Macromolecules

Synthesis and Physical Properties of Thiol-Ene Networks Utilizing **Plant-Derived Phenolic Acids**

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Supporting Information

ABSTRACT: Elastomeric polymer films synthesized through thiol-ene chemistry, suitable in applications as coatings and adhesives due to their ease of preparation and superior physical properties, are traditionally derived from petroleum sources. Of recent interest is the exploration of sustainable alternatives for the precursors to these materials. Here, we report the synthesis of thiol-ene networks through the photoinitiated reaction between allylated plant-based phenolic acids (salicylic acid and 4hydroxybenzoic acid) and a multifunctional thiol, followed by isothermal annealing. Plant-sourced phenolic acids offer many



advantages as biorenewable monomers: their rigid aromatic rings are expected to provide mechanical strength to the resulting polymers and the presence of multiple hydroxyl and carboxyl groups leads to ease of functionalization. Both phenolic acids produced networks with high degrees of homogeneity and few defects, as evidenced by narrow glass transitions and consistency of their tensile behavior with the ideal elastomer model at low-to-moderate strains. The 4-hydroxybenzoic acid based network, which had a higher cross-link density, exhibited a higher glass transition temperature, modulus, tensile strength, and elongation at break as compared to the salicylic acid based network. This work develops fundamental relationships between the molecular structure of the phenolic acids and the physical properties of the resulting networks.

INTRODUCTION

Thiol-ene chemistry offers a versatile platform for polymer synthesis due to its lack of sensitivity to water and oxygen, high conversion and yield, lack of byproducts, rapid reaction rates, solvent-free conditions, and ability to impart spatial and temporal control over the reaction (in the case of photoinitiation).^{1,2} The resulting films offer advantages of low shrinkage and stress,³ and high degree of network homogeneity^{1,2,4,5} relative to other elastomeric materials. Current applications of thiol-ene films include adhesives, soft touch coatings for electronic devices, protective coating on floors and wires, among others.² Although a wide range of ene- and thiolbearing molecules have been investigated for the preparation of thiol-ene networks,^{1,2,4} the vast majority of these studies have utilized petroleum-sourced monomers.

As petroleum is a finite resource and processing of petroleum oils leads to environmental pollution, current efforts in academia and industry promote the utilization of renewable resources for the derivation of polymers.^{6,7} Thiol-ene chemistry is well-suited for the incorporation of plant-sourced materials as mild reaction conditions are employed, and solvent-free syntheses have an even greater environmental benefit. Relatively few studies have reported the derivation of thiol-ene elastomeric films using biorenewable components; some notable examples include the use of vegetable oils and

their fatty acids,^{8–12} carbohydrates,^{13,14} terpenes,¹⁵ and other plant-derived molecules.^{16,1}

In this study, plant-sourced phenolic acids were chosen as components of thiol-ene networks. Phenolic acids are plant metabolites widely distributed in nature.¹⁸⁻²¹ They are often found in plant byproducts including the skins and seeds of fruits and vegetables.^{18–21} Phenolic acids offer many advantages as biorenewable monomers: their rigid aromatic rings are expected to provide mechanical strength to the resulting polymers and the presence of multiple hydroxyl groups and carboxyl groups leads to ease of functionalization. Through the choice of phenolic acid, the number and relative placement of hydroxyl and carboxyl groups can be varied, which is expected to be a convenient method of tuning the physical properties of the resulting polymers.

Herein, the synthesis and properties of thiol-ene networks are described, which were prepared through the reaction of allylated phenolic acids and a multifunctional thiol. Two phenolic acids were investigated: salicylic acid and 4hydroxybenzoic acid. Both phenolic acids contain two functional groups (one carboxylic acid group and one hydroxyl

Received: August 12, 2015 **Revised:** October 12, 2015 group), yet the relative placements of the functional groups vary (i.e., ortho vs para position). Synthetic conditions were developed to prepare thiol—ene networks with high yield and conversion. The thermal and mechanical behaviors of the thiol—ene networks were investigated. This work develops fundamental relationships between the molecular structure of the phenolic acids and the physical properties of the resulting networks. Gaining such knowledge is an important first step toward the widespread implementation of biobased phenolic acids in thiol—ene polymer applications.

EXPERIMENTAL DETAILS

Materials. All chemicals were purchased from Sigma-Aldrich unless otherwise noted below. The phenolic acids used in this study were also purchased from Sigma-Aldrich, though they were chosen for their prevalence in various plant sources. All reagents were used as received without further purification unless noted. Two phenolic acids were employed in this study: salicylic acid (SA, \geq 99%, FG/Halal/Kosher) and 4-hydroxybenzoic acid (4HBA, 99%, ReagentPlus). The chemical structures of both phenolic acids are shown in Figure 1.



Figure 1. Chemical structures of phenolic acids used in this study: (a) salicylic acid (SA) and (b) 4-hydroxybenzoic acid (4HBA).

