

Supporting Information

Ambient Temperature Cross-Linking of a Sustainable, Cardanol-Based Cyanate Ester Via Synergistic Thiol-ene Copolymerization

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Characterization of Networks

Differential Scanning Calorimetry (DSC). All DSC studies were performed on a TA Instruments Q200 differential scanning calorimeter in hermetically sealed, aluminum pans under an N₂ atmosphere. High purity indium was used to calibrate the calorimeter. The cure chemistry of the reaction solutions was analyzed by heating 5 – 10 mg of the reaction mixture from -80 °C to 200 °C at 10 °C/min. Two heating cycles were performed on each sample to determine if curing was complete. DSC scans were also performed on the networks after curing using the specified curing protocols to determine network T_g and the degree of cure.

Thermogravimetric Analysis (TGA). All TGA studies were performed on a TA Instruments Q5000 thermogravimetric analyzer in standard, aluminum pans under a nitrogen or air atmosphere. Samples weighed between 5 – 10 mg and were heated from 25 °C to 600 °C at 10 °C/min. The TGA studies were used to determine the decomposition temperature (T_d), which was defined as the temperature at which 5% mass loss was observed, and the char yield of the networks (mass remaining at 600 °C).

Dynamic-Mode Thermomechanical Analysis (TMA). Dynamic-mode TMA was performed using a TA Instruments Q400-0537 analyzer under 100 mL/min N₂. The bars were cooled to -80 °C, and then the flexural probe was lowered to put a force of 0.10 N on the samples in a three-point bending mode. Samples were then heated at 5 °C/min to 100 °C. The force was modulated ± 0.04 N at a frequency of 0.05 Hz during the cycle. The TMA studies were used to determine the T_{gs} of the thiol-ene polycyanurate networks.

Fourier Transform Infrared (FTIR) Spectroscopy. FTIR studies were performed on a Nicolet 6700 FTIR spectrometer equipped with a liquid nitrogen cooled MCT-A detector. The samples were analyzed using attenuated total reflectance (ATR) with a germanium, single reflection crystal. The FTIR spectra represent an average of 32 scans and have a 4 cm⁻¹ resolution. The monomers, uncured solutions, and cured networks were analyzed to verify full conversion of the cyanate ester peaks.

