Supplementary Information

Photopatterning of Two Stage Reactive Polymer Networks with CO2-Philic Thiol-Acrylate Chemistry: Enhanced Mechanical Toughness and CO2/N2 Selectivity

Adrienne Blevins[1], Mengyuan Wang[2], Michelle L. Lehmann[2,3], Leiqing Hu[4], Shouhong Fan[5], Christopher M. Stafford[6], Jason P. Killgore[7], Haiqing Lin[4], Tomonori Saito[2], Yifu Ding[1,5,]*

[1] Materials Science & Engineering Program, University of Colorado, Boulder, CO, 80303

[2] Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

[3] The Bredesen Center for Interdisciplinary Research and Graduate Education, University of Tennessee, Knoxville, Tennessee 37996

[4] Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, NY, 14260

[5] Membrane Science, Engineering and Technology Center, Paul M. Rady Department of Mechanical Engineering, University of Colorado, Boulder, CO, 80309

[6] Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, MD, 20899

[7] Applied Chemicals and Materials Division, National Institute of Standards and Technology, Boulder, CO, 80305

* Corresponding author. Email: yifu.ding@colorado.edu

Section S1. Additional AFM Scans

Unpatterned Stage 1 and Stage 2 surfaces were scanned with AFM in FFM mode (Figures S1-S3) to get average surface modulus values, which are then compared to the modulus values in FFM scans of patterned samples (Figure 3B-D). Stage 2 samples have a soft, PDMS-enriched layer at the top, so Stage 2 scans on both the top and bottom are presented here. Average modulus values are reported in Table S1.

