Supporting Information

Rapid and Controlled Photo-induced Thiol-ene Wrinkle Formation via Flowcoating

Stephen J. Ma, Norman J. Wagner, Christopher J. Kloxin*

Table of Contents

Figure S1. Custom-built stretching stage for straining elastomers	2
Figure S2. Flowcoating on silicon wafer vs glass slides	3
Figure S3. Film thickness versus coating velocity and monomer concentration	4
Figure S4. Observed thickness scaling deviations of the wrinkle wavelength	5
Figure S5. Modulus of thin films	6
Figure S6. TGA of 1:1.1 PETMP:TATATO thin films with a two hour isothermal hold at 120°C	7
Figure S7. Wrinkle amplitudes of 1:1.1 and 0.7:1.1 thiol:ene film formulations	8



Figure S1. Custom-built stretching stage for straining elastomers. Linear stages (UMR3.5), with attached BM11.5 micrometers (Newport), were mounted on an optical bread board. Machined aluminum brackets were screwed into the linear stage such that the two brackets were separated by 25 mm at the center of the set up. Elastomers were mounted on these brackets, sandwiched with Teflon sheets, and clamped down at the ends. Strain was applied by turning the micrometer to the desired length. This entire optical breadboard set up, including the mounted elastomer, can be submerged under water to transfer polymer thin films from a silicon wafer backing onto the strained elastomer.



Figure S2. Flowcoating on silicon wafer vs glass slides. Flowcoated thiol-ene films (10 wt% monomer in toluene, 7 mm/s) coated on glass slides and silicon wafers yielded similar wrinkle structures across a variety of coating velocities. Glass slides and silicon wafers were precleaned in a UVO cleaner and rinsed three times with toluene prior to coating.



Figure S3. Film thickness versus coating velocity and monomer concentration. A) Film thickness plotted as a function of velocity shows a linear increasing trend. As velocity increases, more monomer is left behind on the flowcoated substrate, thereby increasing the film thickness. B) The film thickness increases with increasing monomer concentration.



Figure S4. Observed thickness scaling deviations of the wrinkle wavelength as film thickness approaches 40 nm; the wavelength scaling on thickness is $\lambda \sim h^{1.43}$ instead of the expected h^1 .



Figure S5. Modulus of thin films. Modulus histograms for AFM peak force tapping measurements of PETMP/TATATO (1:1.1)thin films. A) Poly(styrene) standard with a mean of 3.37 GPa and a standard deviation of 0.87. b) PETMP:TATATO thin filmwith a mean of 3.59 GPa and a standard deviation of 0.34. C) Second replicate of PETMP:TATATO film with an average of 4.75 and a standard deviation of 0.46. D) Third replicate of the PETMP:TATATO thin film with an average of 4.17 and a standard deviation of 0.39. These data indicate that these film thicknesses of the PETMP:TATATO films retain their glassy bulk modulus.



Figure S6. TGA of 1:1.1 PETMP:TATATO thin films with a two hour isothermal hold at 120°C. PETMP:TATATO films were casted and cured with (yellow circle) and without (blue square) a 100°C post cure treatment to remove excess toluene and drive the thiol:ene reaction to completion. As observed, samples exposed to the post-cure heating exhibited a mass loss of half a percent as compared to films that did not undergo the post heating (2% mass loss), indicating toluene was removed in the postcure step.



Figure S7. Wrinkle amplitudes of 1:1.1 and 0.7:1.1 thiol:ene film formulations. A) Film thickness plotted against wrinkle amplitude exhibits an increasing linear trend as predicted by the wrinkle amplitude equation. B) Although the log_{10} (film thickness) plotted again log_{10} (Amplitude) shows a slow of 1.4 ± 0.2 (which deviates from the expected value of 1 (i.e., A~h¹), the scaling is commensurate with the wrinkle wavelength vs film thickness trend.