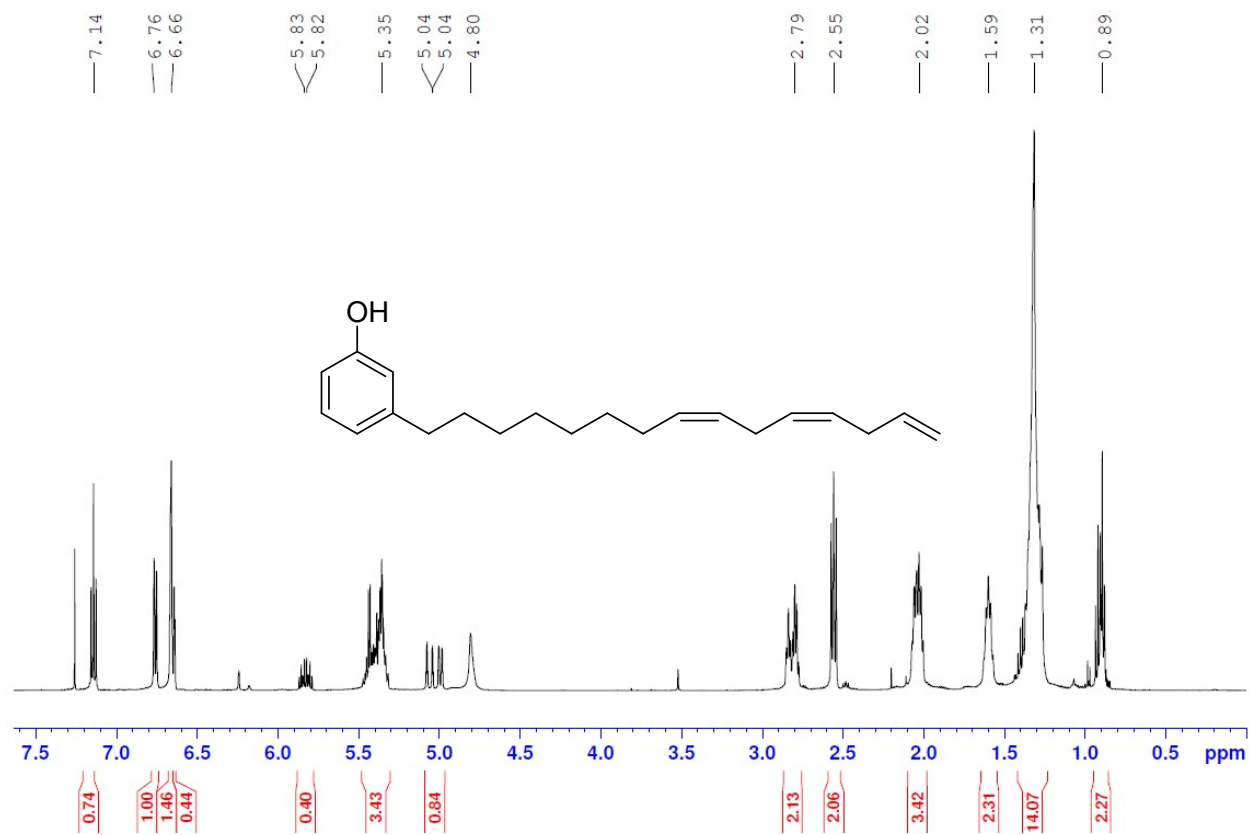


Figure S1. ¹H NMR (CDCl₃) of purified cardanol

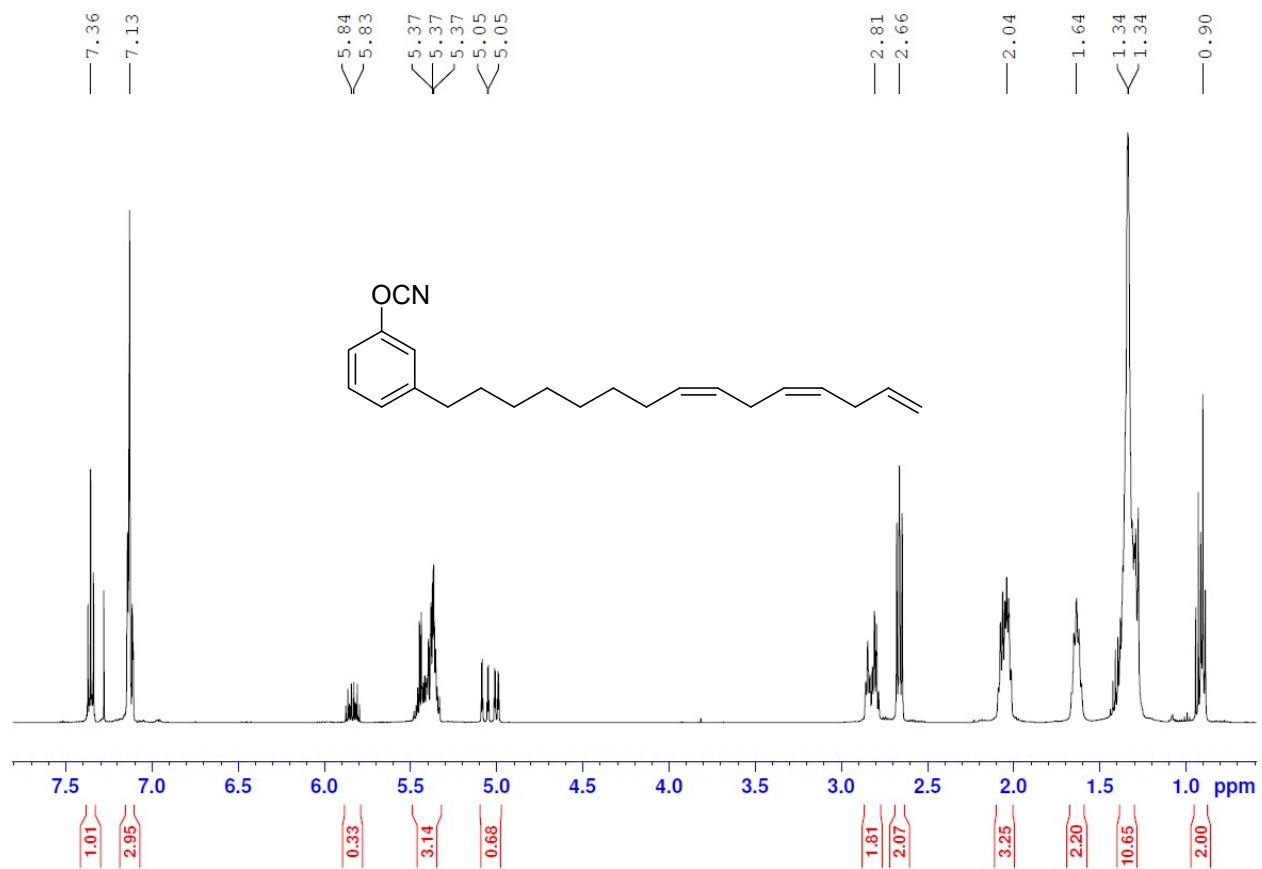


Figure S2. ¹H NMR (CDCl₃) of cyanated cardanol (**1**)