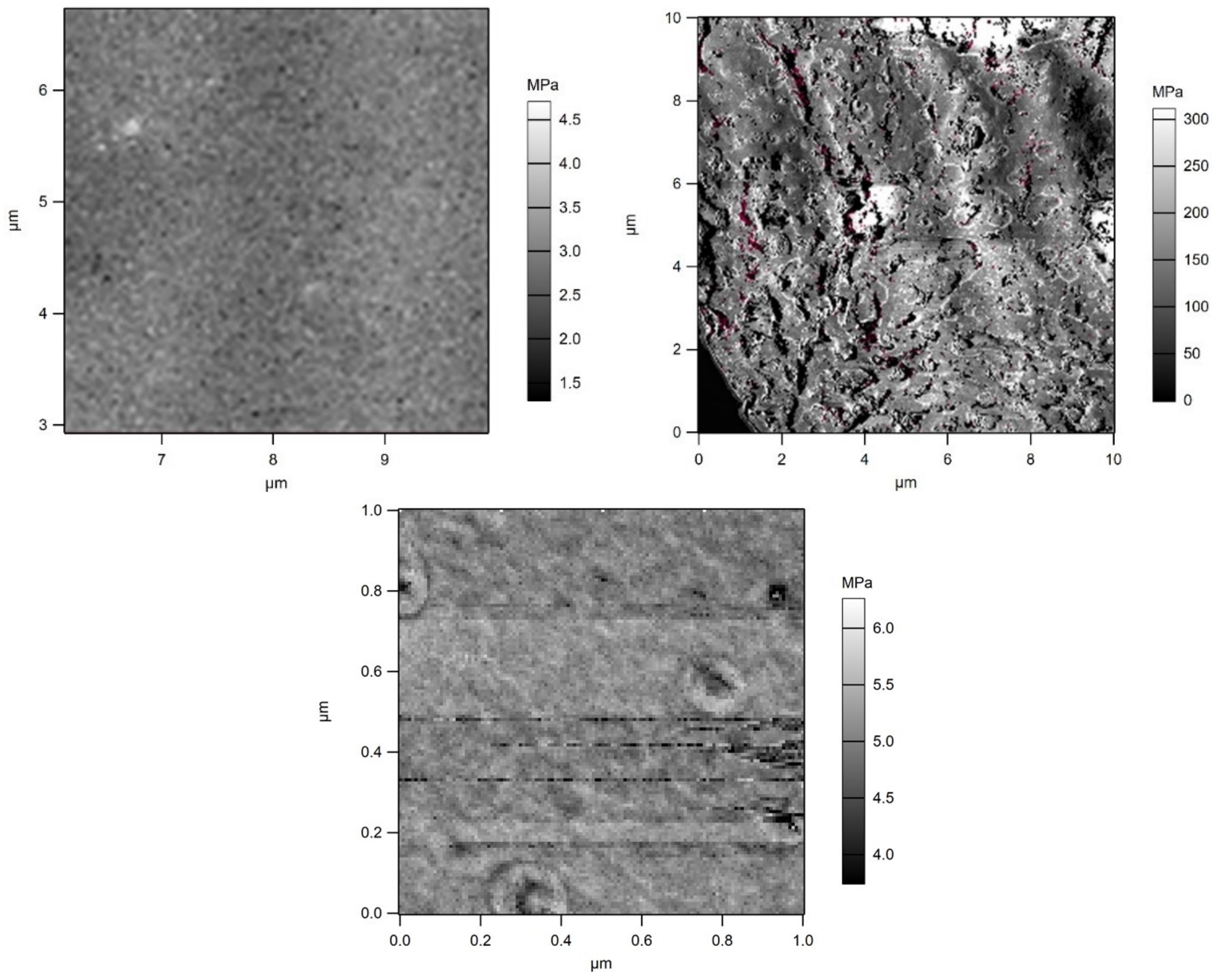

Figure S1. Stage 1 (upper left) and Stage 2 (bottom side, upper right; top side, lower) surfaces for the 1.4:1 formulation.

