Supporting Information

Photo-crosslinked Poly(thioether-*co*-carbonate) Networks Derived from the Natural Product Quinic Acid

Lauren A. Link[†]*, Alexander T. Lonnecker*[†]*, Keith Hearon*[‡]*, Cameron A. Maher*[‡]*, Jeffery E. Raymond*[†]*, Karen L. Wooley**[†]

[†]Department of Chemistry, Department of Chemical Engineering, Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77842-3012, USA
[‡]Department of Biomedical Engineering, Texas A&M University, College Station, TX 77842-3012, USA

Corresponding Author
*Email: wooley@chem.tamu.edu

Experimental Section

Materials: Quinic acid, Amberlyst 15 ion-exchange resin, N,N,N',N'-tetramethylethylenediamine, allyl chloroformate, 2,2-dimethoxy-2-phenylacetophenone, 1,2-ethanedithiol, 2,3-butanedithiol, 1,6-hexanedithiol, trimethylolpropane tris(3-mercaptopropionate), and triallyl-1,3,5-triazine-2,4,6-trione were all used as received from Sigma Aldrich. Tetraethylene glycol bis(3-mercaptopropionate) (Wako Chemical) was also used as received.

Functionalization of QA lactone with allyl carbonate groups: QA lactone (4.081 g, 23.43 mmol) was synthesized as previously described[1] and added to a flame-dried 250-mL schlenk flask nitrogen, DCM (30 mL) was added and the solution was cooled to -5 °C. TMEDA (14.5 mL, 96.8 mmol) was added and allowed to stir at -5 °C for 20 min. To an addition funnel equipped with a pressure equalizing side arm, allyl choroformate (17.8 mL, 168 mmol) was added and diluted with DCM (10 mL). Dropwise addition (~1 drop/5 s) of the allyl chloroformate and DCM mixture to the flask proceeded for about 4 h. The reaction was maintained between -5 °C and -10 °C, stirring rapidly for 2 h after the addition was complete. The reaction was allowed to warm to room temperature and stirred overnight. The thick white solid that remained was dissolved in DCM and filtered. The filtrate was washed twice with deionized water, once with a 10 wt% CuSO4 solution, dried with MgSO4, filtered and concentrated. The crude product was purified by column chromatography (hexane-ethyl acetate, 3:2) to afford tris(alloc) quinic acid (TAQA) (7.406 g, 74%). T_m = -21 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.97-5.88 (m, 3 H, H-10), 5.41 (t, 1 H, *J* = 5.1, 4.6 Hz, H-4) 5.41-5.27 (m, 6 H, H-11), 5.04 (ddd, 1 H, *J* = 11.7, 6.9, 4.5 Hz, H-5), 4.96-4.94 (dd, 1 H, *J* = 6.0, 4.9 Hz, H-3), 4.65-4.62 (m, 6 H, H-9) 3.22-3.18 (ddd, 1 H, *J* = 11.6, 6.1, 2.8 Hz, H-2), 2.57-2.55 (d, 1 H, J = 11.4 Hz, H-2), 2.46-2.41 (ddd, 1 H, *J* = 12.1, 6.9, 2.8, H-6), 2.35 (t, 1H, *J* = 11.9, H-6); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.6 (C7), 153.8 (C8), 153.3 (C8), 152.3 (8), 131.2 (C10), 131.0 (C10), 130.8 (C10), 119.9 (C11), 119.8 (C11), 119.46 (C11), 77.5 (C1), 73.4 (C3), 69.6 (C9), 69.5 (C9), 69.4 (C5), 69.3 (C9), 67.9 (C4), 33.5 (C2), 33.4 (C6); FT-IR (neat, cm^{-1}): 2985, 2956, 1809 (C=O), 1747 (C=O), 1651, 1448, 1425, 1417, 1367, 1274, 1228, 1211, 1161, 1145, 1103, 1083, 1039, 989, 937, 781, 750; HRMS (+ESI) *m/*z calc'd for $C_{19}H_{22}O_{11}$ $[M+K]^+$: 465.08, found 465.0794.