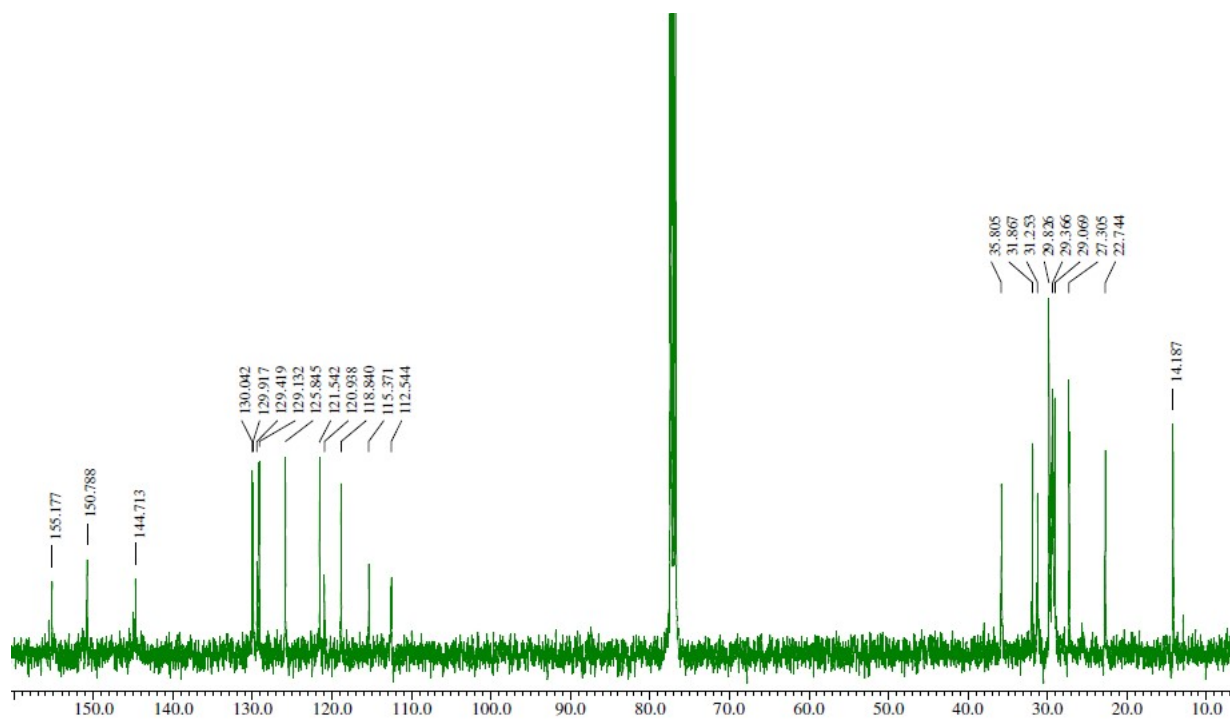


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) of cyanated cardanol (**1**):

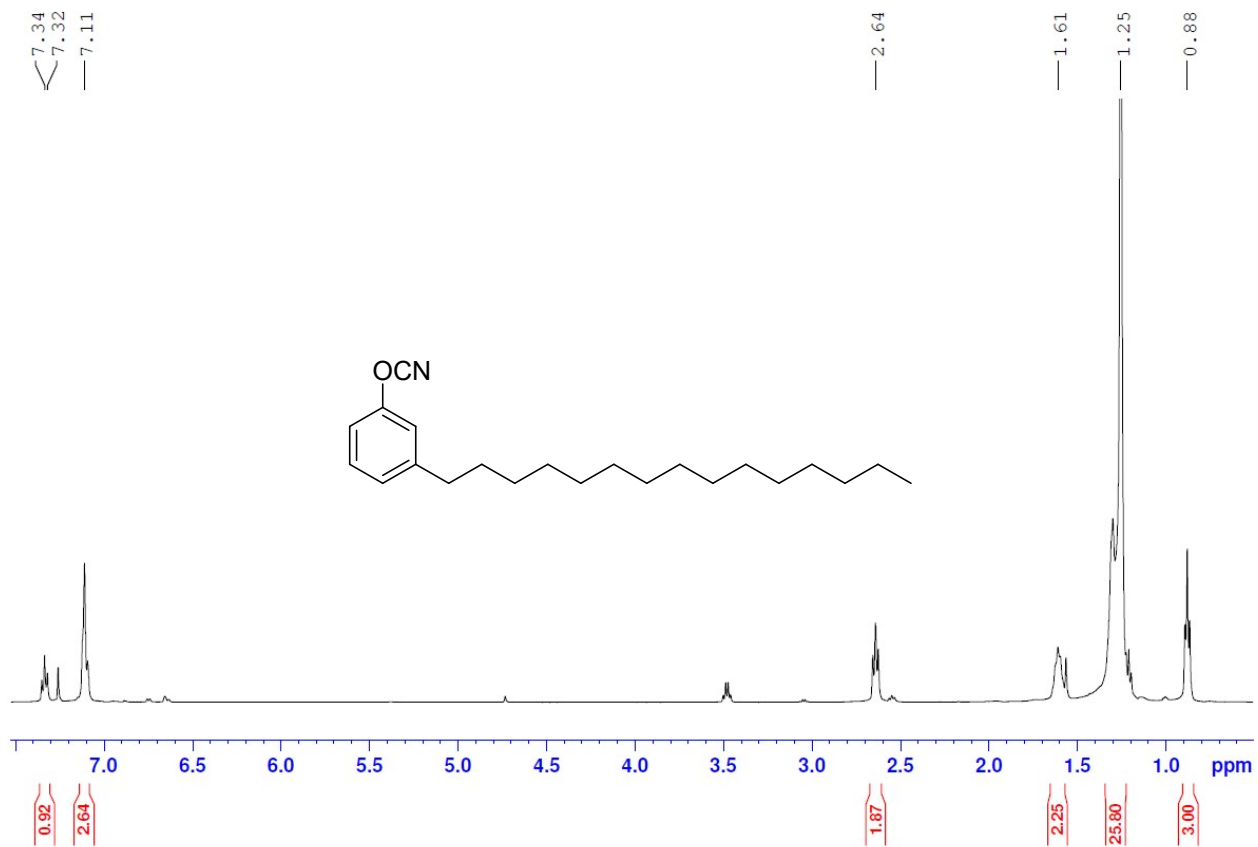


Figure S4. ^1H NMR (CDCl_3) of 1-cyano-3-pentadecylbenzene (**2**):