Other chemicals used were *N*,*N*-dimethylformamide (DMF, BDH, \geq 99.8%, ACS reagent), potassium carbonate (K₂CO₃, \geq 99.0%, ACS reagent), allyl bromide (97%), ethyl acetate (BDH, \geq 99.5%, ACS grade), magnesium sulfate (MgSO₄, BDH, \geq 99.0%, anhydrous reagent grade), 2,2-dimethoxy-2-phenyl-acetophenone (DMPA, 99%), and pentaerythritol tetrakis(3-mercaptopropionate) (PETMP, > 95%).

Nuclear Magnetic Resonance (NMR). The following NMR experiments were performed on a JEOL ECA-400 instrument using deuterated dimethyl sulfoxide (Cambridge Isotope Laboratories, Inc., 99.9% D) as the solvent: ¹H NMR (400 MHz), ¹³C NMR (100 MHz), DEPT 135, COSY, HSQC, and HMBC. Chemical shifts were referenced to the solvent proton resonance (2.5 ppm). All spectra are included in the Supporting Information (Figures S1 and S2).

Fourier Transform Infrared Spectroscopy (FTIR). FTIR spectra were recorded on a Thermo Scientific Nicolet 4700 spectrometer in transmission mode as well as using an attenuated total reflection (ATR) stage (containing a Germanium crystal). The OMNIC Series software was used to follow selected peaks at 1.928 cm⁻¹ resolution using 32 scans. FTIR spectra were collected on allylated monomers and thiol—ene networks (prior to exposure of the sample with UV, after 15 and 30 min of UV exposure, and after 15 min of UV exposure followed by annealing at 150 °C for 10 min).

Monomer Synthesis. The allylation of phenolic acids was conducted following literature procedures.²² Phenolic acid (10.0 g, 72.4 mmol) was dissolved into 340 mL DMF in a 1000 mL glass round-bottom flask equipped with a rubber septum and a magnetic stirring bar. The temperature was maintained at 0 °C using an ice bath. K_2CO_3 (22.0 g, 159 mmol) was added

to the flask (the molar ratio of K_2CO_3 to phenolic acid was 2.20 to 1.00). After 3 min of stirring, allyl bromide (19.3 g, 159 mmol) was added dropwise with a syringe (the molar ratio of allyl bromide to the phenolic acid was 2.20 to 1.00). The solution was stirred at room temperature for 48 h. Distilled water (340 mL) was added and the product was isolated by extraction with ethyl acetate (3*x*), washing with saturated brine, drying over MgSO₄, and concentration *in vacuo*, followed by drying in a vacuum oven at 50 °C, until the NMR peaks associated with DMF (7.96 ppm, 2.94 ppm, 2.78 ppm) were not observed. The yield was 84% for allyl (2-allyloxy)benzoate and 88% for allyl (4-allyloxy)benzoate.

Allyl (2-Allyloxy)benzoate (Referred to as "Allylated SA" in This Manuscript). ¹H NMR (400 MHz, DMSO- d_6): δ 7.65 (dd, J = 7.7, 1.8 Hz, 1H), 7.50 (ddd, J = 8.5, 7.4, 1.8 Hz, 1H), 7.12 (dd, J = 8.5, 0.6 Hz, 1H), 7.00 (ddd, J = 7.7, 7.4, 0.6 Hz, 1H), 6.04–5.93 (m, 2H), 5.44 (ddt, J = 17.3, 1.9, 1.9 Hz, 1H), 5.37 (ddt, J = 17.2, 1.7, 1.7 Hz, 1H), 5.24–5.20 (m, 2H), 4.72 (ddd, J = 5.3, 1.7, 1.3 Hz, 2H), 4.61 (ddd, J = 4.7, 1.9, 1.3 Hz, 2H) ppm. ¹³C NMR (100 MHz; DMSO- d_6): δ 165.4, 157.1, 133.6, 133.2, 132.7, 130.8, 120.3, 120.2, 117.7, 117.0, 113.8, 68.6, 64.9 ppm. FTIR (ATR): 3083, 3017, 2987, 2936, 2877, 1728, 1648, 1601, 1582, 1489, 1450, 1424, 1411, 1377, 1360, 1301, 1245, 1165, 1133, 1102, 1073, 996, 930, 854, 755, 706, 670, 654 cm⁻¹.

Allyl (4-Allyloxy)benzoate (Referred to as "Allylated 4HBA" in This Manuscript). ¹H NMR (400 MHz, DMSO- d_6): δ 7.93 (d, J = 9.0 Hz, 2H), 7.07 (d, J = 9.0 Hz, 2H), 6.10–5.98 (m, 2H), 5.44–5.35 (m, 2H), 5.30–5.24 (m, 2H), 4.76 (ddd, J =5.3, 1.5, 1.5 Hz, 2H), 4.66 (ddd, J = 5.2, 1.5, 1.5 Hz, 2H) ppm. ¹³C NMR (100 MHz, DMSO- d_6): δ 165.0, 162.2, 133.1, 132.9, 131.3, 121.9, 118.0, 117.7, 114.7, 68.5, 64.8 ppm. FTIR (ATR): 3086, 3050, 2989, 2941, 2873, 1714, 1649, 1605, 1581, 1509, 1455, 1421, 1361, 1313, 1268, 1251, 1169, 1102, 1011, 995, 929, 847, 769, 697, 668, 633 cm⁻¹.