General procedure for fabricating thiol/TAQA films: Mixtures of multifunctional thiol and TAQA were prepared based on equal molar functional groups. The amount of photoinitiator, DMPA, was 1 wt% for each mixture. **Table S1** shows the composition for each film. DMPA was first dissolved in the multifunctional thiol and then TAQA was added and blended thoroughly. Each mixture was cast between two glass slides separated by a 0.5 mm spacer, and exposed to UV light (365 nm) on a Fusion curing line system (1 m/min, 15 min). The glass slide molds were removed, and the free-standing films were post-cured at 120 °C for 4 h or as otherwise noted.

Table S1. Sample Compositions.

Sample	Triallyl Monomer[g][a)]	Thiol [g]	DMPA [g]
TEGBMP-*co*-TAQA	0.3060	0.3986	0.0070
TMPTMP-*co*-TAQA	0.3140	0.2946	0.0059
1,6-HDT-*co*-TAQA	0.3904	0.2056	0.0064
2,3-BDT-*co*-TAQA	0.4174	0.1791	0.0060
1,2-EDT-*co*-TAQA	0.4540	0.1484	0.0058
1,2-EDT-*co*-TATATO	0.7683	0.4313	0.0121

[a)] Triallyl monomer was either TAQA or TATATO

Characterization: ^{1}H and ^{13}C NMR spectra were obtained on either a Mercury 300 or an Inova 300 at 300 MHz or 75 MHz, respectively, using the solvent signal as internal reference. Glass transition temperatures (T_g) were measured using differential scanning calorimetry (DSC) by a Mettler-Toledo DSC822 (Mettler-Toledo, Columbus, OH) with a heating rate of 10 °C/min. The

T_g was taken as the midpoint of the inflection tangent upon the third heating cycle and averaged over three samples. Thermogravimetric analysis (TGA) was done under an Ar atmosphere using a Mettler-Toledo TGA/DMA1 with a heating rate of 10 °C/min. IR spectra were obtained from a Shimadzu IR Prestige Attenuated Total Reflectance Fourier-transform Infrared Spectrometer (ATR-FTIR). Dynamic mechanical analysis (DMA) experiments were run in tension to determine thermomechanical profiles for the thermoset poly(thioether-*co*-carbonate) samples. Rectangular DMA specimens (4 mm x 25 mm x 0.4 mm) were machined using a Gravograph LS100 40 W CO_2 laser machining device. All laser machined samples were sanded around the edges using 400, then 600 grit sandpaper. DMA was performed using a TA Instruments Q800 Dynamic Mechanical Analyzer in the DMA Multifrequency/Strain mode in tension using a deformation of 0.1% strain, a frequency of 1 Hz, a force track of 150%, and a preload force of 0.01 N. Each experiment was run from -20 to 180°C using a heating rate of 2°C/min (presented in Figure 1). All other DMA and submersion DMA were performed on a Mettler-Toledo TT-DMA system. DMA data were obtained from Triton Laboratory software and exported to Origin Pro 9.0 for analysis. Kinetic fits were obtained by single or exponential fitting as appropriate, using chi-square analysis to assign fitting component number. Average lifetimes for multi-exponential kinetics are reported as intensity average lifetimes where $t(avg) = \Sigma(a_i \bullet t_i^2) / \Sigma(a_i \bullet t_i)$. Activation energy data were extracted from frequency tan(δ) maxima as fitted with a single Gaussian distribution in the temperature regime. Variable frequency DMA measurements were done from 0.1 to 100 Hz, and the activation energy was averaged over three samples. To determine toughness values, ultimate tensile strengths, and failure strains, tensile testing experiments were conducted to failure on ASTM type V dog bone samples (n = 5) using a dual-column Instron model 5965 tensile tester with a 500 N load cell, 1000 N high temperature pneumatic grips, and a temerature chamber thermally controlled by forced convection heating. The dog bone samples were cut with a 40 W Gravograph LS100 CO_2 laser and edges were smoothed with 180 grit sandpaper. Atomic force microscopy was performed using an Asylum 3D-SA instrument operated in tapping mode with a silicon probe (Vista probes T190, k = 48 N/m, f = 190 kHz - nominal). Surface analysis was performed with IGOR 6.0 software.

Figure S1. ^{1}H NMR spectrum of TAQA.

