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### Abstract

Novel bio-based and dual-curable thermosets were prepared from eugenol derivatives. The curing sequence combined two click reactions, a photoinduced radical thiol-ene reaction followed by a thermally activated thiol-epoxy reaction. Eugenol was transformed into a triallyl (3A-EU) and a diallyl glycidyl derivative (2AG-EU) with high yields, and they were used as starting monomers in order to study the thiol-ene reaction and the dual-curing process, respectively. Three different thiol crosslinkers were tested, one commercially available tetrathiol derived from pentaerythritol (PETMP) and two other that were also synthesized: a trithiol derived from eugenol (3SH-EU) and a hexathiol derived from squalene (6SH-SQ). FTIR and DSC were used to monitor both curing stages and analyze the obtained materials. The results evidenced the occurrence of side reactions that led to incomplete thiol-ene reaction. The dual-curable materials showed higher Tgs than the materials obtained by a simple thiol-ene process and presented higher mechanical and thermomechanical performance.

<b>Keywords</b>	Green chemistry; bio-based; eugenol; dual curing; click reaction; thermosets.
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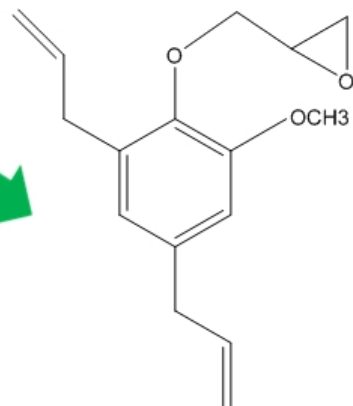
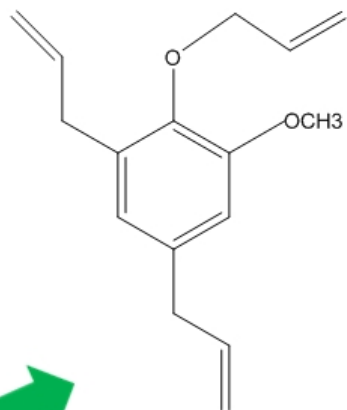
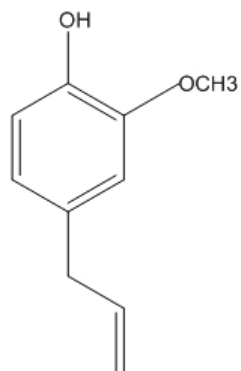
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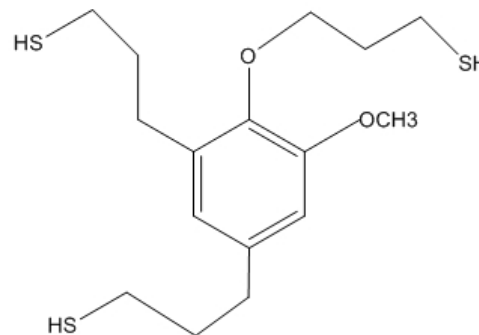
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## **Highlights**

A new diallylglycidyl derivative of eugenol has been prepared>Bio-based thermosets have been prepared by thiol-ene/thiol-epoxy dual curing>Dual cured materials showed better thermomechanical performance than purely photocured



**Thiol-ene  
networks**



**Thiol-ene/  
thiol-epoxy  
networks**

1.



2.



NEW BIO-BASED MATERIALS OBTAINED BY THIOL-ENE/THIOL-EPOXY DUAL CURING  
CLICK PROCEDURES FROM EUGENOL DERIVATES

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## Abstract

Novel bio-based and dual-curable thermosets were prepared from eugenol derivatives. The curing sequence combined two click reactions, a photoinduced radical thiol-ene reaction followed by a thermally activated thiol-epoxy reaction.

Eugenol was transformed into a triallyl (3A-EU) and a diallyl glycidyl derivative (2AG-EU) with high yields, and they were used as starting monomers in order to study the thiol-ene reaction and the dual-curing process, respectively. Three different thiol crosslinkers were tested, one commercially available

tetrathiol derived from pentaerythritol (PETMP) and two other that were also synthesized: a trithiol derived from eugenol (3SH-EU) and a hexathiol derived from squalene (6SH-SQ).

FTIR and DSC were used to monitor both curing stages and analyze the obtained materials. The results evidenced the occurrence of side reactions that led to incomplete thiol-ene reaction. The dual-curable materials showed higher  $T_g$ s than the materials obtained by a simple thiol-ene process and presented higher mechanical and thermomechanical performance.

## **Keywords**

Green chemistry, bio-based, eugenol, dual curing, click reaction, thermosets.

## **1. Introduction**

Green chemistry is synonymous of health and environmental sustainability. Green chemistry explores new ways of preparing chemical substances or materials in more environment-friendly conditions from renewable resources. This concept includes the reduction or elimination of dangerous substances in the design, manufacture, and use of chemical products.<sup>1,2,3</sup> This is the reason behind the increasing demand for novel synthetic polymers made from components derived from renewable sources that has appeared in the recent years.<sup>4,5</sup> The use of natural components allows to reduce the dependence on fossil resources and implies a positive economic impact.<sup>6,7,8,9,10</sup>

