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

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Abstract

Cardanol, a low-cost component of cashew nut shell oil, is a phenolic compound with a 15-carbon unsaturated chain in the position meta to the hydroxyl group. This biorenewable substrate was converted to a cyanate ester resin and blended with a trifunctional thiol at different ratios. Irradiation of the blend with UV light (254 nm) facilitated thiol-ene reactions with concomitant cyclotrimerization of the cyanate ester group without additional heating. This novel synergistic approach allowed for cyanate ester cure under ambient conditions, while enhancing the degree of cross-linking. Through this approach, an elastomeric cross-linked network with a T_g of -2.4 °C was prepared. This material may have potential applications as a toughener for rigid cyanate esters or self-healing materials that can take advantage of the reversible nature of thiol-ene chemistry.

Introduction

The majority of commercial plastics are derived from crude oil, with polymers accounting for approximately 7% of total petroleum use. [1, 2] Clearly, the use of "old carbon" on this scale is unsustainable and requires new approaches to the development of thermoplastic and thermoset materials that can be derived from renewable substrates. [3, 4, 5] Extensive research on sustainable feedstocks that can supplement and eventually replace petroleum has led to many breakthroughs, such as high-performance fuels and materials from biomass sources.[6, 7, 8, 9, 10, 11, 12, 13, 14] Although the transition to bio-based feedstocks will require a paradigm shift in the chemical industry, it will also enable the development of novel materials. The petrochemical industry is focused on a relatively small number of molecules whereas nature produces molecules with a wide diversity of structural characteristics.[15, 16, 17] Leveraging this diversity will provide opportunities to explore unique structural motifs that can impact material properties in unexpected ways.[18, 19, 20, 21, 22, 23, 24, 25, 26, 27]

Phenols are important building blocks for the generation of thermosetting resins and thermoplastics. For example, the hydroxyl groups can be readily transformed into multifunctional cyanate esters, glycidyl ethers, and vinyl esters.[28] Cardanol, the main component obtained from distillation of cashew nut shell liquid (CNSL), is a substituted phenol containing four different molecules with C_{15} hydrocarbon chains in the *meta* position. It is produced globally (Brazil, India, Kenya, China) at ~450,000 metric tons annually, with uses as a building block for novolac resins, surfactants, liquid crystals, and polyurethanes. [28, 29, 30] A small amount of the saturated molecule is present, along with molecules in which the chains have double bonds at the 8, and/or 11, and/or 14-positions (**Figure 1**).[31, 32, 33] Glycidyl ether epoxy resins synthesized from cardanol and bisphenols from cardanol, have several advantages compared to conventional epoxies, exhibiting improved toughness, without the need to utilize an expensive/toxic hardener. [34, 35, 36, 37] Due to the flexible side chains, epoxy cardanol prepolymers were shown to be in a rubbery state at room temperature and could be cured via thermal polymerization.[38] Esterification of cardanol-based epoxidized novolac resins with methacrylic acid has also been shown to generate vinyl ester resins with thermal stability between 260–285 °C.[39, 40, 41] Polybenzoxazine resins synthesized from cardanol exhibited improved toughness attributed to plasticization by the long alkyl chain.[42] These studies demonstrate that cardanol is a versatile substrate that should be exploited for the synthesis of unique cyanate ester networks.

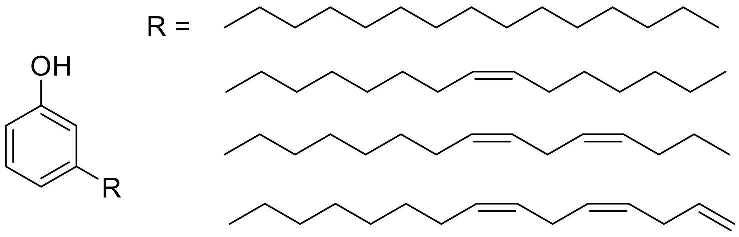


Figure 1. Structure of cardanol.

Cyanate ester resins are used for the fabrication of composite materials with applications in radomes, circuit boards, and satellites due to their low dielectric constants, easy processability, and high thermal stability.[43, 44, 45] Cyanate esters undergo a thermally induced and thermodynamically favored cyclotrimerization to form 1,3,5-substituted triazine rings (**Figure 2**).[46, 47, 48] Therefore, a molecule containing two or more cyanate ester groups can be thermally polymerized, or cross-linked to form a polycyanurate network with glass transition temperatures (T_g) typically between 200 and 300 ºC.[49, 50, 51] The high T_gs, good processability, and low water uptakes afforded by these resins make them useful in a wide variety of demanding environments.[51, 52] A diverse array of cyanate ester resins have been prepared from sustainable phenols. In general, the bio-based resins exhibited thermal and water uptake properties that were either similar or better compared to petroleum-based monomers.[53, 54, 55, 56, 57] The benefits of using a bio-based monomer in place of a conventional monomer are partially negated by the use of relatively toxic methods for the synthesis of thermosetting resins. For example, cyanate esters are typically prepared from phenols through reactions with either cyanogen bromide or chloride in the presence of base. Thus, in parallel with efforts to develop new sustainable materials, greener methods of cyanate ester synthesis are of significant interest.

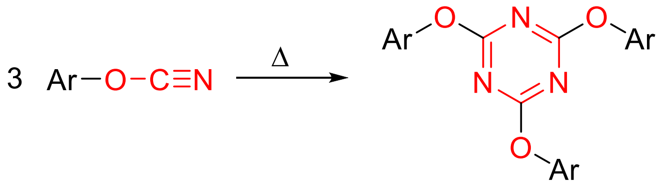


Figure 2. Cyanate ester cyclotrimerization

The uncatalyzed cyclotrimerization of cyanate ester resins generally occurs around 160-250 °C with peak exotherms around 250-350 °C.[46] Added/residual phenols or acidic conditions, catalyze the reaction, allowing for cross-linking at much lower temperatures (~120 °C).[58, 59, 60, 61] Metals can also catalyze the cure of cyanate esters to generate networks with acceptable T_gs (~250 °C). The best conditions for maximizing T_g are obtained when the concentration of the catalyst is below 100 ppm. [62]

The dual functionality of cardanol allows for the synthesis of a resin with both a cyanate ester group and an unsaturated chain in the meta position. This type of monomer can cross-link through both the cyanate ester and alkene groups. There are several approaches through which the alkene functionality can react to form cross-links. For example, the alkenes can be oligomerized at temperatures above 200 °C via thermally induced radical reactions, which can be accelerated by cationic, anionic, and oxidizing agents[63] to primarily form dimers.[64] Another approach to cross-linking alkenes is through thiol-ene chemistry with a polythiol.[65] Depending on the structure of the alkene, polythiol, and cross-link density, either low or high T_g polythiolene networks can result.[66, 67, 68, 69] The combination of thiol-ene chemistry and cyanate ester cyclotrimerization has the potential to form unique networks exhibiting a combination of flexible and rigid components.