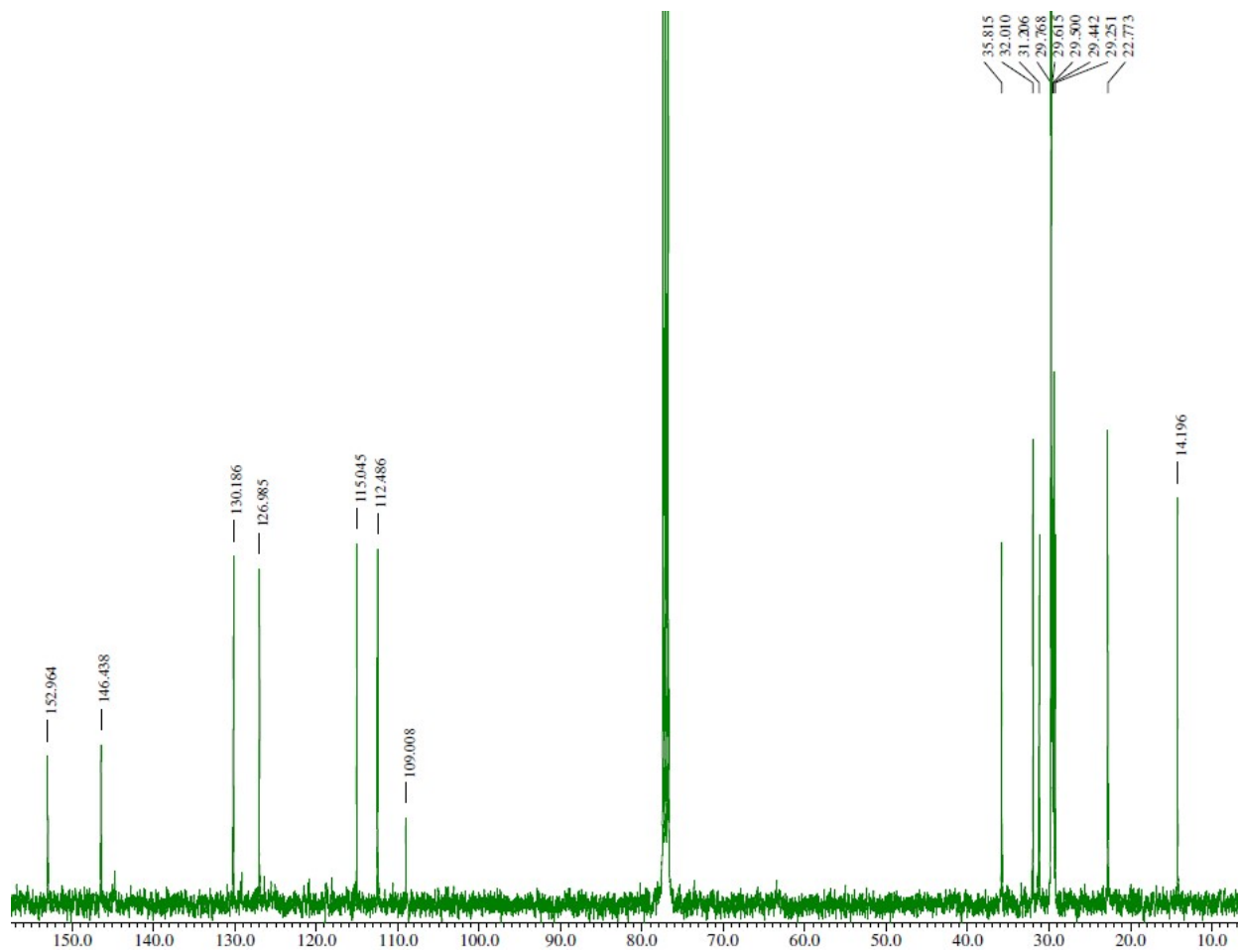


Figure S5. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) of 1-cyanato-3-pentadecylbenzene (2)