Polymer Synthesis. The UV curing of thiol-ene networks followed procedures similar to those reported in ref.¹⁶ The allylated phenolic acid (1.00 g, 4.59 mmol) was mixed with PETMP (1.18 g, 2.29 mmol, stoichiometry based on equal molar functional groups) and 1 wt % of the photoinitiator DMPA (0.0218 g, 0.0851 mmol) at room temperature in a 20 mL vial (using magnetic stirring), which was covered by aluminum foil. The mixture was placed in the following sample holders appropriate for each characterization experiment: (a) between two glass slides with a 0.4 mm glass spacer for TGA, DSC, DMA and ATR-FTIR, (b) between two NaCl windows (32 mm diameter, 3 mm thick) with a 0.05 mm Teflon spacer for transmission-mode FTIR, and (c) in a Teflon dogboneshaped mold following ASTM D638 (bar type 5, thickness 0.4 mm) for tensile testing. The sample was exposed under continuous 365 nm UV light (4 W, Spectroline ENF-240C) for 15 min and transferred to a convection oven at 150 °C for a specified period of time, summarized in Table 1.

Network Synthesized from Allylated SA. FTIR (ATR): 2953, 2929, 1732, 1600, 1582, 1491, 1467, 1452, 1420, 1388, 1352, 1302, 1244, 1166, 1135, 1085, 1047, 1028, 931, 757, 704, 663 cm⁻¹.

Network Synthesized from Allylated 4HBA. FTIR (ATR): 2954, 2921, 1736, 1710, 1605, 1580, 1510, 1468, 1421, 1385, 1353, 1316, 1273, 1251, 1168, 1140, 1105, 1028, 928, 849, 770, 697, 644 cm⁻¹.

Dynamic Mechanical Analysis (DMA). The dynamic mechanical behavior of cured thiol-ene films (following the

Table 1. Curing Protocol for Allylated Phenolic Acids

phenolic acid ^a	UV exposure time (min)	isothermal heating time at 150 °C (min)
salicylic acid (SA)	15	10
4-hydroxybenzoic acid (4HBA)	15	10

"The phenolic acids were allylated and subsequently cured with pentaerythritol tetrakis(3-mercaptopropionate) and a photoinitiator, as described in the Experimental Details.

protocol in the Polymer Synthesis section) was probed using a Q800 dynamic mechanical analyzer (TA Instruments) with a nitrogen environment. Specimens of 0.4 mm thickness were cut with a razor blade to have the following dimensions: 10 mm \times 5 mm \times 0.4 mm (length \times width \times thickness).

Four experiments were conducted: (1) Isothermal strain sweeps were conducted at desired temperatures and using a frequency of 1 Hz to locate the range of strains in the linear viscoelastic region; (2) isothermal frequency sweeps were conducted from 0.1 to 10 Hz at desired temperatures, using a strain within the linear viscoelastic region; (3) time-temperature superposition of the data was performed at 0, 5, 10, 15, 20, 25, 30, and 40 °C, and (4) temperature ramps were conducted at a constant strain and frequency. In the case of time-temperature superposition, the master curve was prepared using the TA Instruments Rheology Advantage Data Analysis software with 30 °C chosen as the reference temperature. The DMA instrumental error on the modulus measurement is reported by TA Instruments to be $\pm 1\%$.

Differential Scanning Calorimetry (DSC). The glass transition temperature (T_g) was measured through DSC experiments conducted using a TA Instruments Q2000 calorimeter, calibrated with an indium standard, with a nitrogen flow rate of 50 mL/min. The cured sample (following the protocol in the Polymer Synthesis section) was placed in the calorimeter (using a Tzero aluminum pan), equilibrated at 40 °C, cooled to -40 °C at a rate of 10 °C/min and heated to 40 °C at a rate of 10 °C/min. The cooling and heating scans were repeated for a total of three measurements. The value of the T_g was determined using the half extrapolated tangents method in the Universal Analysis software.²³ The onset and endset temperatures were also identified with the Universal Analysis software.

Thermogravimetric Analysis (TGA). TGA experiments were conducted with a TA Instruments Q500 analyzer. The sample was cured following the protocol in the Polymer Synthesis section and transferred to the analyzer. The cured sample was heated from 30 to 800 °C at a rate of 10 °C/min in an argon environment (the balance argon purge flow was 40 mL/min and the sample purge flow was 60 mL/min).

Tensile Testing. Tensile testing was carried out with an Instron 5966 universal testing system containing a 2 kN load cell. Dogbone-shaped testing bars (ASTM D638, bar type 5, thickness 0.4 mm) were prepared following the procedure in the Polymer Synthesis section. Pneumatic grips (maximum force 2 kN) were used to affix the sample in the testing frame, at a compressed air pressure of 40 psi. The force and change in length were measured as the sample was elongated at a rate of 10 mm/min. Each measurement was repeated with 5–6 test specimens that broke in the gauge region and did not contain a visible defect at the point of fracture.