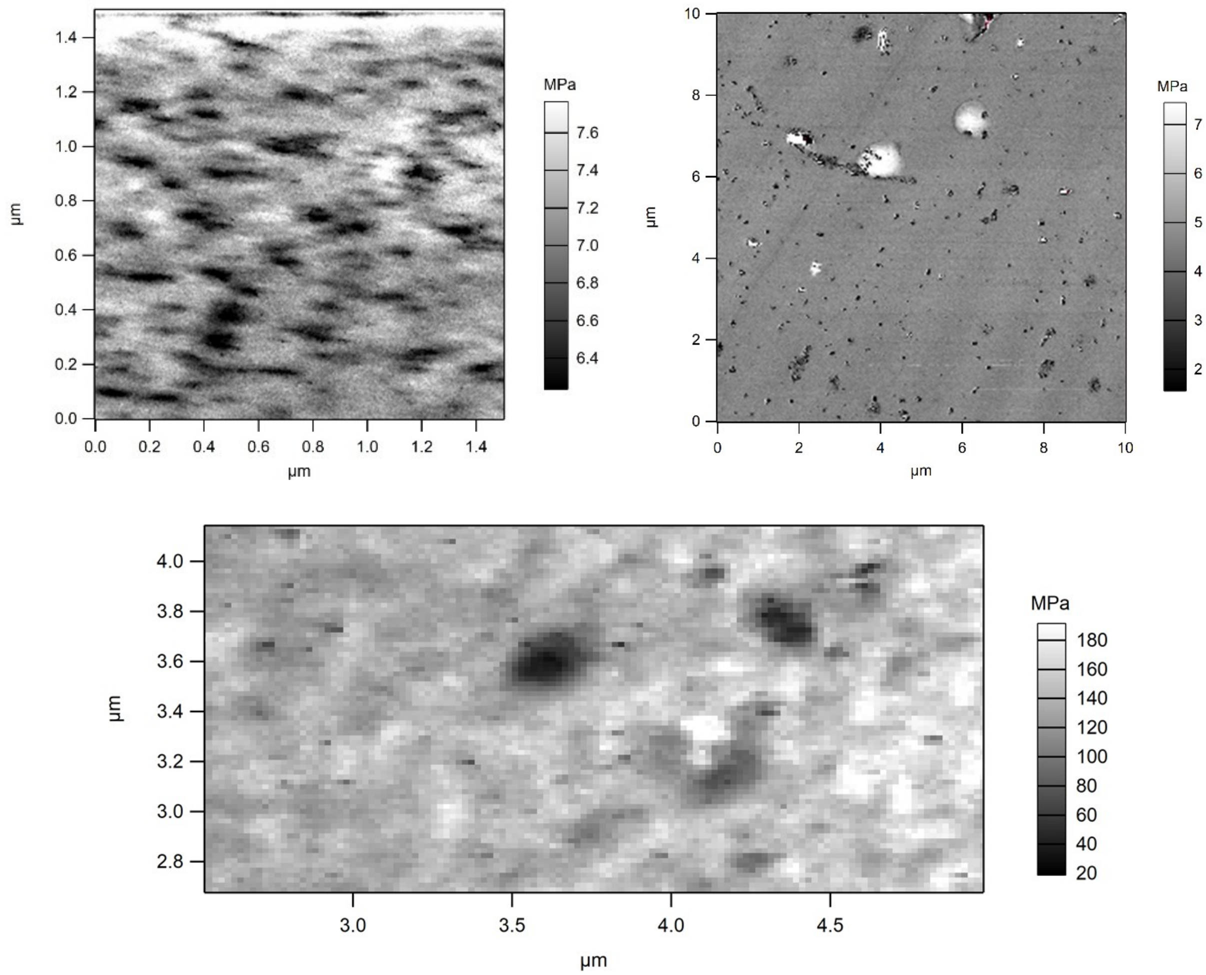

Figure S2. Stage 1 (upper left) and Stage 2 (top side, upper right; bottom side, lower) surfaces for the 3:1 formulation.

