Supporting Information for

Photopolymerization of Lichen Derived Usnic Acid

Ruby R. Zhou^a, Jack L. Vargo^a, Bella G. Andjelkovic^a, Maya G. Vermeer^a, Spencer J. Goyette^b and Bassil M. El-Zaatari^{*a}

a. Davidson College, Department of Chemistry, Box 7120, Davidson, North Carolina 28035, United States

b. Beaty Biodiversity Museum, The University of British Columbia, 2212 Main Mall, Vancouver, British Columbia V6T 1Z4, Canada.

* email: baelzaatari@davidson.edu

Contents

Mate	rials	1
Expe	rimental Methods	1
1.	Differential Scanning Calorimetry (DSC)	1
2.	Thermal Gravimetric Analysis	5
3.	Gel Fraction Study	6
4.	FTIR Experiment	7
5.	UV-Vis	8
6.	Tensile Modulus Measurement	8
Synth	nesis Methods	9
1.	Small Molecule Synthesis	9
2.	Polymer Network Synthesis	11
3.	NMR Data	12

Materials

Commercial reagents were purchased from Sigma-Aldrich (4-pentenoyl chloride, 10undecenoyl chloride, 2,2-Dimethoxy-2-phenylacetophenone, Bis(2,4,6-trimethylbenzoyl)phenylphosphineoxide), Oakwood Chemicals (Eosin Y), or Fisher Scientific ((+)-Usnic Acid, pyridine) and used as received.

Experimental Methods

1. Differential Scanning Calorimetry (DSC)

DSC measurements were performed on polymer network samples with masses ranging between 5 and 10 mg. These samples were placed in aluminum pans and all measurements were performed using a TA Q20 DSC. All samples were performed under N₂ gas. A heating rate of 5 °C/min was performed from -20 to 100 °C. All samples underwent one heating and cooling cycle, before data was recorded. DSC was performed in triplicates for **UA-Net-1** and **UA-Net-2** samples and final Tg was estimated as the midpoint of the transition. The triplicate results for **UA-Net-1** and **UA-Net-2** are shown in Figures S1 through S6.



Figure S1. DSC data of sample 1 of UA-1-Net with the second heating cycle shown as a solid line (heating rate of 5 °C/min). Estimate Tg temperature shown above the curve.



Figure S2. DSC data of sample 2 of UA-1-Net with the second heating cycle shown as a solid line (heating rate of 5 $^{\circ}$ C/min). Estimate Tg temperature shown above the curve.



Figure S3. DSC data of sample 2 of UA-1-Net with the second heating cycle shown as a solid line (heating rate of 5 $^{\circ}$ C/min). Estimate Tg temperature shown above the curve.



Figure S4. DSC data of sample 1 of UA-2-Net with the second heating cycle shown as a solid line (heating rate of 5 °C/min). Estimate Tg temperature shown above the curve.



Figure S5. DSC data of sample 2 of UA-2-Net with the second heating cycle shown as a solid line (heating rate of 5 $^{\circ}$ C/min). Estimate Tg temperature shown above the curve.



Figure S6. DSC data of sample 3 of UA-2-Net with the second heating cycle shown as a solid line (heating rate of 5 $^{\circ}$ C/min). Estimate Tg temperature shown above the curve

2. Thermal Gravimetric Analysis

TGA measurements were performed using a TA Instruments Discovery TGA 550. Samples (between 14-19 mg) were heated from room temperature to 500°C at a rate of 10 °C/min. All samples were run under N₂ gas using aluminum pans. The thermograms of UA-1-Net and UA-2-Net are shown below:



Figure S7. Thermogram of UA-1-Net



Figure S8. Thermogram of UA-2-Net

3. Gel Fraction Study

A polymerized sample (UA-1-NET or UA-2-NET) between 10 and 40 mg, was allowed to swell in toluene at room temperature for 24 hours. The solvent was then removed from the swollen samples and placed in an oven for an additional 24 hours at 100C. The gel fraction was calculated as the ratio of the initial mass to the final mass. All data is shown in Table S1 and S2

Table S1. Initial and final masses for 3 different samples of UA-1-Net in chloroform and the calculated gel fraction.

	Trial 1	Trial 2	Trial 3
Mass initial (g)	0.0356	0.0244	0.020
Mass final (g)	0.0322	0.0220	0.0180
Gel Fraction (%)	90.45	90.16	89.11

Table S2. Initial and final masses for 3 different samples of UA-2-Net in chloroform and the calculated gel fraction.

Trial 1	Trial 2	Trial 3
0.0362	0.0106	0.0148
0.0318	0.0088	0.0139
87.85	83.02	93.92
	Trial 1 0.0362 0.0318 87.85	Trial 1 Trial 2 0.0362 0.0106 0.0318 0.0088 87.85 83.02

Table S3. Initial and final masses for 3 different samples of DAP-Net in chloroform and the calculated gel fraction.

	Trial 1
Mass initial (g)	0.0350
Mass final (g)	0.0303
Gel Fraction (%)	86.57

4. FTIR Experiment

A Nicolet Nexus 6700 Series Fourier transform infrared (FTIR) spectrometer was used to evaluate the disappearance of the thiol peak in PETMP as the polymerization was occurring. The sample was placed in between glass slides, aligned with the laser and a spectrum was taken before and after irradiation of green light. An FTIR spectrum showing the decrease in area of the thiol peak at 2570 cm⁻¹ is shown below.



Figure S9. FTIR plot of the **UA-1**, **PETMP**, and Eosin Y before polymerization (t=0) and after polymerization (t = 1 hour) showing the disappearance of the S-H stretch at 2570 cm⁻¹.