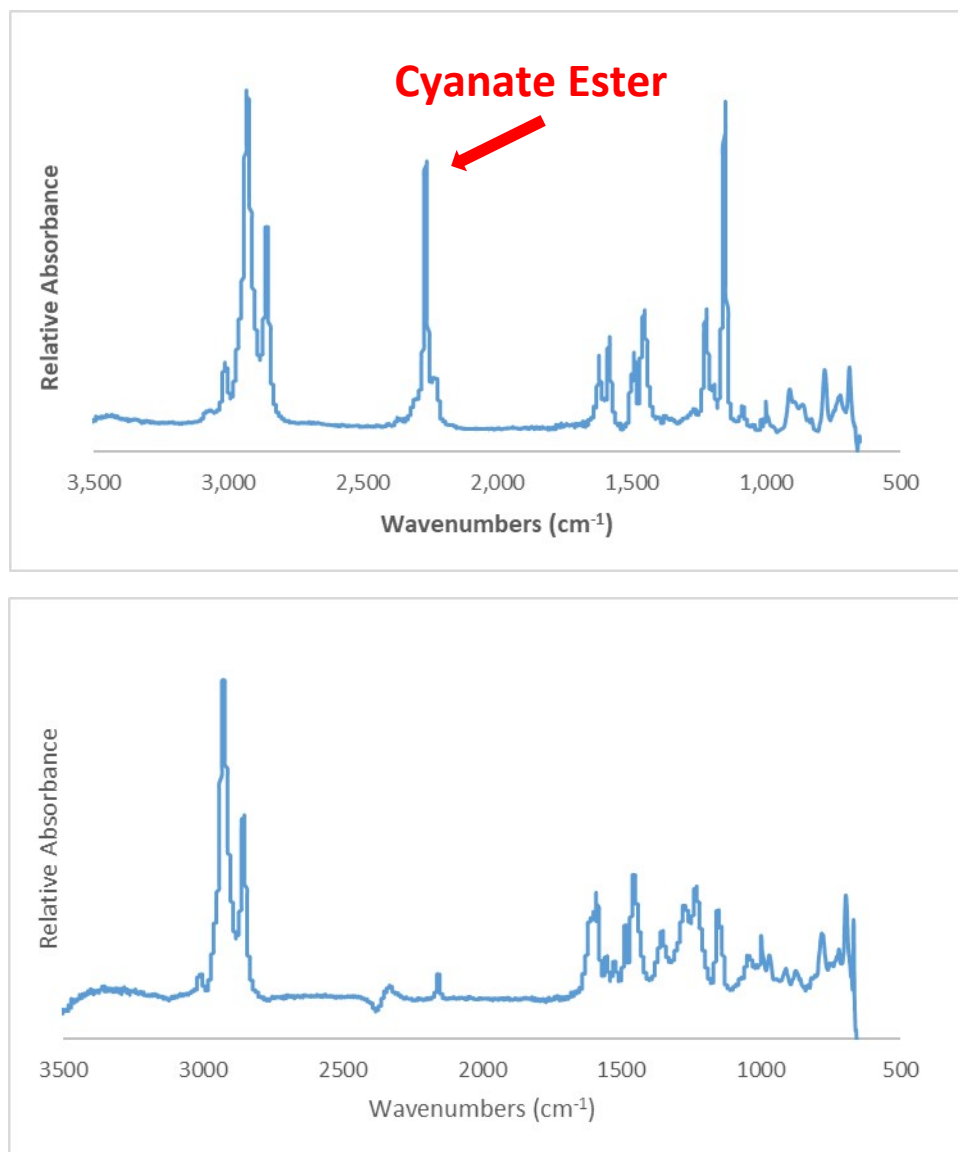


Figure S6. Cardanol cyanate ester and trithiol before UV irradiation (top) and after UV irradiation (bottom)

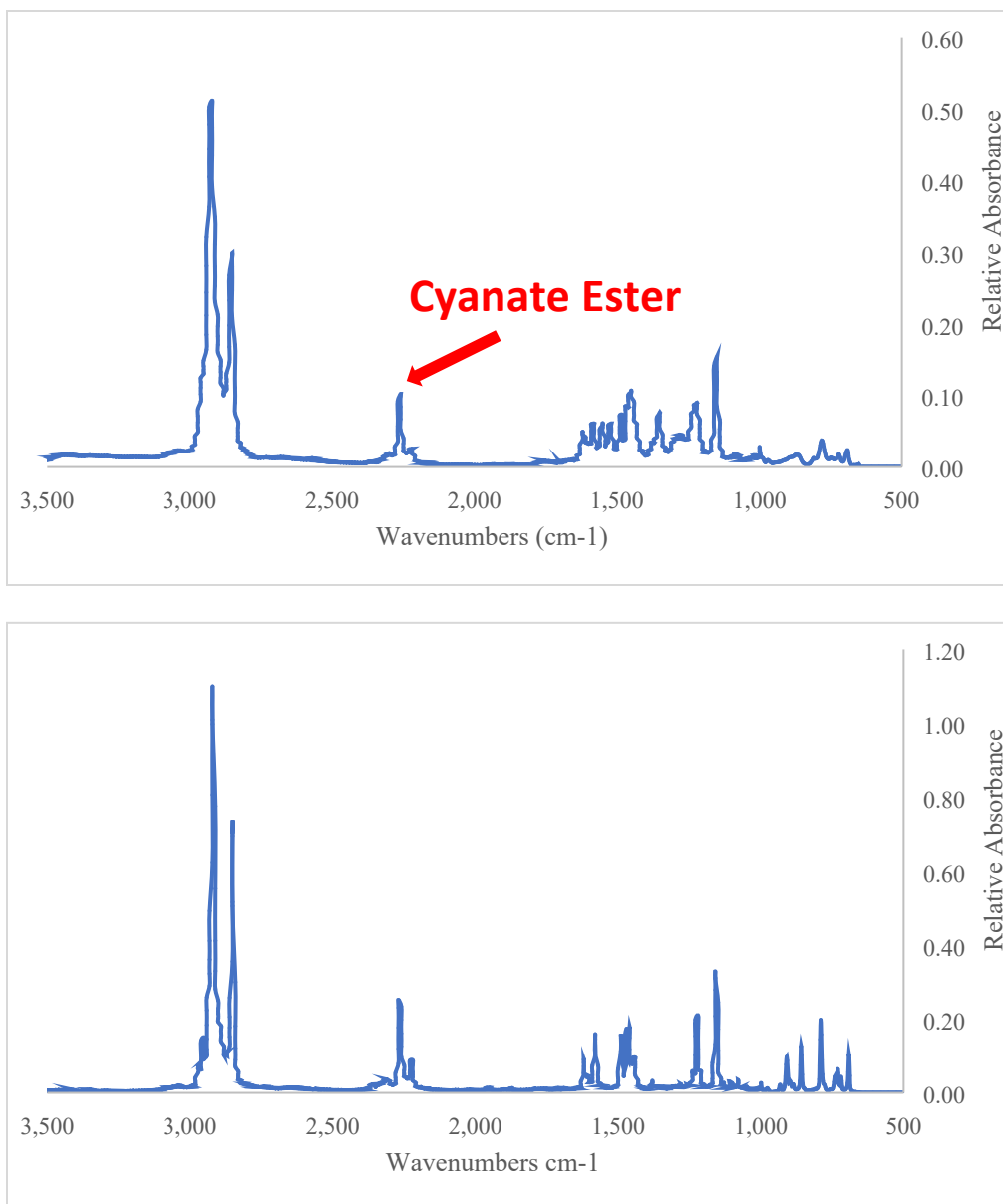


Figure S7. Pentadecyl cyanate ester and trithiol before UV irradiation (top), and after UV irradiation (bottom)