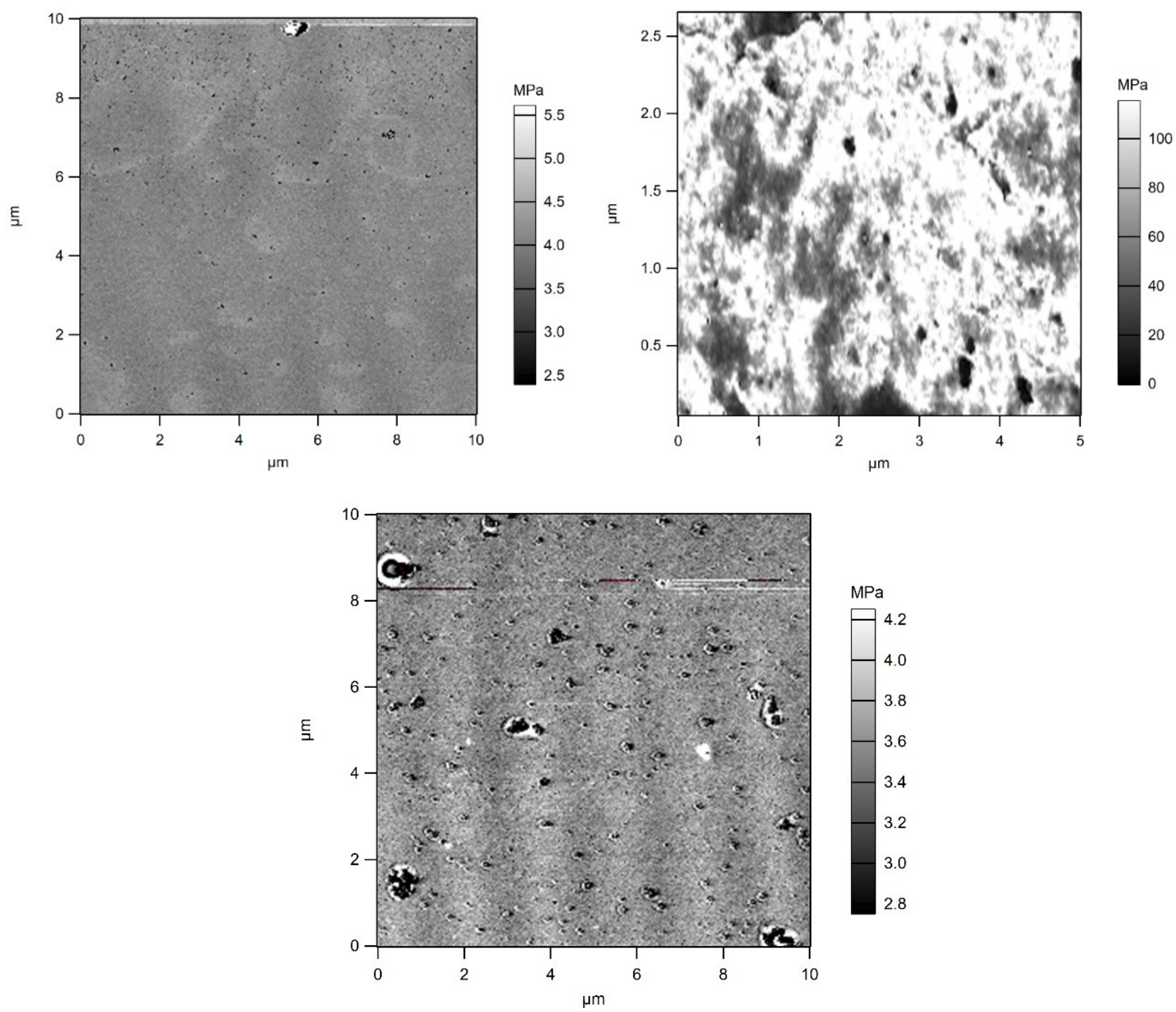

Figure S3. Stage 1 (upper left) and Stage 2 (bottom side, upper right; top side, lower) surfaces for the 5.7:1 formulation.

Table S1. Average surface modulus values for the scans presented in Figures S1-3.

Formulation	Stage 1 Avg. Surface Modulus (MPa)	Stage 2 Front Side Avg. Surface Modulus (MPa)	Stage 2 Back Side Avg. Surface Modulus (MPa)
1.4:1	3.0 ± 0.4	5.0 ± 0.2	155.2 ± 81.1
3:1	7.2 ± 0.7	4.7 ± 0.3	133.5 ± 17.0
5.7:1	4.1 ± 0.2	3.6 ± 0.2	104.9 ± 37.5

Changes in height over the sample surface can confound modulus data in FFM mode. Much of the contrast in Figures S1-3 is reflective of the surface topography. Some of this texture may also indicate phase separation occurring within the films. A comprehensive study of this phase separation is not within the scope of this study. Photopatterning also generates topography on the film surface. The chrome layer on the photomask presses into the film, and creates an effect similar to stamping, once the sample is exposed to UV. The stage 1 regions, in contact with the chrome of the photomask, are pushed down and have a lower height than the stage 1 regions. This effect is visible in Figure S4, which is the height data for the scan in Figure 3C.

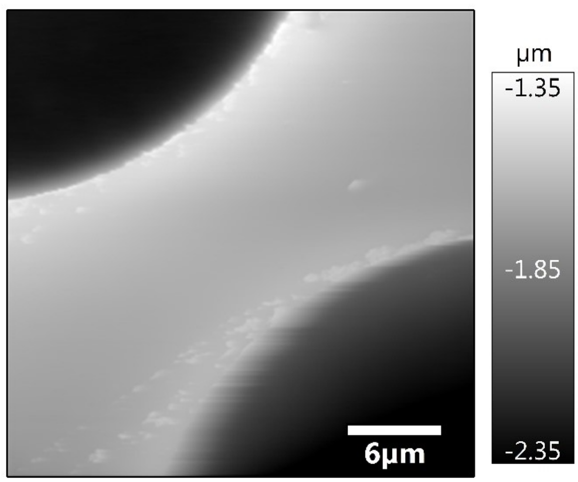

Figure S4. Height channel data for Figure 3A. Stage 1 circles are topographically lower than Stage 2 regions, contributing to the modulus difference in Figure 3A.

Cross-sectional AFM images at both the top, middle, and bottom surfaces of a patterned film of the 3:1 formulation are presented in Figure S5. FFM scans were taken at the top and bottom edges (relative to the UV light source), of the cross-sectional surface. Figure 3D scan area is represented by the red square on the left image at the top of the edge of the sample. These scans give information on the interface width for the pattern. The interface width is 4.5 µm at the top surface and widens out at the bottom surface to 14.7 µm. These scans also confirm the presence of the thin and soft PDMS-rich layer at the top surface only. It shows as the lighter blue strip in S5, left (the dark blue on the edges of the images represent air. Dark blue spots within the sample represent defects generated during the cutting process).