5. **UV-Vis**

UV-visible spectra were taken for **UA-1** and **UA-2** using an Agilent 8453 spectrometer. 50 mg/L samples of each were prepared in chloroform and ran between 250 and 900 nm.

6. Tensile Modulus Measurement

Tensile Modulus (E') measurements were performed using a Universal Extensional Fixture (UXF) on an Anton Paar MCR 302e rheometer. Rectangular samples of **UA-1-Net** or **UA-2-Net** were placed in this fixture at the temperature set to 100°C using a CTD oven. The tensile modulus was measured by performing an amplitude sweep and recording the modulus at an extensional strain of 0.05%. Duplicates for each sample % are shown in the Table below:

Table S4. Tensile Moduli (E') for UA-1-Net and UA-2-Net at 100°C

	Trial 1	Trial 2	Average
E' UA-1-Net (MPa)	7.68	6.78	7.23
E' UA-2-Net (MPa)	5.65	7.31	6.48

Synthesis Methods

1. Small Molecule Synthesis

(R)-4,8-diacetyl-7-hydroxy-2,9a-dimethyl-9-oxo-9,9a-dihydrodibenzo[b,d]furan-1,3-diyl bis(pent-4-enoate) – (**UA-1**)



Usnic acid (2.00 g, 5.8 mmol) was dissolved in chloroform (40 mL). The mixture was then placed in an ice bath, to which 4-pentenoyl chloride (4.10 g, 34.9 mmol) was added, followed by pyridine (2.76 g, 34.9 mmol). The mixture was stirred in the ice bath for 3 h and allowed to stir at room temperature for an additional 24 h. The solution was then washed with water, and the organic layer dried over Na₂SO₄ and evaporated under high pressure. The liquid residue was chromatographed on a silica gel column (10:90 ethyl acetate/hexane) affording the pure product as a viscous yellow oil (1.54 g, 52% yield).

¹H NMR: (400 MHz, CDCl₃) 18.31 (s, 1H), 6.02-5.79 (m, 2H), 5.90 (s, 1H), 5.25-5.10 (m, 4H), 2.86-2.70 (m, 4H), 2.60 (s, 3H), 2.53 (s, 3H), 2.54-2.50 (m, 4H), 1.95 (s, 3H), 1.81(s, 3H).¹³C NMR (101 MHz, CDCl₃): 198.59, 195.16, 192.84, 190.90, 177.83, 171.01, 170.90, 153.60, 148.96, 148.40, 136.80, 136.38, 123.64, 118.81, 116.10, 115.94, 115.87, 106.13, 98.81, 59.56, 33.97, 33.34, 32.12, 31.08, 28.73, 28.53, 26.20, 10.61. MS-MALDI m/z predicted for $C_{28}H_{28}O_{9:}$ 509.1806; measured: 509.1822

(R)-4,8-diacetyl-7-hydroxy-2,9a-dimethyl-9-oxo-9,9a-dihydrodibenzo[b,d]furan-1,3-diyl bis(undec-10-enoate) (**UA-2**)



Usnic acid (1.00 g, 2.9 mmol) was dissolved in chloroform (40 mL). The mixture was then placed in an ice bath, to which 10-undecenoyl chloride (2.1 g, 17.4 mmol) was added, followed by pyridine (1.38 g, 17.4 mmol). The mixture was stirred in the ice bath for 3 h and allowed to stir at room temperature for an additional 45 h. The solution was then

washed with water, and the organic layer dried over Na₂SO₄, and then evaporated under high pressure. The liquid residue was chromatographed on a silica gel column (5:95 ethyl acetate/hexane) affording the pure product as a viscous golden yellow oil (0.39 g, 20% yield).

¹H NMR: (400 MHz, CDCl₃) 18.30 (s, 1H), 5.90-5.82 (m, 2H), 5.89 (s, 1H), 5.02 (m, 4H), 2.75-2.53 (m, 10H), 2.04 (m, 4H), 1.96 (s, 3H), 1.85-1.65 (m 4H), 1.81(s, 3H), 1.48-1.31 (m, 20 H).¹³C NMR (101 MHz CDCl₃): 198.16, 194.91, 192.47, 190.59, 177.61, 171.38, 171.27, 153.22, 148.71,148.09, 139.01,138.95, 123.20, 118.39, 115.87, 114.03,113.99, 105.82, 98.43, 59.27, 34.33, 33.82, 33.61, 31.76, 29.16-28.71 (12 Cs, aliphatic*), 25.85, 24.45, 24.34, 10.20. MS-MALDI m/z predicted for $C_{40}H_{52}O_{9}$: 677.3684; measured: 677.3724

* Not all 12 peaks were individually observed due to close proximity to each other (see Figure S14 for more details)

Synthetic Notes:

- 3 and 4 equivalents of the alkenoyl chloride were also able to provide the desired product in lower yield, but with less side products as established by TLC.
- All flash columns were performed using a CombiFlash Rf 200 (Teledyne Isco)

2. Polymer Network Synthesis

Polymer films were prepared by mixing a 1:1 mol ratio (alkene: thiol functional groups) of **UA-1** or **UA-2** and Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP). 3 wt% of Eosin Y and 10 wt% of methanol were added to the mixture and vortexed for a minute. The mixture was then cast in between two glass slides using a 0.32 mm spacer. The glass slides containing the sample was then cured by irradiating 535 nm light for 2 hours using a WheeLED lamp (Mightex). The polymerized samples were then taken out of the glass slides and postcured in the oven at 100°C for an additional 2 hours.



Pictures of UA-1-Net and UA-2-Net are shown below:

Figure S10. Pictures of UA-1-Net (left) and UA-2-Net (right) rectangular samples

3. NMR Data