RESULTS AND DISCUSSION

Allylation of Phenolic Acids. NMR was used to monitor the progress of the allylation reaction (Figures 2 and S1 and



Figure 2. ¹H NMR data obtained from (a) allylated SA and (b) allylated 4HBA. Additional spectra are included in Figures S1 and S2.

S2). The ¹H NMR spectrum of salicylic acid (SA) is shown in Figure S1.²⁴ The peaks located at 13.93 and 11.27 ppm indicate the presence of carboxyl and hydroxyl groups in SA before allylation. The ¹H NMR spectrum of allylated SA is shown in Figures 2a and S1.^{25,26} No peaks are detected at 13.93 and 11.27 ppm, indicating the disappearance of the hydroxyl and carboxyl groups. The peaks located in the region of 4-6 ppm correspond to the allyl groups in the allylated SA. The ratio of the peak area associated with the CH₂-O protons on the allyl group (4.58-4.69 ppm) to the peak area associated with the aromatic protons (6.80-7.90 ppm) should theoretically be 2:4 if there is complete conversion of the carboxyl and hydroxyl groups to allyl groups. Using the data shown in Figure 2a, this ratio is 2.02:4.00, which is very close to the theoretical prediction. The reaction conversion was calculated to be 99.5%, using the integrals of peaks associated with aromatic protons (refer to Figure S1, which shows ¹H NMR data obtained on allylated SA prior to extraction). Allylated SA was isolated in a 84% yield. The 4-hydroxybenzoic acid (4HBA) was allylated following the same procedures. The ¹H NMR spectra of 4HBA²⁷ and allylated 4HBA^{25,26,28} are shown in Figures 2b and S2. The reaction conversion was 99.6%, and the allylated 4HBA was isolated in a 88% yield. These results are summarized in Table 2.

FTIR Characterization of the UV Curing of Allylated Phenolic Acids. FTIR was used to monitor the photoinitiated thiol—ene reaction between the allylated phenolic acids and the tetra-functional thiol PETMP (Scheme 1), which follows the

 Table 2. ¹H NMR Characterization of Phenolic Acid

 Allylation

phenolic acid	% conversion	peak area of CH_2O on allyl group:peak area of aromatic protons ^a	% yield
SA	99.5	2.02:4.00 (2:4)	84
4HBA	99.6	2.00:4.00 (2:4)	88
^{<i>a</i>} Theoreti	cal ratio is give	en in parentheses.	

well-established step-growth radical mechanism outlined in Scheme S1.^{1,2} Allyl ethers generally exhibit high reactivities in the thiol–ene reaction,² and thiol–allyl ether systems exhibit high propagation rates relative to rates of chain transfer.²⁹

The FTIR spectra obtained upon UV curing of allylated SA and allylated 4HBA are shown in Figure 3 (assignment of vibrational modes is summarized in Table S1). In both spectra, the reduction of the peak located at 2570 cm⁻¹ (S-H stretching) indicates high conversion of the thiol. An increase in the intensity of the peak located at 2950 cm^{-1} (alkane C–H stretching) is attributed to the formation of the network structure upon curing. The decreases in the following peak intensities over time indicate the decrease in concentration of the allyl groups on the allylated phenolic acids upon curing: 932 and 996 cm⁻¹ (olefinic = C–H bending), 1647 cm⁻¹ (C=C stretching), and 3080 cm⁻¹ (olefinic =C-H stretching). We cannot observe whether the peaks associated with the allyl groups disappear completely, as they are all located in the vicinity of neighboring peaks (refer to Figure 3 and inset). In the case of the peak located at 932 cm⁻¹, it is clear that a distinct peak remains after UV curing; this peak may be attributed to unreacted allylated phenolic acid, or alternatively may come from C-O stretching of ester groups present in both the phenolic acids and PETMP.^{30,31} Tables S2 and S3 quantify the reaction conversion, using the maximum peak absorbance of the S–H stretching peak at 2570 cm⁻¹. As increasing the UV exposure time beyond 15 min did not result in any appreciable differences in the FTIR spectra or conversion, 15 min was chosen as the UV exposure time for both allylated phenolic acids (Table 1).

Allylated SA and allylated 4HBA have similar chemical structures: each contain two allyl groups, placed at different positions on the aromatic ring (*ortho* and *para* positions, refer to Figure 1). As these two allylated phenolic acids show similar

curing behavior, we can conclude that the placement of the allyl groups with respect to one another does not have a large effect on the UV curing behavior.

We quantified the biorenewable content in the thiol-ene networks, by calculating the wt % of phenolic acid in the final material. The SA and 4HBA networks each contain 29 wt % renewable content (i.e., derived from the phenolic acids, which are found in plant sources), respectively. To put this into perspective, we conducted a similar calculation for reported literature studies, and found that the biorenewable content in prior studies on thiol-ene networks ranged from 20 to 58%.^{8-10,12-16} One strategy to increase the total biorenewable content in our materials would be to employ a multifunctional thiol derived from a renewable resources, in addition to the allylated phenolic acids.

