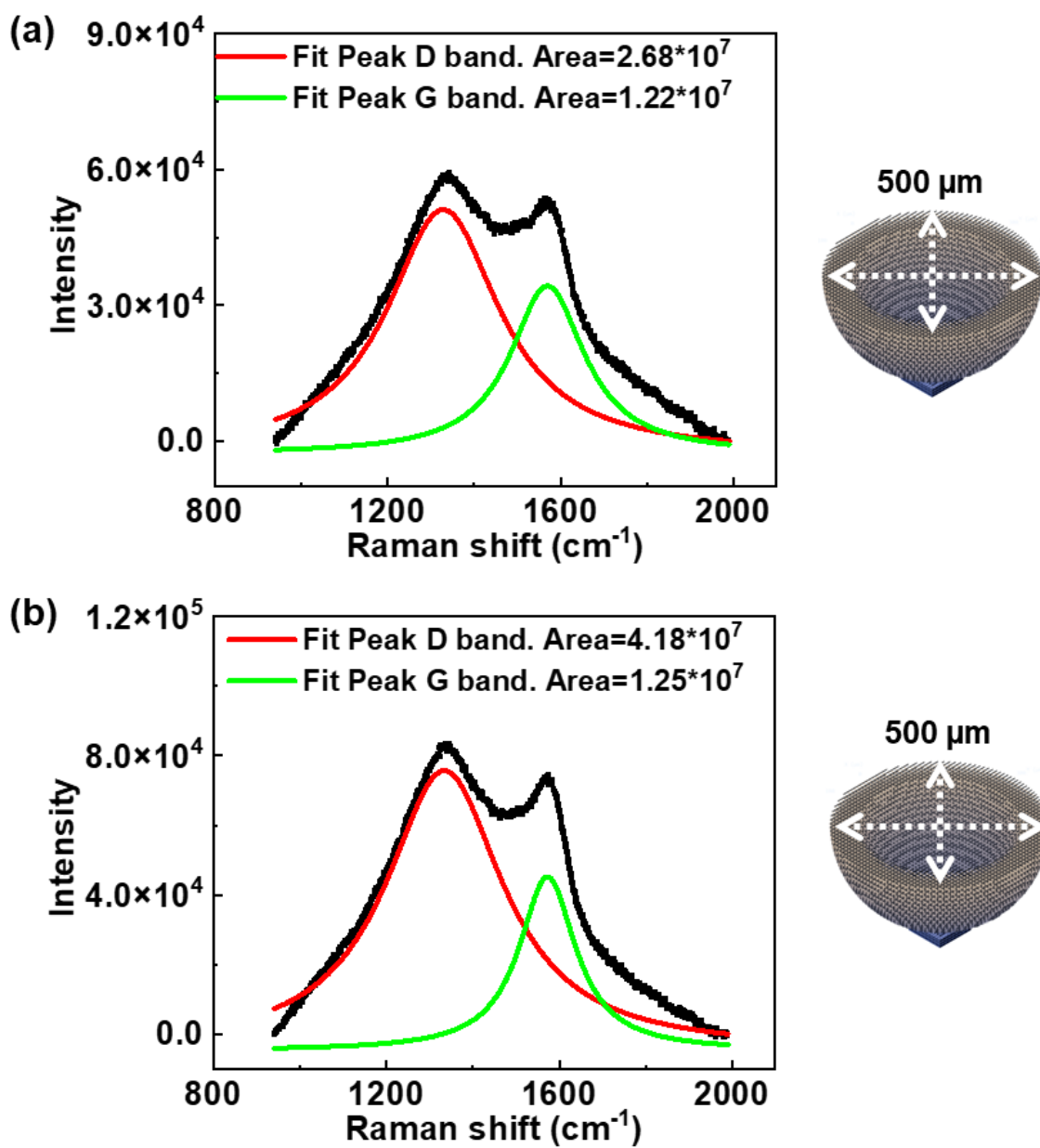


Figure S2. Calculation of I_D/I_G by curve fitting. The samples used for this calculation were two foam structures printed with a laser power of 50 mW and a scan speed of 10 mm/s and then pyrolyzed at (a) 500 and (b) 550 °C, respectively. The ramp rate is 15 °C/min and the pyrolysis time is 5 min.