To investigate a dual-cure mechanism leveraging both cyanate ester cyclotrimerization and thiol-ene chemistry for network formation, we studied the synthesis of a novel cardanol-based cyanate ester resin and subsequent cross-linking cure with a trifunctional thiol containing a cyclohexane core. Through this approach we were able to leverage the exothermic thiol-ene reaction to initiate cyclotrimerization of the cyanate ester groups at ambient temperatures.

Experimental

General. The starting materials were obtained from Sigma Aldrich, TCI, and Oakwood Chemicals and used as received. Primaset LeCy was obtained from Lonza. NMR spectra were collected with a JEOL 300 MHz or Bruker Avance II 500 MHz NMR spectrometer. ^1H and ^{13}C NMR chemical shifts are reported versus the deuterated solvent peak [chloroform-d_6: δ 7.27 (^1H), 77.37 (^{13}C)]. UV irradiation was conducted with a VWR UV-AC Dual Hand Lamp (Dual 254/365 nm UV), 115 V, 0.16 A. Cardanol (~90% pure, mixture of four components) was obtained from Cardolite as a brown viscous liquid. Cardanol was purified as previously described. [70] Briefly, cardanol (100g) was diluted in MeOH (350 mL) and ammonium hydroxide (190 mL, 25%). The mixture was stirred vigorously for 15 min and was then extracted with hexanes (4x200 mL). The organic extracts were washed with 5% HCl (100 mL) and water (100 mL). The organic layer was then stirred with activated charcoal (10 g) for 10 min before being filtered through Celite. The filtrate was dried over $MgSO_4$ and the hexanes removed under reduced pressure to yield cardanol as a red liquid. The ^1H NMR spectrum (**Figure S1**) showed a mixture of isomers with different degrees of unsaturation in the alkyl chain and was consistent with literature results.[70] On average, 2.15 alkenes were present per molecule.

Synthesis of cardanol cyanate ester (1). Cardanol (2.0 g, 6.7 mmol, 1.0 equiv) and cyanogen bromide (0.85 g, 8.05 mmol, 1.2 equiv) were dissolved in 20 mL of diethyl ether. The mixture was cooled to -60 °C, and triethylamine (0.97 mL, 7.05 mmol, 1.05 equiv) diluted in 1 mL of diethyl ether was added dropwise to the solution. The reaction was stirred for 1 h while warming to 0 °C, which resulted in a cloudy beige mixture. The mixture was filtered and the solvent removed under reduced pressure. The red residue was dissolved in diethyl ether (10 mL) and washed with water (3 x 10 mL). The collected organic layer was dried with $MgSO_4$, filtered, and the solvent removed under reduced pressure to yield 1.73 g (80 %) of a red oil. Filtration through a short silica plug with dichloromethane as eluent yielded 1.63 g (74 %) of **1** as a light amber oil. ^1H NMR ($CDCl_3$): δ 7.36 (t, *J* = 8, 1H), 7.13 (s, 3H), 5.37 (m, 3H), 5.05 (dd, *J* = 24, 16 Hz, 1H), 2.81 (m, 2H), 2.66 (t, *J* = 8 Hz, 2H), 2.04 (m, 3H), 1.64 (m, 2H), 1.34 (bs, 11H), 0.90 (m, 2H), Anal. calcd for $C_{22}H_{29}NO$: C, 81.69; H, 9.04; N, 4.33. Found: C, 81.28; H, 9.63; N, 4.25. $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 156.18, 150.79, 144.71, 130.04, 129.92, 129.42, 129.13, 125.85, 121.54, 120.94, 118.84, 115.37, 112.54, 35.81, 31.87, 31.25, 29.83, 29.45, 29.37, 29.29, 29.07, 27.31, 27.27, 22.74, 14.19.

Synthesis of 1-cyanato-3-pentadecylbenzene (2). In a similar manner to the synthesis described above, 3-pentadecyl phenol (2.05 g, 6.7 mmol, 1.0 equiv) was cyanated to yield 1.70 g (80%) of crude 1-cyanato-3-pentadecyl benzene (**2**) as a yellow oil. Filtration through a short silica plug with dichloromethane as eluent yielded 1.68 g (74 %) of a white crystalline powder. ^1H NMR ($CDCl_3$): δ 7.34 (m, 1H), 7.11 (bs, 2H), 2.64 (m, 2H), 1.61 (bs, 2H), 1.25 (bs, 25H), 0.88 (m, 3H). Melting point = 43 °C. Anal. calcd for $C_{22}H_{35}NO$: C, 80.19; H, 10.71; N, 4.25. Found: C, 80.03;

H, 10.54; N, 4.09. $^{13}C\{^{1}H\}$NMR ($CDCl_3$): δ 152.96, 146.44, 130.19, 126.99, 115.05, 112.49, 109.01, 35.82, 32.01, 31.21, 29.77, 29.62, 29.50, 29.44, 29.25, 22.77, 14.20.

Synthesis of trithiol (3).[71] Thioacetic acid (31.28 g, 410.3 mol) was charged into a 5-liter round bottom flask. Air was bubbled into the thioacetic acid using a fritted tube. 1,2,4-Trivinylcyclohexane (20.65 g, 126.7 mol) was added dropwise using an addition funnel over a period of 2.5 hours. An exotherm was observed, but the temperature was maintained at 32 °C using an ice bath. After 4 h, the ice bath was removed and the reaction mixture was stirred for an additional 16 h while air was bubbled through the reflux condenser. The excess thioacetic acid was removed under reduced pressure at approximately 100 °C. 52.0 g of crude trithioester were obtained. GC analysis confirmed that the reaction went to completion.