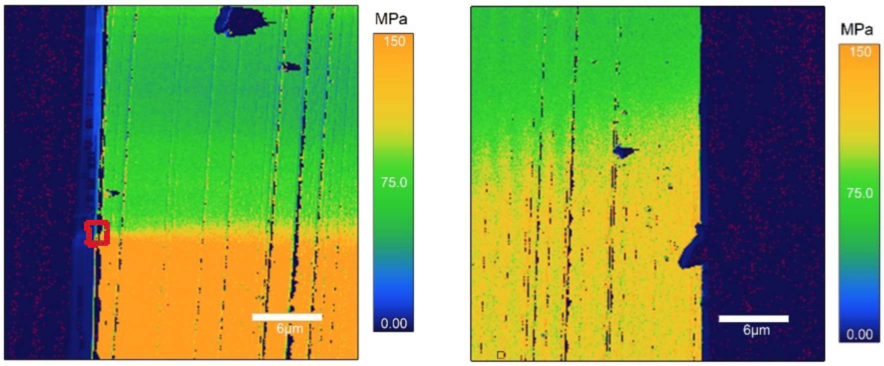

Figure S5. (left) Cross-section view of the top edge of the 3:1 formulation circular-patterned sample. Four regions are visible: free space, the thin PDMS-rich region, Stage 1, and Stage 2 regions. The red outline shows where Figure 3D was scanned. (Right) cross-section view of the bottom edge of the same sample. Stage 1, 2, and free space regions can be seen. No PDMS-rich layer is observed. The widening of the interface can be observed.

Section S2. WCA and XPS data investigating the soft PDMS-rich layer on top of photopatterned samples

Water contact angle measurements are shown in Figure S6. The top surface of Stage 2, which has the soft layer present, is much more hydrophobic than Stage 1. The soft layer cannot be seen on the backside of the sample in Figure S5 (right), and this is also confirmed by the water contact angle measurement on the backside of the sample, which is much closer to the Stage 1 value.

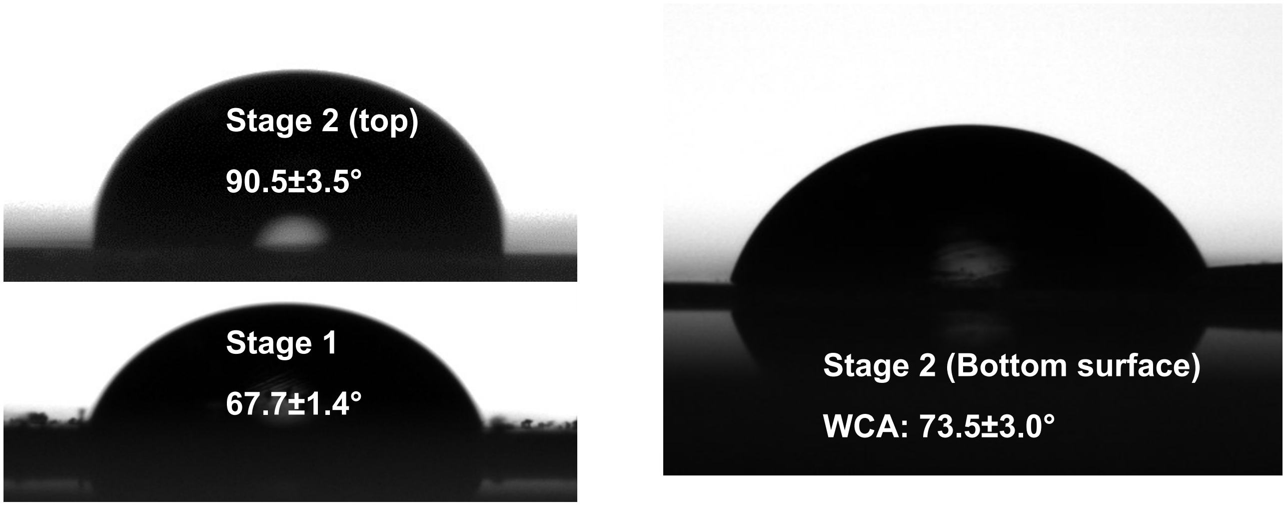

Figure S6. Water contact angle measurement images.