Table S1. Direct insertion probe mass spectroscopy data at different temperatures

Sample	Temperature	Major m/z peaks
Unpolymerized IP-Q	150 °C	41, 69, 113
Polymerized IP-Q	225 °C	39, 69, 113, 309
	235 °C	41, 69, 113, 309
	295 °C	41, 56, 69, 113, 154, 309

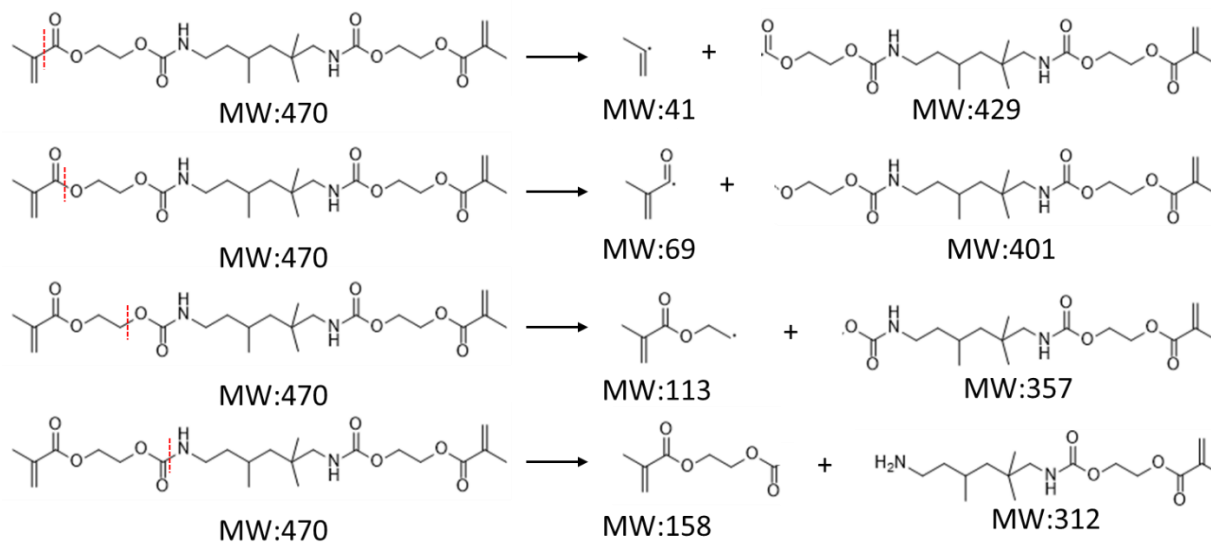


Figure S3. Possible chain scission processes that occur during pyrolysis based on Table S1. The mismatch between the observed peaks and proposed fragments may originate from the high temperature of ion source (~250 °C).