The thioester (52.0 g, 0.13 mol, 1.0 equiv) and NaOH (18.98 g, 0.47 mol, 3.5 equiv) in $MeOH/H_2O$ (100 mL,95:5) were added to 100 mL of $MeOH/H_2O$ (95:5) and refluxed overnight. An amber solution resulted after 12 h. The reaction mixture was added to a mixture of ice/1 M HCl, which was extracted with diethyl ether (3 x 100 mL). The product was purified by vacuum distillation (140-150 °C, 0.05 mmHg) to obtain 20.6 g of the trithiol as a pale yellow oil (60% yield). The ^{1}H NMR of the product was consistent with previous reports.[65]

Synthesis of 4,4′-(propane-2,2-diyl)bis(2-allyl-1-cyanatobenzene) (4). 4,4′-(propane-2,2-diyl)bis(2-allylphenol) (1.93 g, 6.24 mmol, 1.0 equiv) and cyanogen bromide (1.98 g, 18.72 mmol, 3.0 equiv) were dissolved in 60 mL of anhydrous THF. The solution was cooled to -78 °C and triethylamine (1.74 mL, 12.48 mmol, 2.0 equiv) diluted in ~3 mL of THF was added dropwise. The solution was stirred for 3 h while warming to 0 °C, and transitioned to a white cloudy mixture upon warming. The salt was filtered off and the THF removed under reduced pressure. The residue was dissolved in 60 mL of DCM, washed with water (3 x 50 mL), dried over Na_2SO_4, filtered, and then concentrated under reduced pressure. Purification on silica gel (3:1, hexanes: ethyl acetate) gave 1.34 g (60% yield) of a clear oil ($R_f = 0.5$). The NMR spectra were consistent with a literature report. [72]

Preparation of networks. The thiol and cyanate ester networks were prepared using the blend ratios outlined in **Table 1**. Cure implies the cyclotrimerization of the cyanate ester and disappearance of the C-N triple bond stretching frequency in the FTIR spectra. Samples from 1.20-3.00 -SH:O-CN ratios did solidify, indicating thiol-ene chemistry occurred, but significant cure of the cyanate ester was not observed in the FTIR spectra. The samples in **Table 1** were cross-linked via UV irradiation without the addition of external heat. Stirring (~15 min) of cyanate ester and thiol was required to achieve sufficient mixing of the components prior to UV cure. Sample sizes ranged between 25-35 mg and were cured on glass microscopic slides. To prepare cured bars for TMA analysis, aluminum molds (2 mm x 2 mm x 20 mm) were stamped from heavy-duty aluminum foil pressed into silicone molds. The blends were poured into the molds, treated with UV radiation (254 nm) (1” distance between sample and the lamp) for 10 min, degassed under vacuum (~50 torr) at room temperature until bubbles no longer formed, and then cured under a nitrogen atmosphere to prevent oxidation. The cure protocol for the networks was 50 °C for 1 h, 100 °C for 2 h, 160 °C for 2 h, 170 °C for 2 h, and a final cure at 210 °C for 24 h. The dark red rubbery samples were then allowed to cool to room temperature and were removed from the molds.

Table 1. Effect of thiol concentration on the ambient temperature cyclotrimerization of **1** with UV light

-SH:-OCN Ratio	Result
0.05	No Cure
0.10	No Cure
0.20	No Cure
0.60	Partial Cure
0.80	Partial Cure
1.00	Complete Cure

–SH:-OCN ratios up to 3.00 were screened, but no significant cross-linking via cyclotrimerization was observed at the higher ratios due to dilution effects

General curing procedure for cyanate esters 1, 2, 4 and commercial LeCy. Cyanate ester (~300 mg, 1.0 equiv) and trithiol **3** (1.0 equiv of S-H to each cyanate ester group) were mixed together. Structures of the cyanate esters studied in this work can be found in **Figure 3**. A drop of the mixture (~35 mg) was dispensed onto a microscope slide and subjected to UV (254 nm) irradiation for 30 min at ambient temperature. In the case of compound **2**, heat was applied (40 °C) to melt the cyanate ester. For compound **2** and LeCy, which do not contain side- chains with alkenes, alkene-containing compounds at different concentrations were added (**Table 2**)

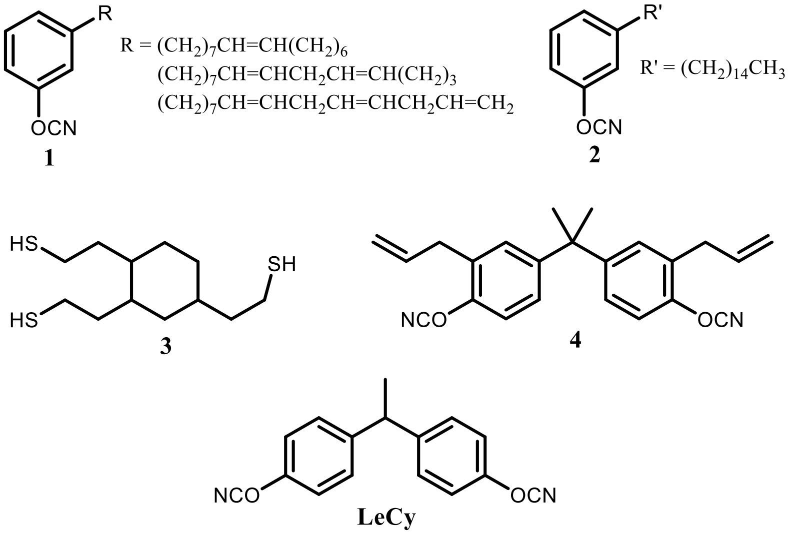


Figure 3. Cyanate esters (**1**, **2**, **4**, LeCy) studied in this work and the trithiol (**3**) used for cross-linking reactions with unsaturated side-chains.

Table 2. Cross-linking conditions utilized for compounds **1**, **2**, **4**, and LeCy with trithiol **3**

Compound	T (°C)[a]	Additive (equivalents of alkene)[b]
1	25	-
2	40	-
2	40	1-octadecene (1.0 equiv)
4	25	-
LeCy	25	-
LeCy	25	1-octadecene (1.0 equiv)
LeCy	25	*trans*-anethole (1.0 equiv)
LeCy	25	*trans*-anethole (3.0 equiv)
LeCy	25	1,7-octadecene (1.0 equiv)
LeCy	25	1,7-octadecene (3.0 equiv)

[a]Hot plate temperature—local temperatures may have been higher due to UV irradiation and the exotherm from the thiol-ene reaction. [b]Equivalents of alkene are in relation to cyanate ester groups.

Characterization of Networks

Networks were evaluated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mode thermomechanical analysis (TMA) and Fourier Transform Infrared Spectroscopy (FTIR). Details can be found in the supporting information.

Results and Discussion

For the cyanate ester compound **1**, the ^{1}H NMR spectrum showed a mixture of isomers (4 compounds) with different degrees of unsaturation in the alkyl chain. The lack of a phenol peak and shifting of the aromatic peaks, showed complete conversion to the cyanate ester. On average, 2.15 alkenes were present per molecule (**Figure 4**). The FTIR spectrum displayed a diagnostic peak for the cyanate ester group at 2240 cm^{-1} (**Figure 5**).