XPS data, Table S2, also confirmed that the softer layer has an increased Si content, potentially indicating higher PDMS content.

Table S2. Chemical composition of Stage 1 and Stage 2 sample surfaces for the 3:1 formulation from XPS measurement.

	C 1s [at.%]	O 1s [at.%]	Si 2p [at.%]
Stage 1 top surface	64.11 ± 0.17	24.55 ± 0.09	11.34 ± 0.19
Stage 2 top surface	61.32 ± 0.33	23.89 ± 0.03	14.78 ± 0.36

Section S3. Calculating rule-of-mixtures permeability predictions.

The rule of mixtures permeability prediction (*P*) is calculated by the volume-fraction weighted permeability for each component:

$$P = v_A P_A + v_B P_B$$

where v_A and v_B are the volume fractions of components A and B, and P_A and P_B are the permeabilities of each component on its own. Data for volume fractions are all based on the representative data from AFM of the 3:1 formulation, as the behavior is assumed to be similar across all formulations. There are 4 primary regions to take into consideration: Stage 1 (subscript 1), pattern interface (subscript i), Stage 2 (Subscript 2), and the soft, PDMS enriched layer (subscript P):

$$P = v_1 P_1 + v_i P_i + v_2 P_2 + v_P P_P$$

Permeabilities for each component are taken for each formulation based on unpatterned permeability measurements. P_P is taken to be pure Stage 1 value since it is so soft, P_1 is taken to be the partially cured permeability value since partial curing was observed in Figure 3C, and P_i is the average of Stage 2 and the partial cure value, all values listed in Table S3. Calculations for volume fractions are listed below.

Pattern unit cell dimensions based on Figure 3A:

Stage 1 circle diameter (*d*): (46.7 ± 1.3) µm

Cell edge length, (*e*): (61.3 ± 1.2) µm

Interface width between Stage 1 and Stage 2 regions from Figure S4:

Near top surface: 4.5 µm

Near bottom surface: 14.7 µm

Average interface width (l_i): 9.6 µm

Average film thickness (*t*): 150 µm

PDMS-enriched soft layer thickness (t_p): 0.25 µm

Total volume: $V_T = e^2 t$

Volume of Stage 1 region: $V_1 = \pi\left(\frac{d - l_i}{2}\right)^2(t - t_p)$

$$v_1 = \frac{V_1}{V_T}$$

Volume of interfacial region: $V_i = \pi l_i d(t - t_p)$

$$v_i = \frac{V_i}{V_T}$$

Volume of Stage 2 region: $V_2 = \left(e^2 - \pi\left(l_i d + \left(\frac{d - l_i}{2}\right)^2\right)\right)(t - t_p)$

$$v_2 = \frac{V_2}{V_T}$$

Volume of soft layer: $V_p = t_p(e^2)$

$$v_p = \frac{V_p}{V_T}$$

Results for overall rule of mixtures permeability predictions are found in Table S3.

Table S3. Permeability values for unpatterned samples for each formulation and gas tested, as well as rule of mixtures predictions based on volume-fraction weighting.

	P_1 (Barrer)	P_i (Barrer)	P_2 (Barrer)	P_p (Barrer)	P (Barrer)
1.4:1 – CO_2	120	82	44	172	80.3
1.4:1 – N_2	24	17.5	11	47	17.2
3:1 – CO_2	42	30.5	19	52	30.0
3:1 – N_2	7	5.5	4	12	5.44
5.7:1 – CO_2	38	30	22	78	29.7
5.7:1 – N_2	6	4.25	2.5	11	4.18

To double check that the highly permeable PDMS-rich layer does not impact permeability predictions, a similar calculation is made where the soft layer is not included, and the thickness of Stage 1, interfacial, and Stage 2 regions are equal to *t*, instead of $(t\text{-}t_p)$:

$$P = v_1 P_1 + v_i P_i + v_2 P_2$$

The results show an overall decrease of predicted permeability values, but at only a 0.1 % to 0.5 % difference, which is negligible. An example is the predicted N_2 permeability of the 3:1 formulation patterned sample. In the calculation without the soft layer, predicted permeability is predicted to be 5.43, as opposed to 5.44, a 0.18 % difference.