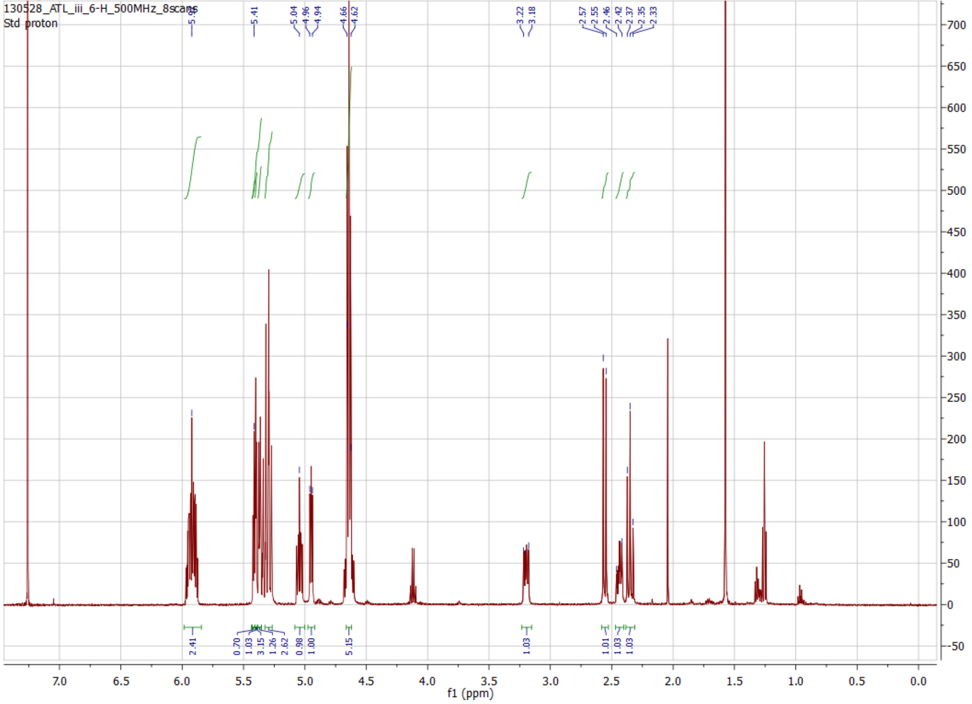


Figure S2. ^{13}C NMR spectrum of TAQA.

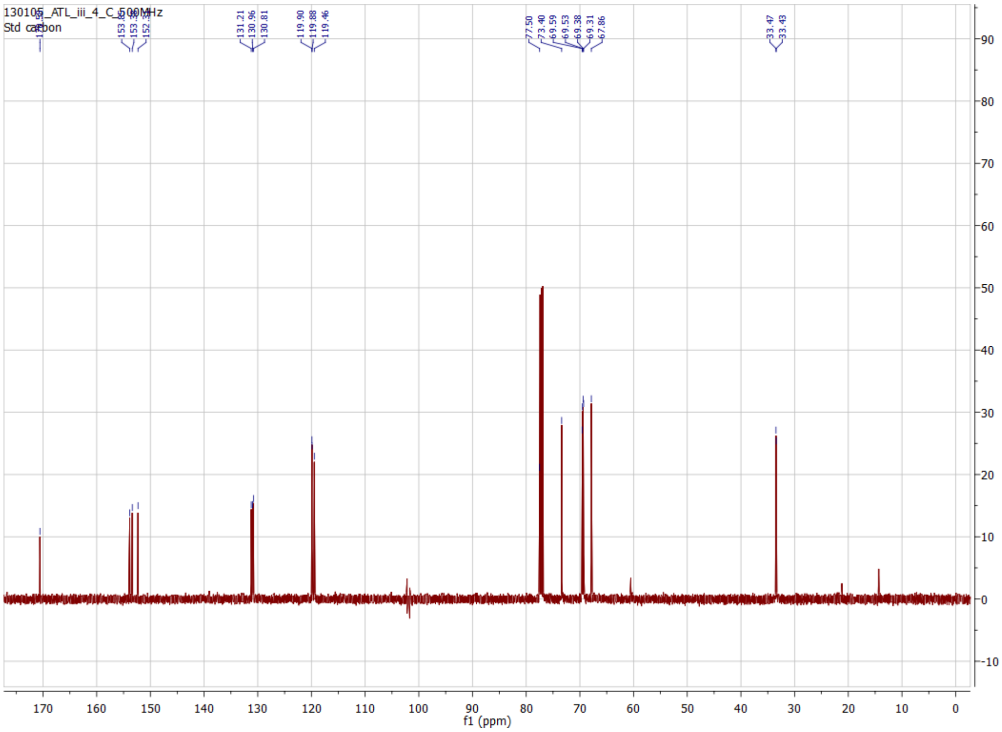


Figure S3. COSY NMR spectrum of TAQA.