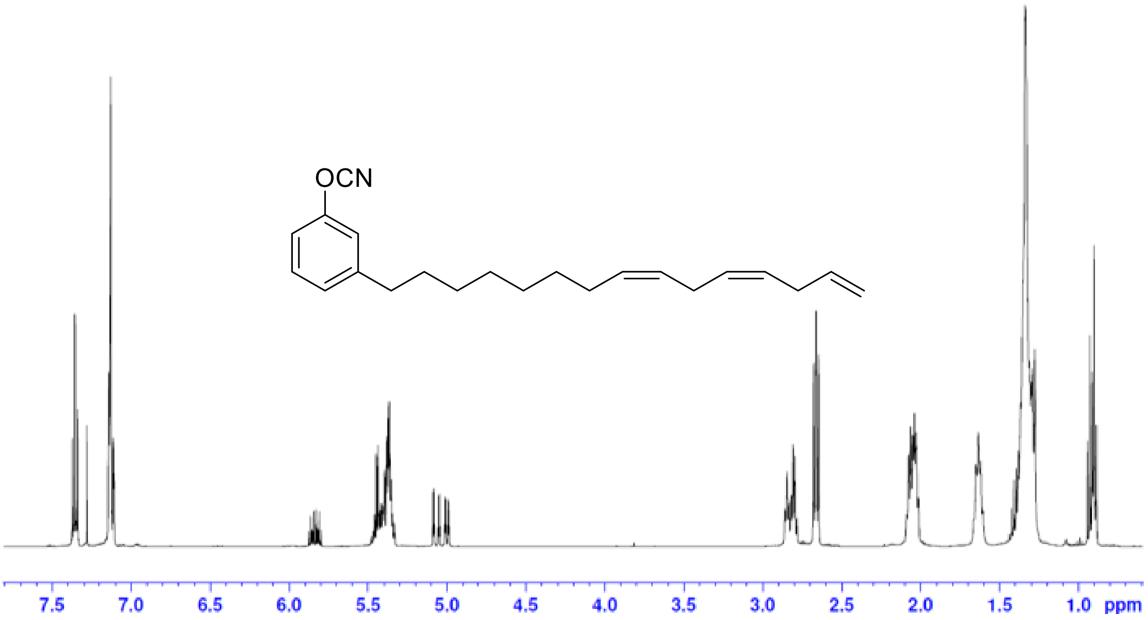


Figure 4. ^{1}H NMR ($CDCl_3$) spectrum of compound **1**.

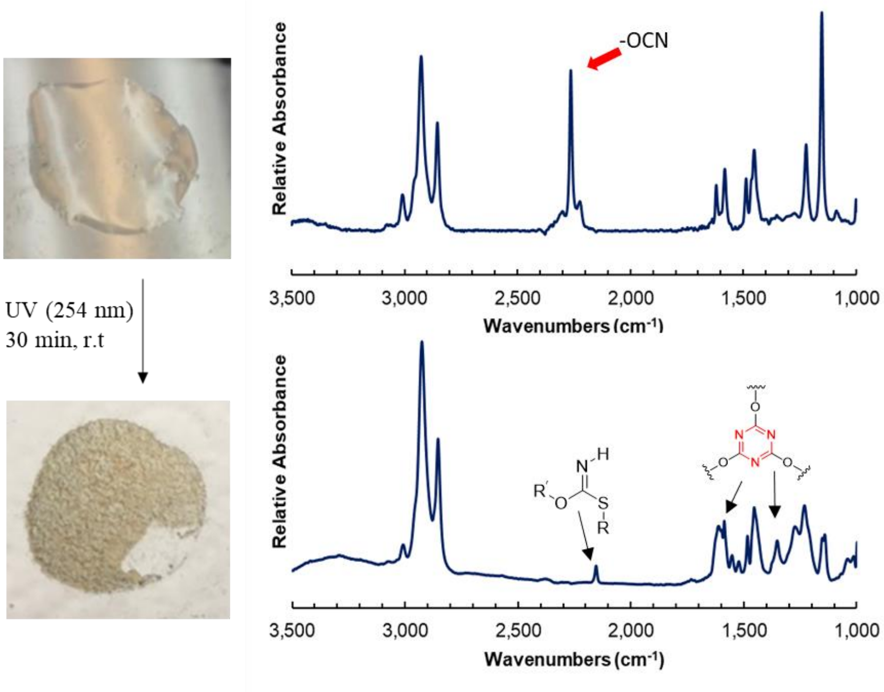
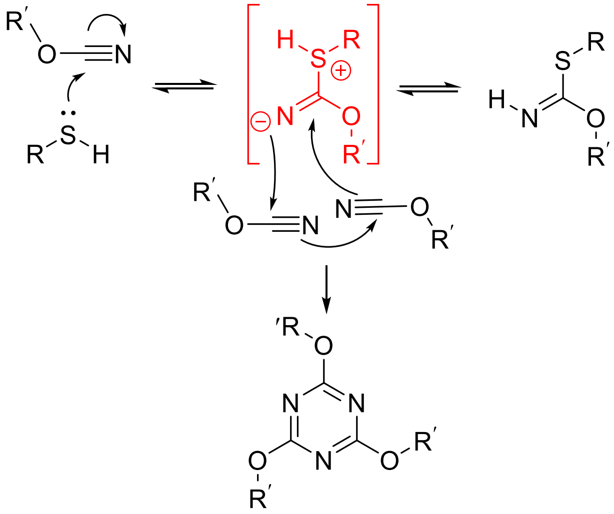
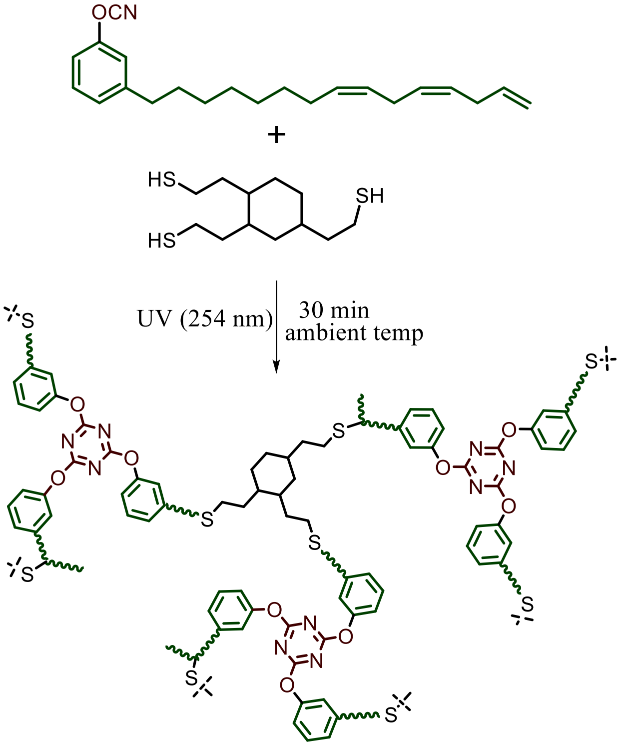


Figure 5. Digital images of an uncured mixture of **1** and **3** (top left, -SH:-OCN ratio of 1) and cross-linked network (bottom left, 254 nm UV irradiation, 30 min). FTIR spectra of the uncured mixture (top right) and cross-linked network (bottom right).