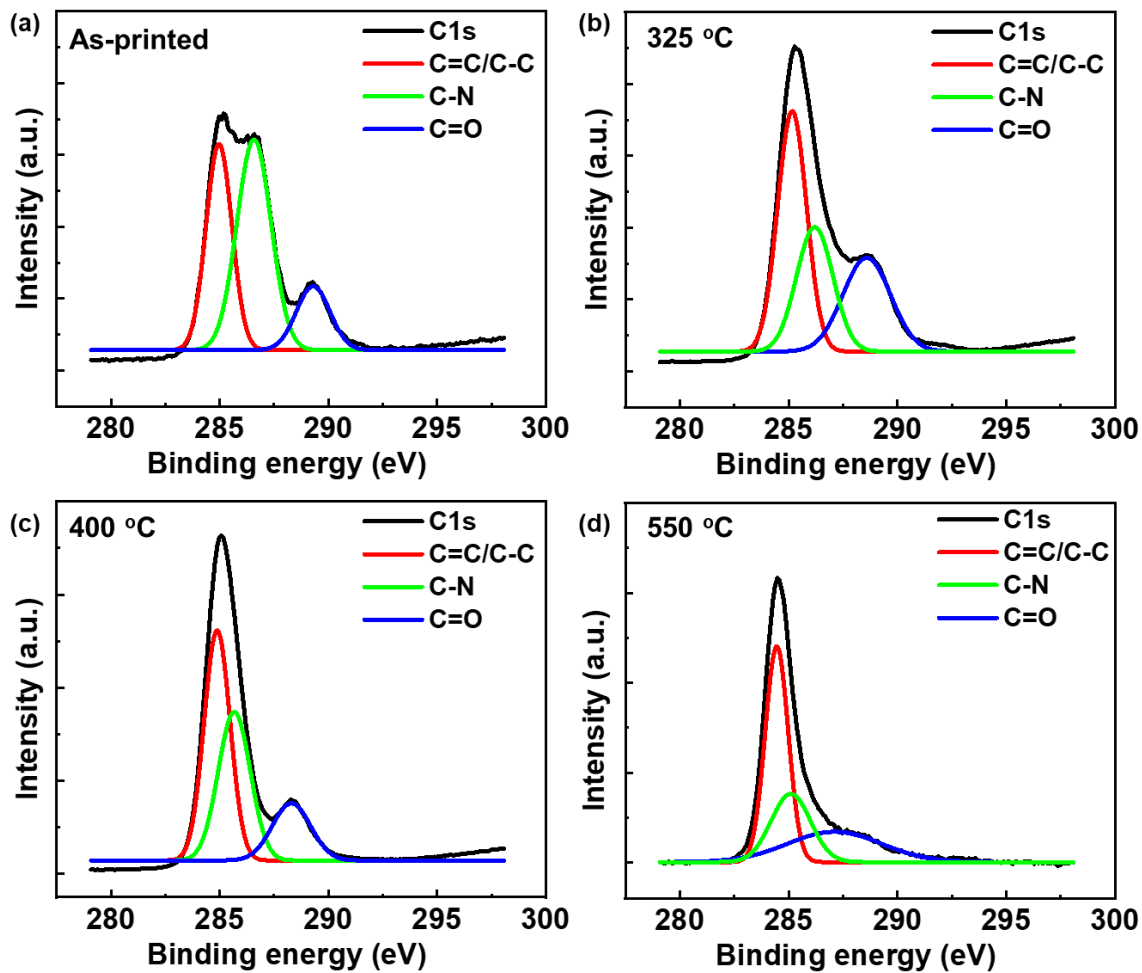


Figure S4. XPS C1s spectra for (a) as-printed IP-Q thin film, and films pyrolyzed at (b) 325, (c) 400, and (d) 550 °C, respectively. The ramp rate is 10 °C/min and the pyrolysis time is 30 min.