Isothermal Post-Curing of Thiol–Ene Networks. Differential scanning calorimetry (DSC) was used to identify the appropriate isothermal annealing time for the thiol–ene networks following UV exposure. Thiol–ene networks prepared from allylated phenolic acids were first exposed to UV for 15 min, and then encapsulated in a Tzero aluminum pan for characterization through DSC. The heat flow as a function of temperature was measured through subsequent heating and cooling scans (Figure 4). It is clear that the T_g increased after heating the sample to 150 °C (i.e., compare first and second heating scans); further heating of the samples did not significantly impact the T_g (i.e., compare second and third heating scans).

Thiol—ene networks were prepared through 15 min of exposure to UV followed by isothermal curing in a convection oven at 150 °C (the reaction conversion increased after the 150 °C postcure, detailed in Tables S2 and S3). In Figure 5, the T_g is plotted as a function of the isothermal curing time at 150 °C. For both SA and 4HBA-based networks, the T_g did not change upon increasing the isothermal annealing time beyond 10 min. For this reason, we chose to use 10 min of isothermal annealing at 150 °C for the preparation of the thiol—ene networks in this study. The UV and isothermal curing protocols are summarized in Table 1.

Thermal and Mechanical Properties of Thiol–Ene Networks. The thermal and mechanical characteristics of thiol–ene networks derived from allylated phenolic acids were



Scheme 1. Photoinitiated Thiol-Ene Reaction between the Allylated Phenolic Acids and the Tetra-Functional Thiol PETMP



Figure 3. FTIR data (transmission mode) obtained from a mixture of PETMP, photoinitiator, and (a) allylated SA and (b) allylated 4HBA: before curing (red solid curve), after 15 min of UV exposure (green solid curve), and after 30 min of UV exposure (blue dashed curve). The following peaks are highlighted: 932 and 996 cm⁻¹ (olefinic = C-H bending, allyl group), 1647 cm⁻¹ (C=C stretching, allyl group), 2570 cm⁻¹ (S-H stretching, PETMP), 2950 cm⁻¹ (alkane C-H stretching, polymer network), and 3080 cm⁻¹ (olefinic = C-H stretching, allyl group).



Figure 4. DSC heat flow as a function of temperature for thiol—ene networks derived from (a) allylated SA and (b) allylated 4HBA. Samples were exposed to UV for 15 min, encapsulated into an aluminum pan, and subsequently cycled through three consecutive heating and cooling sequences in the DSC (at a rate of 10 $^{\circ}$ C/min): first heating scan (black dotted curve), second heating scan (red solid curve), and third heating scan (blue dashed curve).

investigated using a combination of techniques: DSC, TGA, tensile testing, and DMA.

Thermal Characterization. DSC was employed to characterize the glass transition temperature (T_g) of thiol-ene networks that were prepared through exposure to UV for 15 min followed by isothermal curing at 150 °C in a convection oven (following the protocol in Table 1). To investigate the reproducibility of the extent of curing of the samples, and resulting T_g values, the T_g was measured for three distinct regions of the same specimen, and this process was repeated for three separate specimens (i.e., nine measurements total for each type of thiol-ene network). T_g measurements were obtained for each sample upon repeated heating and cooling scans. Tables S4 and S5 show all T_g results; the transitions observed in the first, second, and third heating scans were comparable to one another, within the error of the measurement. The average and standard deviation values obtained during the first heating scan are provided in Table 3. The 4HBA network exhibited a higher T_g than the SA network. Aging the samples for 7 days at room temperature did not have a significant impact on the value of the T_g (Table 3). The T_g 's of both networks are lower than room temperature, as is typically observed in thiol—ene networks, which contain flexible thioether linkages.³²

The thermal degradation properties of the networks were explored with TGA, and the results are summarized in Table 3. The two types of networks have similar onset degradation



Figure 5. Glass transition temperature (T_g) as a function of isothermal curing time at 150 °C (following 15 min of exposure to UV) for thiol– ene networks derived from allylated SA (blue \blacksquare) and 4HBA (red \bigcirc). The data points shown were obtained from four distinct regions of the same specimen (which were isothermally cured for different lengths of time). The results of the first heating scan are shown in this figure.

Table 3. Thermal Properties of Thiol–Ene Networks Derived from Phenolic Acids^a

phenolic acid	T _g (°C), as-prepared ^b	T_{g} (°C), after 7 days of room-temperature aging ^b	onset degradation temperature (°C) ^c
SA	3.1 ± 2.1	3.2 ± 2.4	341.9
4HBA	8.0 ± 1.2	8.2 ± 1.2	343.0

"Samples were prepared following the protocol in Table 1. ^bNine total measurements using DSC were obtained for each sample, from three distinct regions of three separate specimens. The results presented in this table were obtained from the first heating scan; the full data set is shown in Tables S4 and S5. ^cDetermined from TGA.

temperatures, around 342–343 °C, which is significantly higher than the chosen isothermal postcuring temperature of 150 °C. Therefore, it is expected that little sample degradation occurs during the curing process.