To evaluate if **1** could be efficiently cross-linked via a dual-cure mechanism, **1** was mixed with trithiol **3** (1.0 equiv of thiol to cyanate ester) and a droplet of the resulting solution was transferred to a microscope slide. At ambient temperature, exposure to UV irradiation (254 nm) for 30 min caused solidification of the droplet into a thin film. FTIR analysis revealed nearly complete disappearance of the cyanate ester peak at 2240 cm^{-1} and the growth of peaks at ~1550 and 1350 cm^{-1}, which represent formation of the polycyanurate network (**Scheme 2** and **Figure 5**). A small peak (~2150 cm^{-1}) was also formed and is attributed to a trace of residual imidothioate formed by nucleophilic attack of a thiol group on the carbon of a cyanate ester group.[73] This reaction enhances the nucleophilicity of the nitrogen and promotes the formation of the cyanurate ring system (**Scheme 1**).[74] To our knowledge, this is the first example of ambient temperature cure of a cyanate ester resin.



Scheme 1. Imidothioate assisted trimerization of cyanate esters.

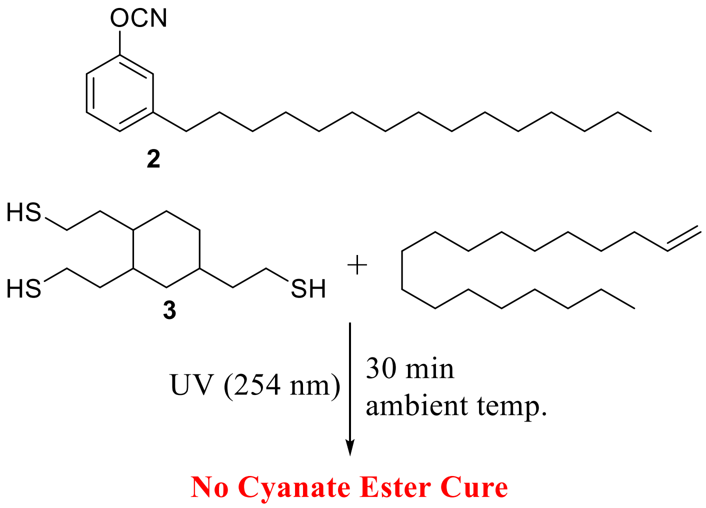


Scheme 2. Ambient temperature cure of **1** with trithiol **3** and UV irradiation. Sinuous lines are used to denote cardanol C_{15}-side-chains.

To evaluate the impact of thiol concentration on the cyclotrimerization reaction, mixtures with S-H:(O-CN) ratios in the range of 0.05 - 1.00 were studied (**Table 1**). Under the conditions employed, the concentration of the thiol had a significant effect on network cure. At both low and high concentrations of thiol, no evidence of significant cyclotrimerization of the cyanate ester group was observed. In contrast, nearly complete cure was observed when one equivalent of trithiol was added, and partial curing was observed at ratios of 0.6-0.8. The degree of cyclotrimerization was determined qualitatively based on the residual intensity of the cyanate ester peak in the FTIR spectra.

We initially considered two mechanisms for the thiol-promoted polycyanurate formation. First, it is well known that phenols can facilitate the cure of cyanate esters via an acid catalyzed route.[58] Thiols, which have pKas in a similar range as phenols (~10), could be catalyzing the reaction in a similar manner.[75] In order to test that hypothesis, we attempted to cross-link the mixture under similar conditions with the saturated analogue of the cardanol cyanate ester (**2**). The absence of alkenes in the side chain eliminated the potential for thiol-ene chemistry between the side chain and the trithiol. After exposure to UV irradiation for 30 min, FTIR analysis showed no reduction in the cyanate ester peak or growth of peaks attributable to the cyanurate ring system. This control experiment suggested that alkenes were a critical factor influencing cyanate ester reactivity.

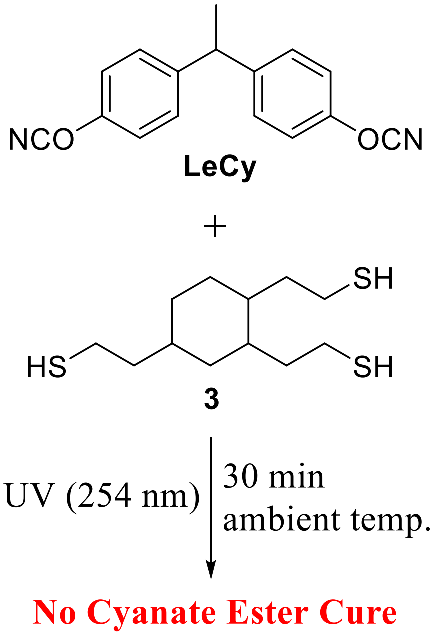
Reaction of a thiol with an alkene is an exothermic reaction (~60 to 100 kJ/mol).[76, 77] The thiol-ene reaction coupled with the exothermic cyclotrimerization of the cyanate ester group (~100 kJ/mol)[78] should be sufficient to generate enough heat to catalyze the global cross-linking of the network. This type of approach is similar to that employed during frontal polymerization.[79] For example, Viner showed that the exothermal heat from a free radical polymerization of trimethylolpropane triacrylate (TMPTA-n) could initiate the polymerization of a cyanate ester with an amine catalyst. The subsequent cyanate ester cure exotherm created a propagating heat front that promoted full cure of the resin.[80] To provide further insight into the current mechanism, 1-octadecene was added to the mixture of **2** and trithiol **3**. The same molar ratio of alkenes was utilized as that present when conducting cross-linking reactions with **1**. 1-Octadecene contains a terminal alkene, which should undergo a more facile thiol-ene reaction with thiols. In contrast, **1** contains less reactive internal alkenes in addition to terminal alkenes. UV irradiation of the blend containing 1-octadecene did not result in significant cross-linking of the cyanate ester groups as observed by FTIR spectroscopy (**Scheme 3**). It seems likely that the lack of a reaction is due in part to the increased dilution of the mixture. In addition, considering the alkene is no longer attached to the molecule with the cyanate ester group, the exothermic thiol-ene reaction no longer produces direct localized heating of the cyanate ester groups. This type of dilution effect was also a factor during attempts to cure **1** when high concentrations of polythiol (S-H:-OCN > 1.2) were present. Therefore, the results suggest that for the reaction to occur without the application of additional heat, a careful balance between the concentration of alkene groups, thiols, and cyanate ester groups must be maintained.