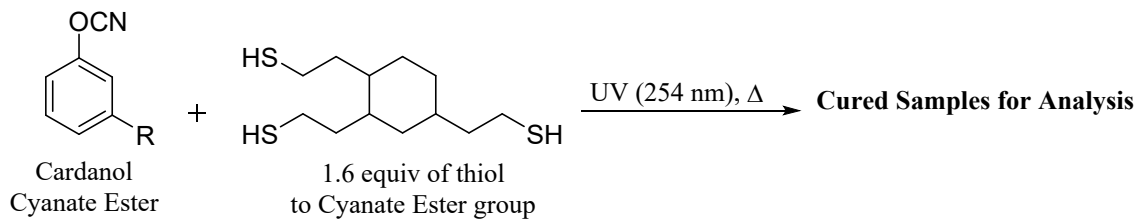


Figure S8. UV irradiation with 1.6 equiv of trithiol, followed by thermal curing of the cardanol cyanate ester resin

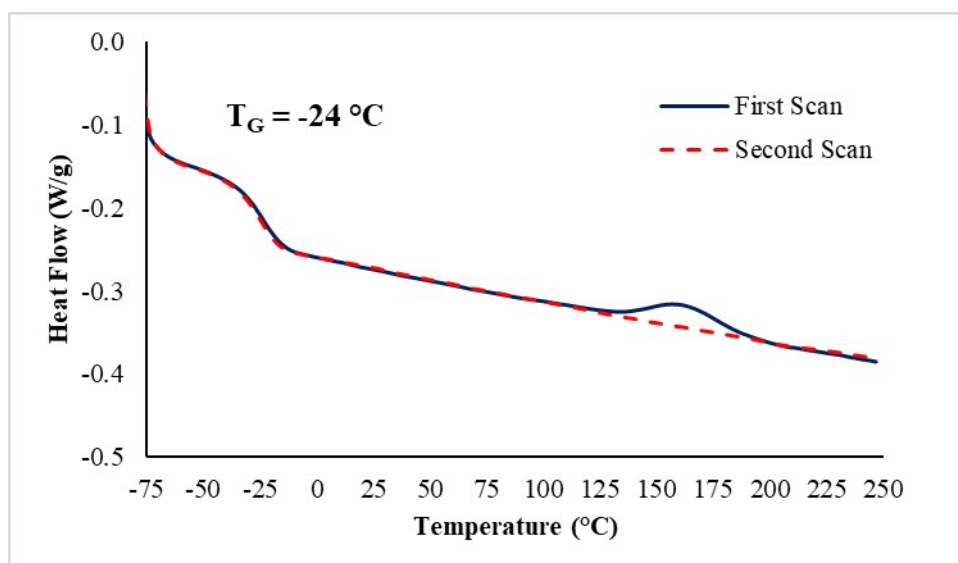


Figure S9. DSC of cured cardanol cyanate ester with 1.6 equiv. of thiol

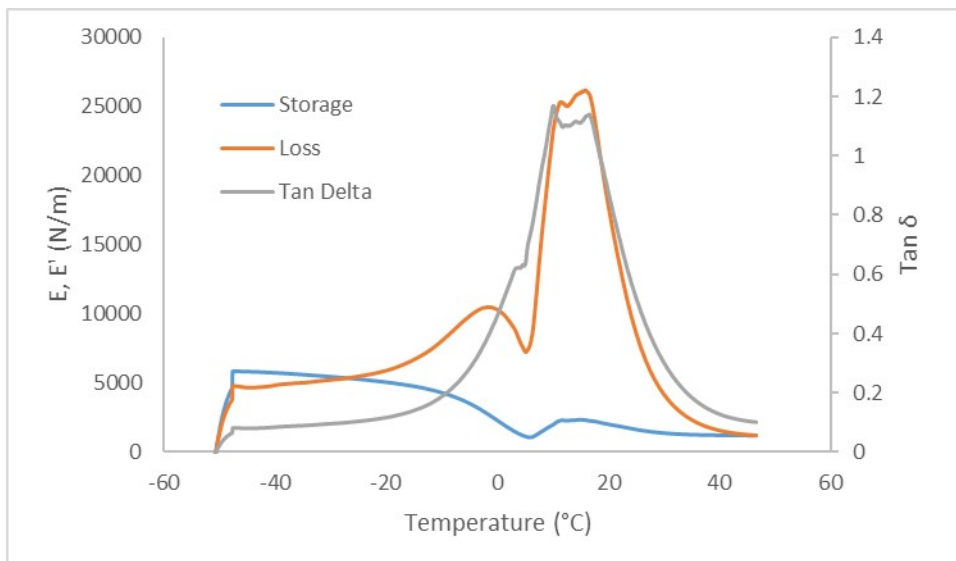


Figure S10. TMA of cured cardanol cyanate ester with 1.6 equiv. of thiol

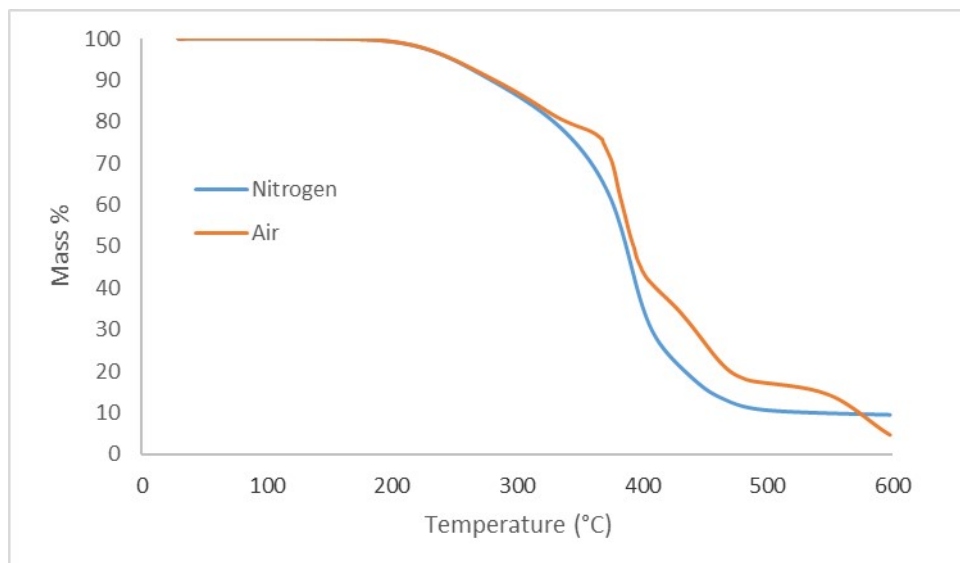


Figure S11. TGA of cured cardanol cyanate ester with 1.6 equiv. of thiol

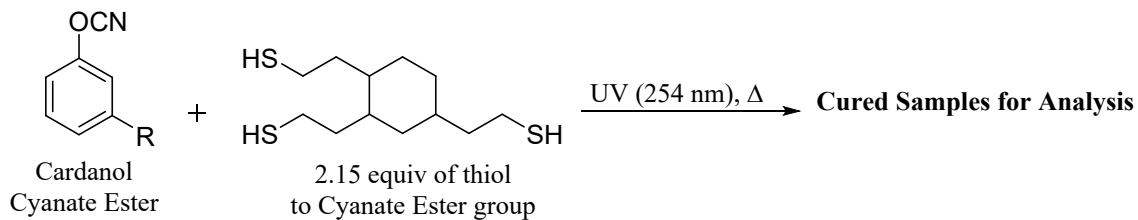


Figure S12. UV irradiation with 2.15 equiv of trithiol, followed by thermal curing of the cardanol cyanate ester resin