Dynamic Mechanical Analysis. Dynamic mechanical analysis (DMA) was used to explore the dynamic moduli of the thiol-ene networks. The storage (E') and loss (E'') moduli were probed as a function of strain (using frequency = 1 Hz) at selected temperatures (Figure S3). A strain in the linear viscoelastic region was chosen at each temperature and used to examine the frequency-dependence of E' and E'', as shown in Figure S4 at selected temperatures. Time-temperature superposition was applied to the frequency-dependent E' and E''.

Reduced moduli $(E'_r \text{ and } E''_r)$ were first obtained by multiplying each modulus by a vertical shift factor, b_T :^{33,34}

$$b_T = \frac{T_0}{T} \tag{1}$$

$$E'_{r} = b_{T}E' \tag{2}$$

$$E''_{r} = b_{T}E'' \tag{3}$$

where the reference temperature, T_0 , was taken to be 30 °C. The reduced moduli were then shifted horizontally by applying a horizontal shift factor, a_T , at each temperature

$$\omega_{\rm r} = a_{\rm T}\omega \tag{4}$$

where ω_r represents the reduced frequencies. At each temperature, a_T was identified as that required to produce a smooth and continuous master curve. The master curves containing the shifted data are shown in Figure 6.

The Williams–Landel–Ferry (WLF) equation is wellestablished for describing the temperature-dependence of a_T for polymers at temperatures above or in the vicinity of the T_g :³⁵

$$\log a_T = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)}$$
(5)

The WLF equation fit to the shift factor as a function of temperature is shown in Figure 7. In both networks, the data



Figure 7. Temperature-dependent shift factor, a_T , for thiol—ene networks derived from allylated SA (blue **D**) and allylated 4HBA (red O). Curves indicate the fit of the WLF equation to the data (for SA, solid blue curve, $C_1 = 9.64$ and $C_2 = 82.47$ K; for 4HBA, solid red curve, $C_1 = 5.85$ and $C_2 = 53.15$ K).



Figure 6. Master curves for the reduced (a) storage modulus (E'_r) and (b) loss modulus (E''_r) of thiol–ene networks derived from allylated SA (blue \blacksquare) and allylated 4HBA (red \bigcirc).

Table 4. Cross-Link Density and Homogeneity of Thiol-Ene Networks Derived from Allylated Phenolic Acids^a

cross-link density		width of glass transition (T_g)	
E' in rubbery plateau (MPa) ^b	$v_c ({\rm mol/cm^3})^c$	T_{g} width (°C) from DMA ^d	T_{g} width (°C) from DSC ^e
7.11	$(0.94 \pm 0.05) \times 10^{-3}$	9.6	5.8 ± 0.9
11.6	$(1.53 \pm 0.04) \times 10^{-3}$	10	6.3 ± 0.5
		cross-link density E' in rubbery plateau (MPa) ^b $v_c \ (mol/cm^3)^c$ 7.11 $(0.94 \pm 0.05) \times 10^{-3}$ 11.6 $(1.53 \pm 0.04) \times 10^{-3}$	$\begin{tabular}{ c c c c c c } \hline c cross-link density & width of glass the set of th$

"Samples were prepared following the protocol in Table 1. ^bMeasured at 30 °C, in the plateau region of Figure 6 (at $\omega = 1$ Hz). ^c v_c was calculated using eq 6. The sample-to-sample error of E' was estimated as the error measured for the Young's modulus through tensile testing (Table 5), through which multiple specimens were tested. Using this standard deviation, the standard deviation on the cross-link density was estimated to be 0.05 and 0.04 mol/cm³ for the SA and 4HBA networks, respectively. ^dFull width at half-maximum of peak observed in tan δ as a function of temperature (Figure S5) ^eDifference of the onset and endset temperatures (Figure S6)

are consistent with the WLF equation. C_1 is an empirical parameter; however, C_2 can be described as $C_2 = f_r / \alpha_{\hat{p}}$ where f_r is the fractional free volume of the material at the reference temperature and α_f is the coefficient of thermal expansion of the free volume ($\alpha_f \sim \alpha_1 - \alpha_g$ where α_1 and α_g are the coefficients of expansion of the liquid and glassy states, respectively). C_2 is significantly higher for the SA network as compared to the 4HBA network; this may imply differences in the values of f_r and α_f for these materials.