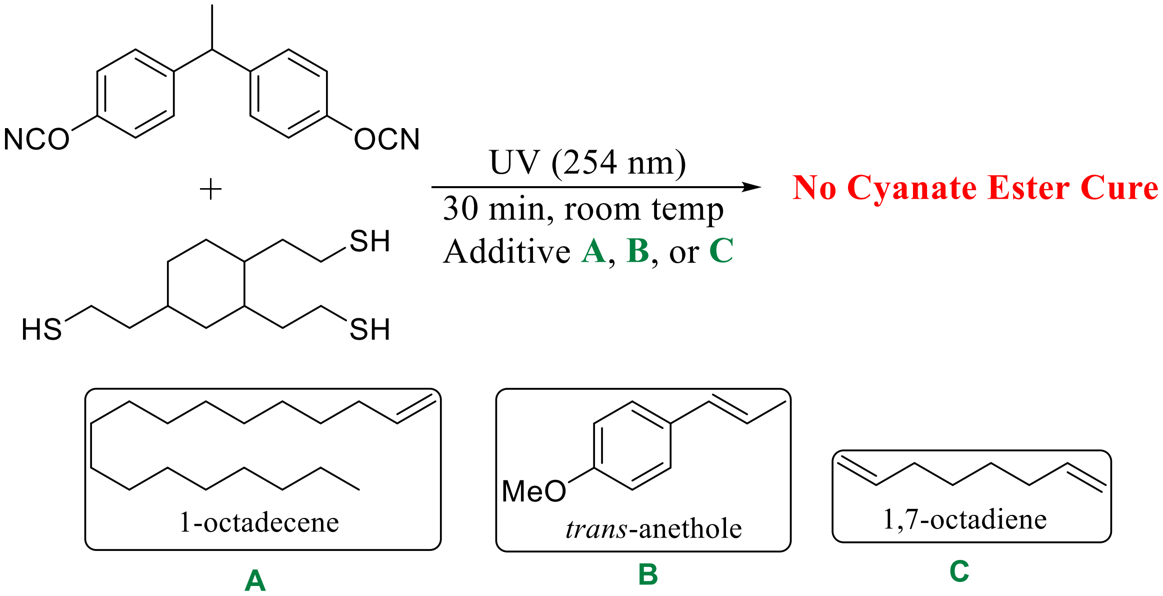
Scheme 3. Attempted cure reaction of **2** with **3** and 1-octadecene.

To provide further insight into the cyclotrimerization mechanism for mixtures of **1** and **3**, a control reaction was conducted with the commercial cyanate ester LeCy (**Scheme 4**). LeCy was selected due to its low melting point (29 °C) and well-studied cure chemistry.[81] As observed in the attempted cure reactions with compound **2**, addition of **3**, followed by UV irradiation, did not result in cyclotrimerization of the cyanate ester groups of LeCy at ambient temperature. The absence of alkenes suitable for reaction with the trithiol eliminated the production of sufficient heat to catalyze the cyclotrimerization reaction. Varying the amount of thiol in the mixture (0.05, 0.10, and 1.00 equivalents of -SH to -OCN) had no impact on the results. In a similar manner to the experimental protocol for **2**, different alkenes were added to the mixture of LeCy and the trithiol **3**. No cyanate ester cure was observed, regardless of the molecular weight and structure of the added alkene

(**Scheme 5**). In addition to dilution effects, the results provided additional evidence that it may be necessary for the alkene to be covalently bonded to the cyanate ester resin. The presence of an isotropic system allows for the heat generated during the thiol-ene reaction to induce the cyclotrimerization of the cyanate ester groups in a localized fashion.



Scheme 4. Attempted cross-linking of LeCy with trithiol **3** and exposure to UV irradiation.



Scheme 5. Attempted cure of LeCy with a trithiol and various alkenes under UV irradiation.

To further evaluate the thiol-catalyzed cross-linking of **1**, various blends of **1** and **3** were subjected to UV irradiation while applying moderate thermal energy. Heating samples at 50 °C on a hot plate during UV irradiation resulted in complete conversion of cyanate ester groups to cyanurate ring systems when up to three equivalents of -S-H to -OCN were present (**Table S4**). It should be noted that heating either **2** or commercial LeCy mixtures with **3** to 50 °C did not result in the cure of those blends. The low-temperature heating results with LeCy and **2** further demonstrated the pivotal role of exothermic thiol-ene chemistry in the low temperature cross-linking mechanism.

To extend and generalize the results observed with **1**, we attempted the dual cure (cyclotrimerization and thiol-ene cross-linking) of 4,4′-(propane-2,2-diyl)bis(2-allyl-1-cyanatobenzene) (**4**), with trithiol **3**. A previous study describing the cross-linking reaction of **4** with trimethylolpropane tris(3-mercaptopropionate) (TPTMP) under UV irradiation in the presence of a photosensitizer showed evidence of an efficient thiol-ene reaction, but no definitive sign of cylotrimerization through the cyanate ester groups. [72] In our experiment, we only observed partial reaction of the cyanate ester groups at ambient temperature (**Figure 6, Scheme 6**). It was expected that rapid thiol-ene chemistry with concomitant cyanate ester cyclotrimerization would occur because there are two primary alkenes in **4** that are close in proximity to the cyanate ester groups. In addition, due to the shorter chains present in **4**, the concentration of alkenes in the reaction mixture is significantly higher than when **1** is used as the cyanate ester component. In contrast, the results suggest that the higher reactivity of the primary alkenes resulted in rapid vitrification upon reaction with the thiols, preventing further cross-linking through the cyanate ester groups. In order for this reaction to proceed to completion, the reaction temperature would