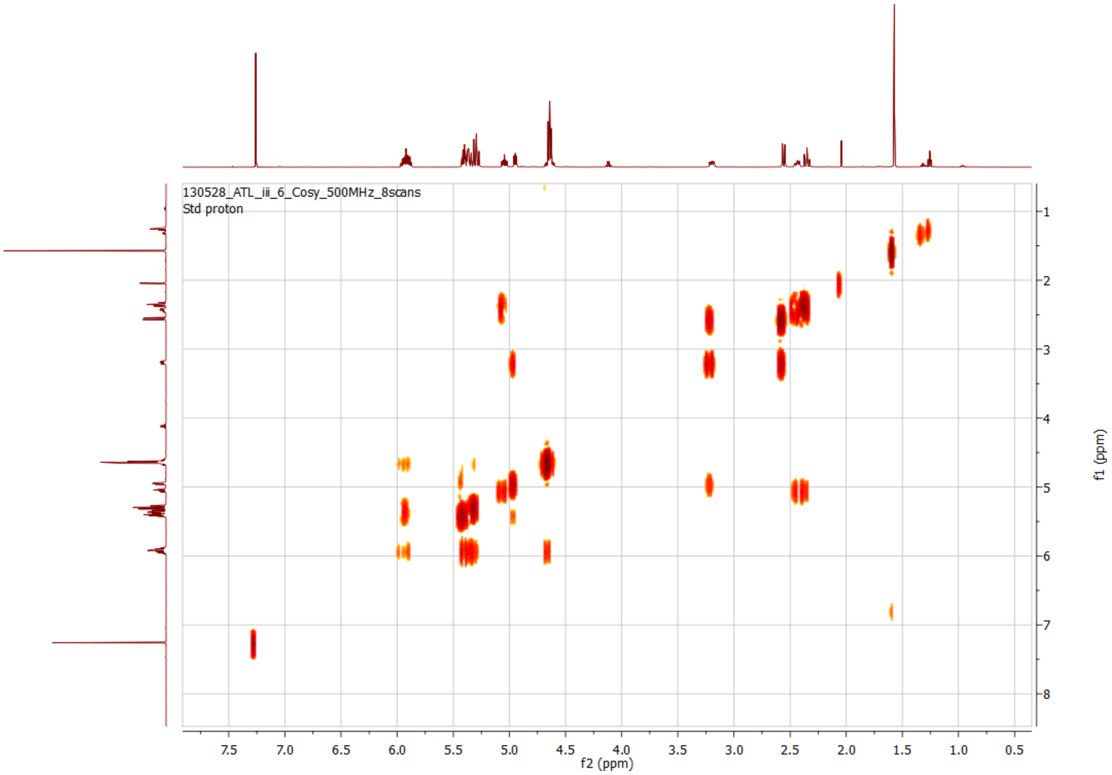


Figure S4. HSQC NMR spectrum of TAQA.