Network Structure and Homogeneity. Following the theory of rubber elasticity,³⁶ the cross-link density (v_c) of a network is calculated from E' in the rubbery plateau region of the plot of E' vs ω :

$$v_c = \frac{E'}{3RT} \tag{6}$$

where *R* is the gas constant. The cross-link densities calculated using the data in Figure 6 are summarized in Table 4. Allylated SA, which contains neighboring allyl groups, produces a network structure with bulky aromatic groups intruded into network, thus reducing the cross-link density compared to that produced from allylated 4HBA. The higher modulus (Table 4) and T_g (Table 3) of the 4HBA network are attributed to its higher cross-link density.^{37,38}

Previous studies on thiol—ene networks have indicated the presence of highly homogeneous networks, as evidenced by the sharpness of the glass transition.^{1,2,4,5} In our study, a similarly sharp transition is observed in the DSC and DMA data, shown in Figures S5 and S6. This is in contrast with the behavior observed in free radical and sulfur cross-linked networks with greater levels of inhomogeneity.^{39–43} The SA and 4HBA networks exhibit glass transitions with similar widths (Table 4), indicating a comparable degree of homogeneity in the two networks.

Tensile Behavior and the Ideal Elastomer Model. The mechanical properties of the networks were probed with tensile testing. Tensile experiments were conducted on multiple specimens for each network type (reported in Figure 9a and Figures S7 and S8); the average values of relevant parameters are shown in Table 5. The 4HBA network exhibits a higher tensile modulus, tensile strength, and elongation at break as compared to the SA network. We will discuss the physical basis for this behavior with respect to two phenomena: (1) the effect

Table 5. Tensile Properties of Thiol–Ene Networks Derived from Allylated Phenolic Acids

phenolic acid	tensile strength (MPa)	elongation at break (%)	modulus (MPa)	toughness (MPa)
SA	2.7 ± 0.3	25.0 ± 2.2	10.8 ± 0.4	0.36 ± 0.06
4HBA	3.7 ± 0.3	29.6 ± 2.4	12.4 ± 0.3	0.57 ± 0.09

of cross-link density of the network and (2) the effect of the molecular structure of the phenolic acid.

As the higher plateau modulus of the 4HBA network implies a greater cross-link density, the effect of cross-link density on the tensile parameters must first be considered. References 44 and 45 summarize the expected behavior of an elastomer as the cross-link density is increased: the tensile modulus increases with increasing cross-link density whereas both the tensile strength and toughness exhibit maximum values at intermediate cross-link densities. Therefore, the increase in the modulus, tensile strength and toughness of the 4HBA network, as compared to the SA network (Table 5), may simply be explained by differences in cross-link density (where the 4HBA network has the higher cross-link density); however, in traditional rubber materials these trends are observed in the regime of relatively low cross-link densities. In the regime of high cross-link densities, it is expected that as the cross-link density increases, the modulus would still increase, but the tensile strength and toughness would decrease.

We also consider the effect of the molecular structure of the phenolic acid on the tensile properties of the networks. When the material is macroscopically deformed, the strands within the network undergo microscopic changes which include alignment, rotation, displacement, bond rotation, and bond stretching, and the stress may become localized, particularly in the presence of a heterogeneous network.⁴⁶ The ultimate macroscopic rupture of the material at high elongations originates with the breaking of individual bonds.^{47,48} A microscopic view of the two phenolic acid—based networks shows important distinctions between them (Figure 8). In the



Figure 8. Diagram of expected forces exerted on an individual phenolic ring in a strand within the network that is aligned with the direction of applied force.

4HBA network, phenolic rings are aligned directly within the strand. In contrast, in the SA network, the placement of the phenolic network is offset from the strand. We hypothesize that the relative placement of the bonds along the phenolic ring (i.e., *ortho* vs *para* position) may lead to differences observed in the mechanical behavior of the networks, such as the higher modulus and elongation at break observed in the 4HBA network.

We now examine the stress-strain behavior of these networks with respect to the ideal elastomer model, described by 36



Figure 9. (a) Representative data showing tensile stress (σ) as a function of strain (ε); (b) tensile data plotted to highlight consistency with the ideal elastomer model eq 7), where λ is the stretch ratio; and (c) tensile data plotted in the Mooney–Rivlin format (following eq 8). In all figures, the solid blue and solid red curves indicate data obtained from of thiol–ene networks derived from allylated SA and allylated 4HBA, respectively. The dashed black curves indicate the fit of the ideal elastomer model eq 7 to the data. Data were obtained on multiple independent specimens of each sample type, and all results are shown in Figures S7 and S8. Data obtained at $1/\lambda > 0.95$ were not included in plot c, based on uncertainties in the tensile testing measurements at these strain values ($\varepsilon < 0.05$).⁴⁹

$$\sigma = \frac{E}{3} \left(\lambda - \frac{1}{\lambda^2} \right) \tag{7}$$

where λ is the stretch ratio ($\lambda = 1 + \varepsilon$, where ε is the strain) and E is the tensile modulus (Young's modulus). Figure 9b shows a plot of the tensile data, formatted to highlight consistency with the ideal elastomer model. The tensile behavior of the SA network was consistent with the ideal elastomer model for the entire range of strains that were examined; the sample fractured at a strain of 0.250 \pm 0.022. The 4HBA network exhibited ideal behavior up to a strain of 0.202 \pm 0.008, and became nonideal at higher strain values.