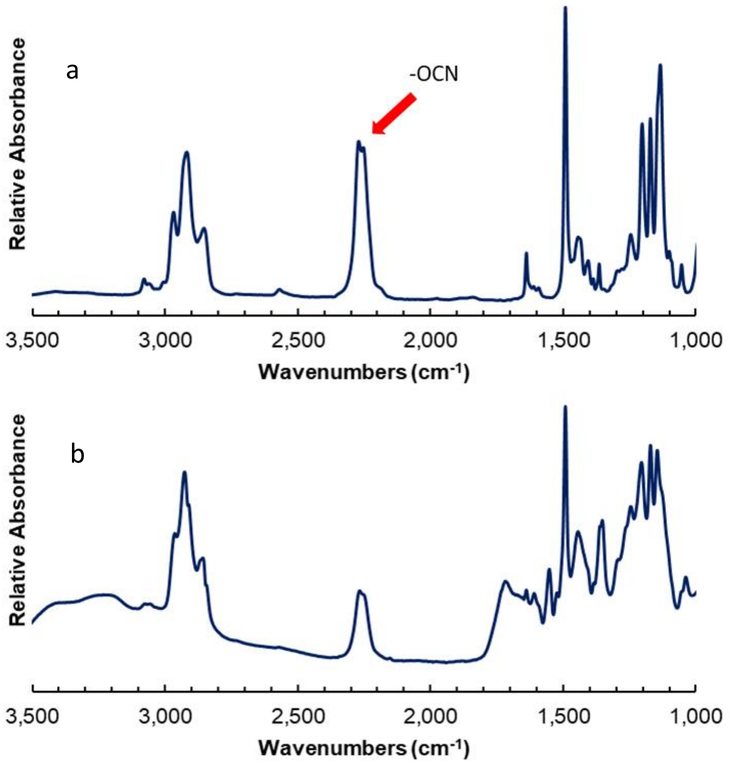
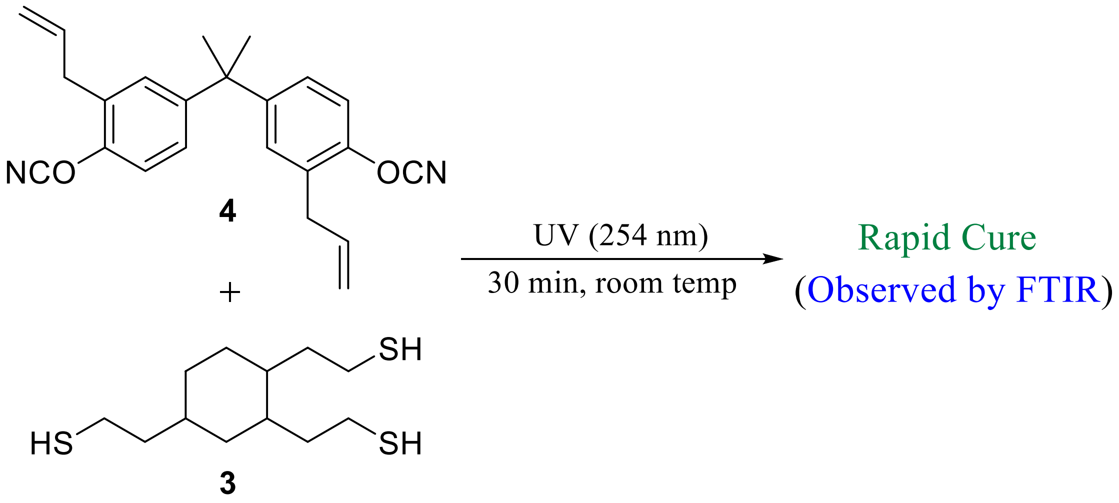


Figure 6. FTIR spectra showing partial cyclotrimerization of the cyanate ester in 4,4′-(propane-2,2-diyl)bis(2-allyl-1-cyanatobenzene) (**4**) upon blending with **3** and UV light exposure. a) Uncured mixture and b) partially cured mixture after exposure to UV radiation.



Scheme 6. Ambient temperature cure of **4** with trithiol **3** under UV irradiation.

need to exceed the T_g of the growing network. This could be accomplished through the addition of external heat.

Thermal properties of networks prepared from 1 and 3

To analyze the thermomechanical properties of cross-linked networks prepared from **1** and **3** (**C1**), bars and pucks of the cured material were fabricated. After initial exposure to UV irradiation, the samples were further cured in a vacuum oven according to the heating cycle described in the Experimental Section. The UV curing protocol described in this work is suitable for films, but to ensure the complete cure of bulk polymer samples, we subjected the mixtures to a thermal cure cycle after the initial UV irradiation. DSC analysis of the cured samples showed a high degree of cure for the bulk samples with a residual cure enthalpy of only 8.54 J/g (**Figure 7**).

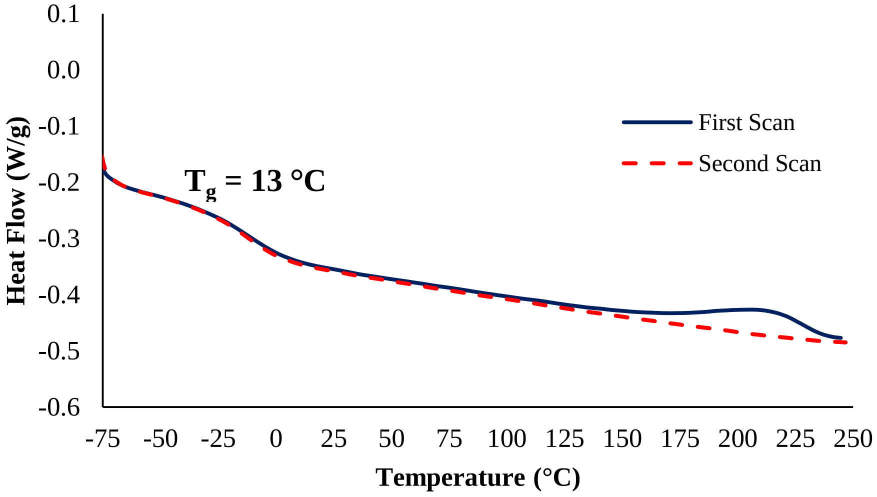


Figure 7. DSC of a cross-linked cardanol cyanate ester trithiol blend (**C1**) with an -S-H/-O-CN ratio of one.