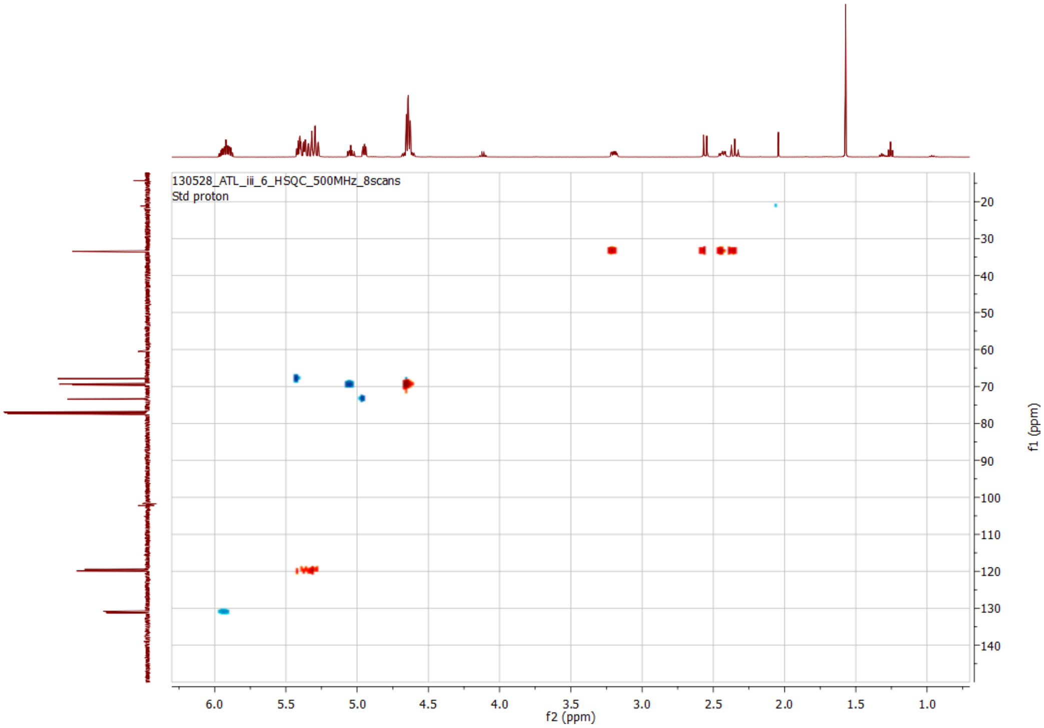


Figure S5. Glass transition temperatures (T_g) of TAQA films as a function of post-cure time at 120 °C, determined by DSC. For each formulation and post-cure time the T_g was averaged from three samples, and the error bars represent the standard deviation.

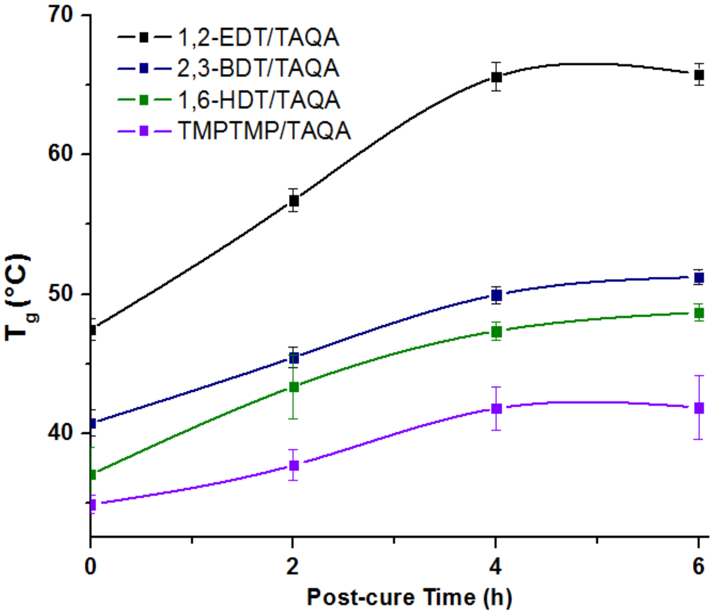


Figure S6. Repeat of *in situ* relaxation measurement (Figure 6) after 24 h. Storage modulus was measured as a function of time over 15 h obtained by DMA while submerged in PBS at 37 °C.