The ideal elastomer model makes the following assumptions regarding the structure of the network: $^{36,50}(1)$ all elastic chains in the network have the same length, (2) all cross-link junctions have the same functionality, (3) the network is homogeneous, and (4) each effective elastic chain obeys Gaussian statistics. Network imperfections such as dangling ends, loops, trapped entanglements, and other inhomogeneities are not accounted for in the ideal network model.^{41,49} In step-growth reactions such as in the formation of thiol-ene networks, the first two assumptions are likely valid, as the network is produced through the reaction of two complementary types of multifunctional molecules (where the functionality of each type of molecule is held constant). As discussed previously, the narrowness of the glass transition implies the networks are relatively homogeneous (i.e., Table 4). We will now evaluate the network for the presence of defects and non-Gaussian strand conformations, which would lead to nonideal behavior.

A Mooney-Rivlin plot is a convenient method of identifying nonideal behavior in networks. The Mooney-Rivlin model is defined as 51,52

$$\frac{\sigma}{(\lambda - \lambda^{-2})} = 2C_1 + \frac{2C_2}{\lambda} \tag{8}$$

where C_1 and C_2 are empirical constants. In the case of an ideal network, C_2 is equal to 0. The tensile data can be replotted in the Mooney-Rivlin format, as shown in Figure 9c. Over the full range of strain values examined, the SA network behavior was consistent with the ideal network model, in which $C_2 = 0$ (for the SA network, $C_2 = -0.07 \pm 0.32$), indicating the absence of network defects and applicability of Gaussian statistics to describe the chain conformations.^{53,54} At low to moderate strain values ($\varepsilon < 0.202 \pm 0.008$, which corresponds to $1/\lambda >$ 0.832), the behavior of the 4HBA network was also consistent with the ideal network model ($C_2 = -0.35 \pm 0.34$), and at high strain values ($\varepsilon > 0.202$ and $1/\lambda < 0.832$), the 4HBA network became non-Gaussian and deviated from the ideal network model (C_2 = 5.05 ± 0.13).^{49,55} Agreement with the ideal network model (and resulting observation of $C_2 = 0$ in the Mooney-Rivlin format) is typically only observed for traditional networks in their highly swollen states;⁵⁶ such behavior in the nonswollen state is further evidence of the high degree of homogeneity and lack of defects in these thiol-ene systems.

CONCLUSIONS

Biorenewable thiol—ene networks were synthesized through the photoinitiated reaction between allylated plant-based phenolic acids (salicylic acid, SA, and 4-hydroxybenzoic acid, 4HBA) and a multifunctional thiol (PETMP). Allylation of the phenolic acids proceeded to high conversion and yield for both SA and 4HBA. The thiol—ene reaction was monitored through the use of FTIR, which showed high conversion of both thiol and allyl functional groups. A two-step curing procedure for the

networks was developed which involved UV curing followed by isothermal annealing. The thermal and mechanical properties of the resulting thiol-ene networks were evaluated. Both networks exhibited high thermal degradation temperatures. The glass transition temperature, plateau modulus, and corresponding cross-link density of the 4HBA network were greater than that of the SA network. The width of the glass transition temperatures of the SA and 4HBA networks were found to be consistent with one another and quite narrow. The narrow width of the transition indicates a high degree of homogeneity of these networks, consistent with prior studies on thiol-ene networks. The tensile behavior of both networks were well-described by the ideal elastomer model at low and moderate strains. At higher strains, the behavior of the SA network could not be examined (as fracture occurred at strain = 0.250), while the 4HBA network exhibited deviations from the ideal network model (at strains greater than 0.202), likely due to the presence of non-Gaussian chain conformations. A Mooney-Rivlin plot revealed a slope of 0 over a wide range of strains for both networks, indicating lack of network defects and chain entanglements. In the case of the 4HBA network, the Mooney-Rivlin plot showed a deviation in the positive direction when the strain was greater than 0.202. The 4HBA network exhibited a higher tensile modulus, tensile strength, and elongation at break as compared to the SA network. The mechanical property differences between the networks are hypothesized to originate from the differing cross-link densities of the two networks as well as the impact of the molecular structure of the phenolic acids on the macroscopic deformation behavior in these materials.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.5b01796.

NMR spectra obtained on the allylated phenolic acids, including ¹H NMR, ¹³C NMR, DEPT 135, COSY, HSQC, and HMBC (Figures S1 and S2), assignment of FTIR vibrational modes (Table S1), thiol-ene reaction conversion quantified through FTIR (Tables S2 and S3), glass transition temperatures determined through DSC using repeat measurements on various specimens (Tables S4 and S5), storage and loss moduli as a function of strain (Figure S3) and frequency (Figure S4) determined through DMA, tan δ as a function of temperature determined through DMA (Figure S5), raw DSC data (Figure S6), stress-strain curves for each specimen measured and included in the average values of the tensile parameters reported (Figures S7 and S8), and general reaction scheme for the photoinitiated thiol-ene polymerization (Scheme S1) (PDF)

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Notes

The authors declare no competing financial interest.

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