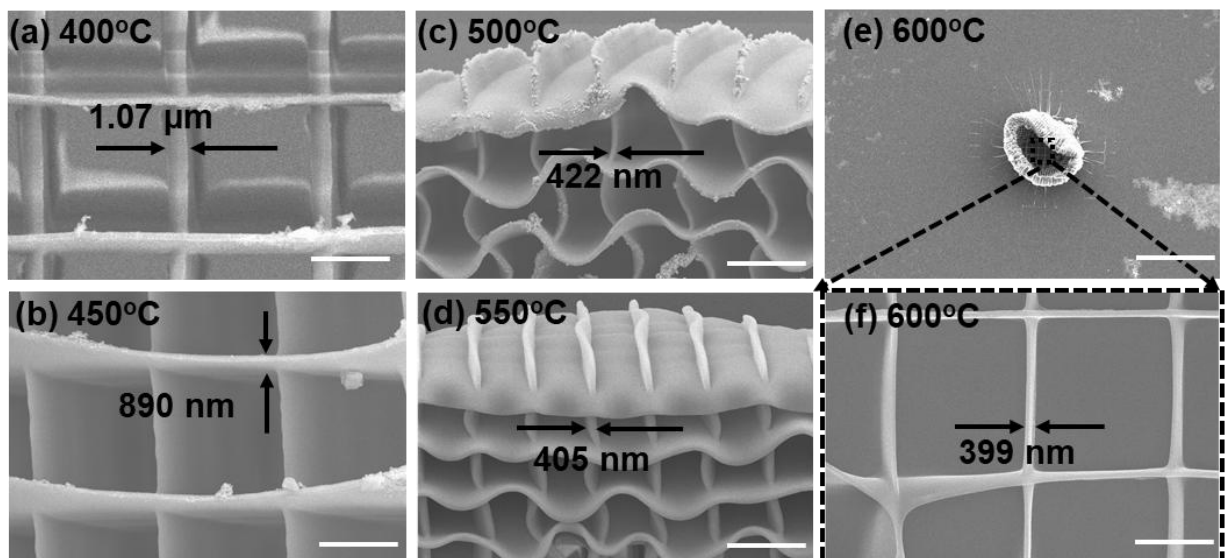
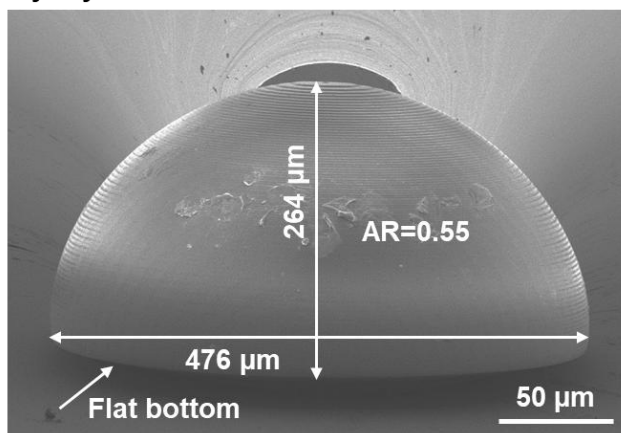


Figure S5. SEM and optical images collected from samples that were pyrolyzed at different temperatures, with ramp rate and pyrolysis time fixed at 15 °C/min and 5 min respectively. Scale bar: 100 μm for (e) and 5 μm for others.

Pyrolyzed 360 °C



Pyrolyzed 420 °C

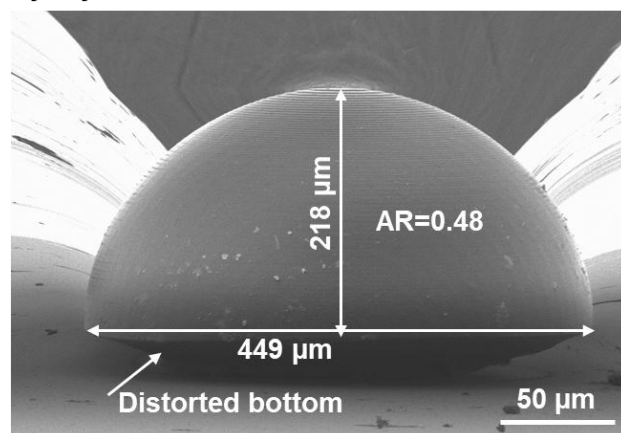


Figure S6. Side-view SEM images of shell structures pyrolyzed at 360 and 420 °C respectively. Based on the SEM measurement, the aspect ratio (AR) decreases from 0.55 to 0.48, which confirms the LSM results that shape deformation occurs in this temperature range.