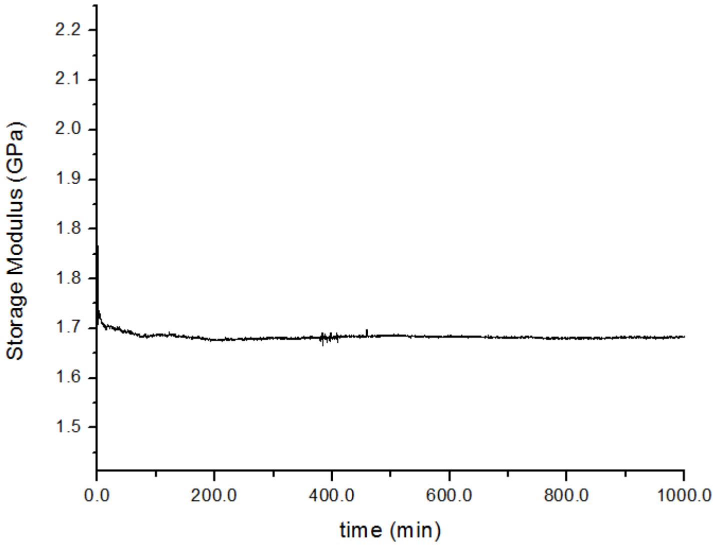
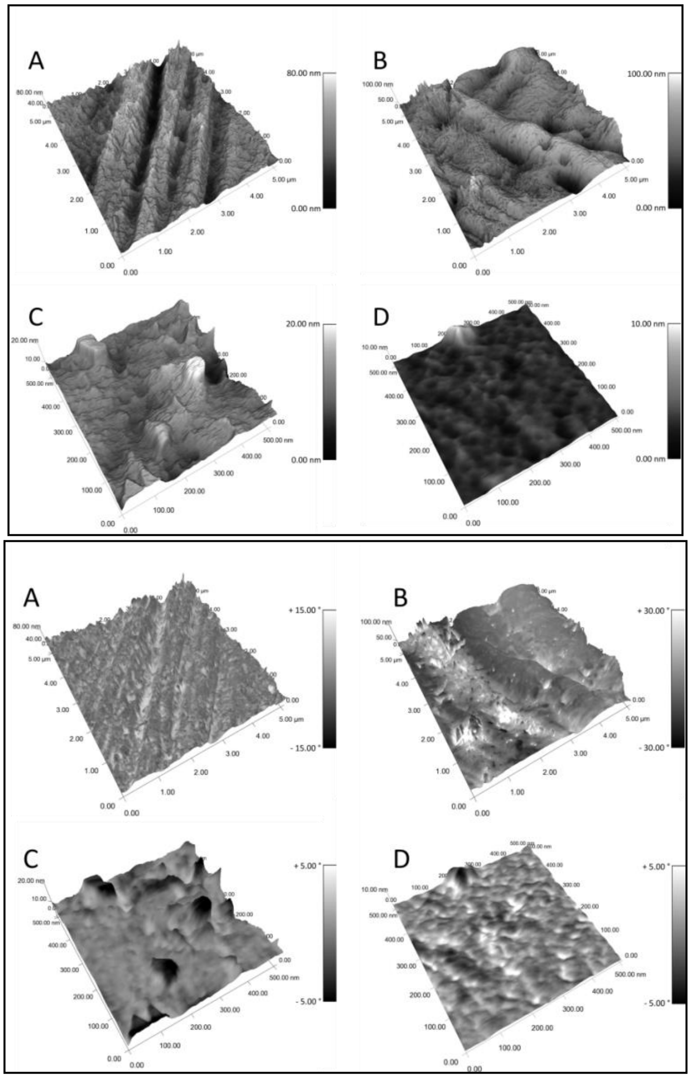


Figure S7. Tapping AFM of 1,2-EDT-*co*-TAQA dry and wet (after 15 h submersion in PBS). **Top:** Height profile **(A)** dry 5 µm^2 (RMS roughness = 12 nm), **(B)** wet 5 µm^2 (RMS roughness = 16 nm), **(C)** dry 500 nm^2 (RMS roughness = 2.4 nm), **(D)** wet 500 nm^2 (RMS roughness = 1.2 nm). **Bottom:** Phase contrast and height profile overlay **(A)** dry 5 µm^2 (phase range = ± 15 °) **(B)** wet 5 µm^2 (phase range = ± 65 °) **(C)** dry 500 nm^2 (phase range = ± 6.0 °) **(D)** wet 500 nm^2 (phase range = ± 11 °). The height profiles show an increase in the height of small features at 5 µm^2 and smoothing of features at 500 nm^2 after 15 h of solvent immersion. The drastic increase in phase range indicates a less homogeneous matrix in terms of surface energy at the nanoscale, *e.g.* a greater difference in tip-surface interaction energies.



References

1. Garg, N. K.; Caspi, D. D.; Stoltz, B. M., The Total Synthesis of (+)-Dragmacidin F. *J. Am. Chem. Soc.* **2004,** *126*, 9552-9553.