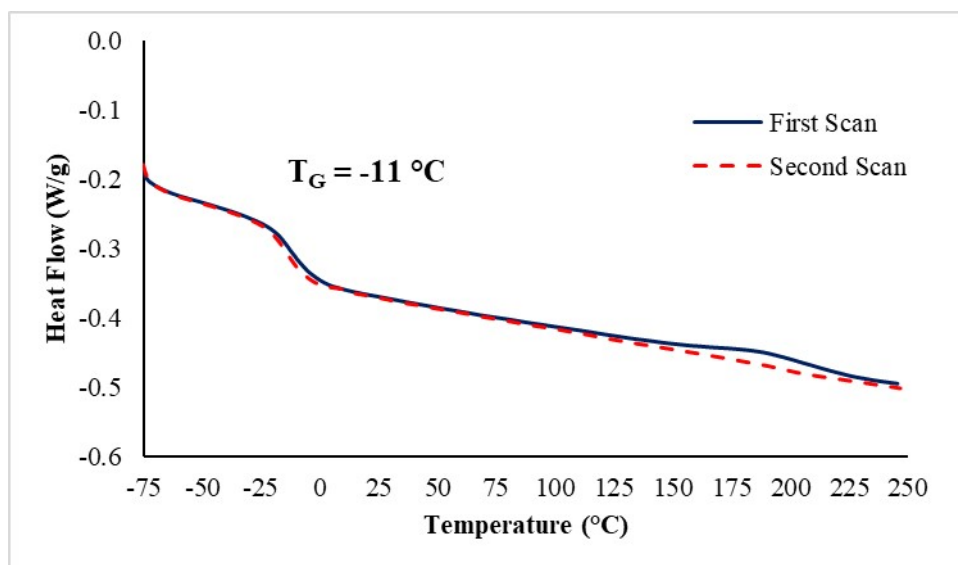


Figure S13. DSC of cured cardanol cyanate ester with 2.15 equiv. of thiol

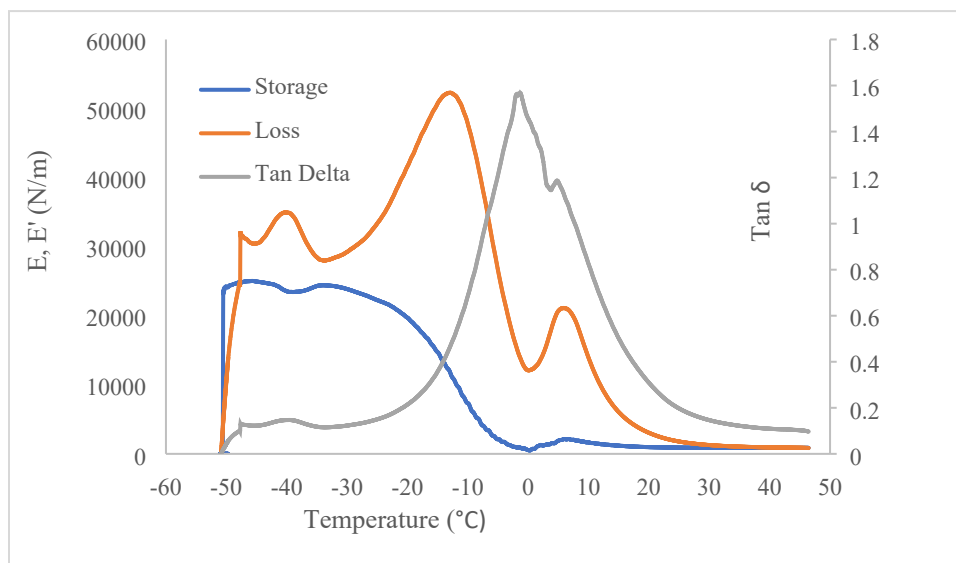


Figure S14. TMA of cured cardanol cyanate ester with 2.15 equiv. of thiol

Table S1. DSC results for cured samples of cardanol cyanate ester with thiol

Thiol Equiv. to Cyanate Ester	T _g (°C)
1.0	-13.0
1.6	-24.0
2.15	-10.7

Table S2. TMA results for cured samples of cardanol cyanate ester with thiol

Thiol Equiv. to Cyanate Ester	T _g , Storage (°C)	T _g , Loss (°C)	T _g , tan δ (°C)
1.0	-9.9	-2.4	9.4
1.6	-15.3	-6.4	4.6
2.15	-23.1	-13.0	-1.3

Table S3. TGA results for cured samples of cardanol cyanate ester with thiol

Equiv. of Thiol to Cyanate Ester	5% Mass Loss Nitrogen (°C)	Char Yield Nitrogen (%)	5% Mass Loss Air (%)	Char Yield Air (%)
1.0 equiv.	256	9.12	268	3.26
1.6 equiv.	248	9.50	249	4.68
2.15 equiv.	260	1.86	259	0.65

Table S4. Summary of the cure reactions of **1** and trithiol, under UV irradiation at 50 °C.

Equiv. of Thiol to Cyanate Ester	Result
1.20	Complete Cure
2.00	Complete Cure
3.00	Complete Cure

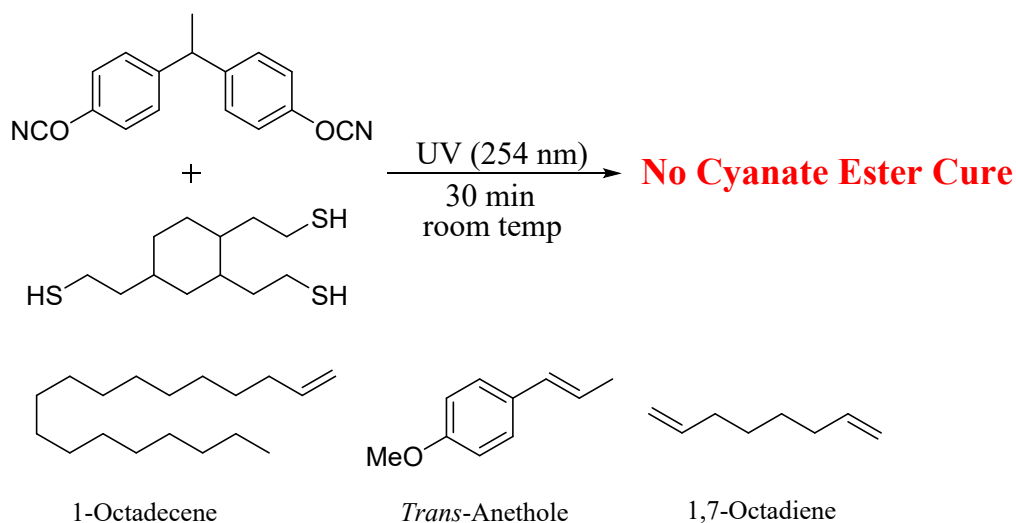


Figure S15. Attempted cross-linking reaction of commercial LeCy with Thiol, UV, and various alkenes

Experimental procedure for initiating LeCy cross-linking with 1-octadecene. LeCy (300 mg, 1.14 mmol, 1.0 equiv), trithiol (200 mg, 0.76 mmol, 1.0 equiv of thiol to cyanate ester group), and 1-octadecene (576 mg, 2.28 mmol, 1.0 equiv of alkene to cyanate ester group) were mixed together. The mixture was dispensed as a drop onto a microscope slide and irradiated with UV (254 nm) for 30 minutes. FTIR showed mostly alkene and drowned out seeing the cyanate.