Thermomechanical analysis (TMA) of **C1** showed a T_g (loss) at –2.4 °C (**Figure 8**). The low T_g and rubbery properties of the material are unusual for standard cured networks of cyanate esters and can be attributed to the long aliphatic chains present in the cardanol molecule, along with the flexible cross-links derived from the thiol-ene reaction. In comparison, a cardanol based cyanate ester novolac resin previously studied, exhibited a modest T_g of 160 °C.[28, 57] It should be noted that thermal cyclotrimerization of cyanate ester **1**, without thiol, resulted in a liquid, which further emphasizes the need for the thiol for the generation of a highly cross-linked network. Thermogravimetric analysis (TGA) revealed T_d's of 256 °C and 268 °C in nitrogen and air,

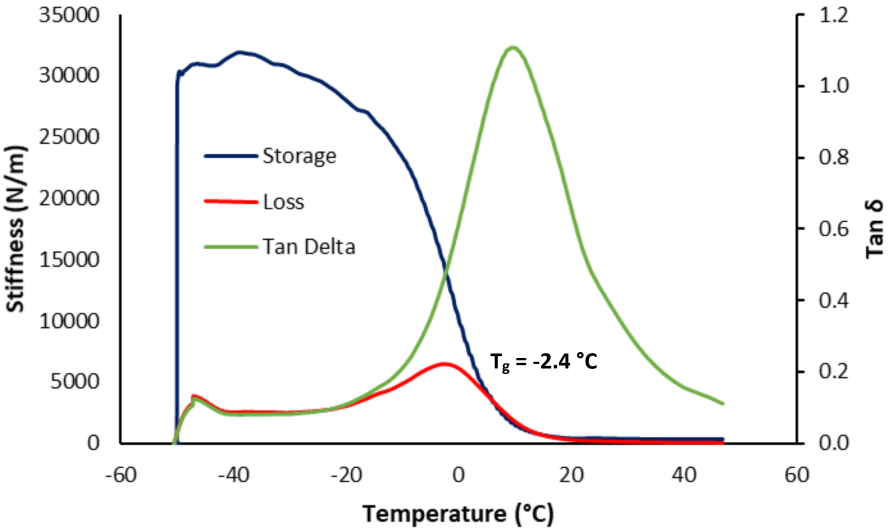


Figure 8. Thermomechanical analysis (TMA) of **C1** (-S-H:-O-CN =1)

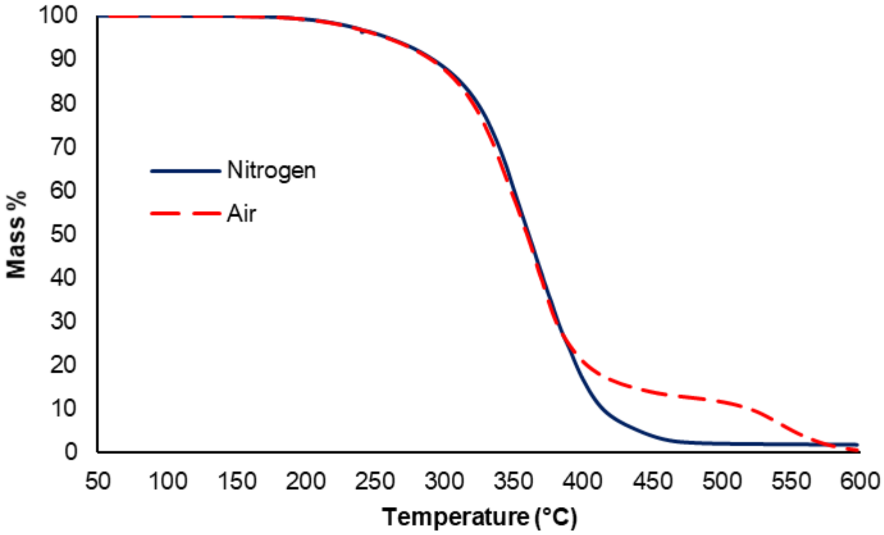


Figure 9. Thermogravimetric Analysis (TGA) of **C1** (-S-H:O-CN = 1)

respectively (**Figure 9**). The highest rate of mass loss was observed at 388 °C (N_2) and 380 °C (air) with 20% mass loss occurring at 349 °C (N_2) and 374 °C (air). Due to the low T_g of this material, **C1** can not be used directly for high temperature applications, however, it may have applications as a toughening agent that could be isotropically incorporated into brittle, high T_g cyanate ester networks.

There are a number of approaches for toughening thermoset networks. For example, semi-interpenetrating polymer networks (SIPNs) can be prepared by blending thermoplastics with thermosetting resins.[82] Alternatively, blending epoxidized vegetable oils with conventional epoxy resins results in composite materials with increased toughness.[83, 84, 85] In a similar manner to the latter approach, **C1** could be used to improve the fracture toughness of cyanate ester thermoset networks.[86] The flexibility and elastomeric properties of **C1** can be clearly seen in **Figure 10**.

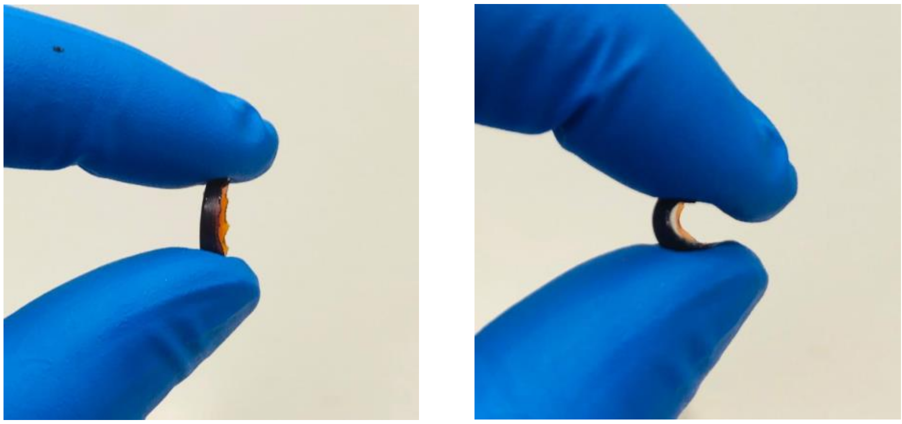


Figure 10. Demonstration of the flexibility of **C1**.

Conclusion

This work describes the first example of ambient temperature cross-linking of a cyanate ester resin initiated with UV irradiation. The results suggest that the activation energy for cyclotrimerization is provided by exothermic thiol-ene reactions between alkenes in the side-chain of the cardanol-based cyanate ester and a trithiol. Studies with additional additives and monomers confirm that the concentration and reactivity of the alkene groups are critical factors which dictate the degree of cure achieved under ambient conditions, and the amount of additional thermal input (if any) required to achieve a high cross-link density. Although the focus of this study was a low T_g bio-rubber derived from cardanol, a variety of novel monomers containing pendent alkene groups could be studied as components of higher T_g materials that can be cross-linked via an “out-of-autoclave” process. This advance holds great promise for composite repair and low-cost production of composite parts. The study of cardanol-based cyanate ester bio-rubbers and their ability to toughen brittle thermosetting resins is of continued interest. One objective of future research is to gain a better understanding of the degree of cure (both thiol and cyanate ester conversion) in generalized thiol-ene/cyanate ester networks. Experimentation on this topic is ongoing in our laboratory.

Conflicts of Interest

A US patent application related to this work has been filed.

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