Experimental procedure for initiating LeCy cross-linking with *trans*-anethole. LeCy (300 mg, 1.14 mmol, 1.0 equiv), trithiol (200 mg, 0.76 mmol, 1.0 equiv of thiol to cyanate ester group), and

trans-anethole (338 mg, 2.28 mmol, 1.0 equiv of alkene to cyanate ester group) were mixed together. The mixture was dispensed as a drop onto a microscope slide and irradiated with UV (254 nm) for 30 minutes. No cure of the cyanate ester was observed by FTIR.

LeCy (300 mg, 1.14 mmol, 1.0 equiv), trithiol (200 mg, 0.76 mmol, 1.0 equiv of thiol to cyanate ester group), and *trans*-anethole (1.0 g, 6.84 mmol, 3.0 equiv of alkene to cyanate ester group) were mixed together. The mixture was dispensed as a drop onto a microscope slide and irradiated with UV (254 nm) for 30 minutes. No cure of the cyanate ester was observed by FTIR.

Experimental procedure for initiating LeCy cross-linking with 1,7-octadiene. LeCy (300 mg, 1.14 mmol, 1.0 equiv), trithiol (200 mg, 0.76 mmol, 1.0 equiv of thiol to cyanate ester group), and 1,7-octadiene (126 mg, 1.14 mmol, 1.0 equiv of alkene to cyanate ester group) were mixed together. The mixture was dispensed as a drop onto a microscope slide and irradiated with UV (254 nm) for 30 minutes. No cure of the cyanate ester was observed by FTIR.