There are several biomass resources that have been proposed to prepare new biobased materials as rosin,<sup>11,12,13,14,15</sup> fatty acids,<sup>16</sup> gallic acid,<sup>17</sup> tannins,<sup>18,19</sup> itaconic acid,<sup>20</sup> lignin,<sup>21,22</sup> vanillin,<sup>23</sup> cardanol,<sup>24</sup> succinic acid<sup>10</sup> and furan

derivatives.<sup>25,26</sup> Eugenol (4-allyl-2-methoxyphenol), obtained from the essential oil of clove tree, is highly attractive as feedstock for development of new materials, since it is a phenolic compound that can be further modified to reach the convenient functionality and a rigid structure.<sup>27,28</sup> This aromatic compound is used in the pharmaceutical industry and therapeutic medicine because it has properties of reduction on blood sugar, triglyceride and cholesterol levels.<sup>29</sup> In addition, it can act as antioxidant agent preventing typical processes of oxidation of lipids in the first stages of inflammatory processes working as captor agent of free radicals.<sup>30</sup> According to that, eugenol derivatives can be a good alternative to get monomeric compounds without toxicological issues.

Recently, many researchers opted for the use of eugenol to prepare new biobased materials. Donovan et al.<sup>31</sup> prepared adhesives by thiol-ene reactions from an eugenol derivative as vinylic compound and pentaerithritol triallylether and PETMP as thiols. Increasing the concentration of eugenol derivative in the thiol-ene network resulted in improved adhesion on a variety of substrates, including glass, aluminium, steel and marble. In another study, Yoshimura et al.<sup>32</sup> prepared new materials by thiol-ene reactions from a triallyl derivative of eugenol. This compound was prepared by allylation of eugenol, followed by a Claisen reaction, and further allylation of the phenol formed. Three different thiols were used to crosslink but the materials obtained did not reach  $T_g$  values higher than 10 °C and therefore their applicability was quite limited.

Green engineering is another concept strongly related to green chemistry. It focuses on the optimization of processes and systems to maximize mass, energy, space, and time efficiency. Renewable rather than depleting

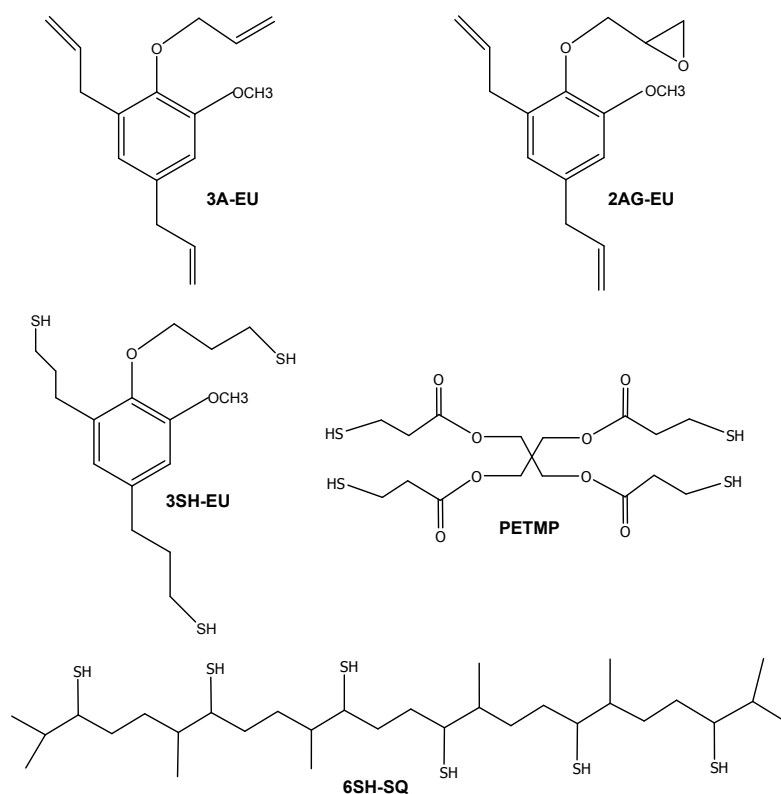
material and energy inputs are other concepts included in the green engineering principles.<sup>33</sup>

Dual curing procedures have been proposed for clean and efficient processing, which facilitates manufacturing and assembling, reducing the waste production. Dual curing methodologies consist in a first stage of curing leading to a stable intermediate material, which upon application of a second stimulus, undergoes further reaction and crosslinking to achieve the ultimate properties.

In a previous study, we developed a completely sequential dual curing procedure based in a first photochemically induced thiol-ene reaction followed by a thermal thiol-epoxy reaction, using commercially available diglycidylether of bisphenol A (DGEBA), triallylisocyanurate (TAIC) and pentaerythritol tetrakis(3-mercaptopropionate) (PETMP).<sup>34</sup> This procedure allowed us to obtain materials with tailored intermediate and final properties by just changing the formulation composition, and to store them for a certain time in the intermediate state before the final application and completion of the curing process. Due to the toxicological issues of DGEBA and TAIC, the substitution of these monomers by other bio-based derived from a renewable feedstock such as eugenol could contribute to obtain safer thermosetting materials from more sustainable procedures.

Considering both green chemistry and engineering concepts, in the present study the preparation of new sustainable materials from eugenol by thiol-ene or the combination of thiol-ene and thiol-epoxy click reactions will be tackled. The strategy of using dual curing by combination of thiol-ene and thiol-epoxy is aimed at increasing the  $T_g$  of the final materials, whereas at the same time improvements in the processability could be reached. As starting monomers, we

have prepared different compounds derived from eugenol with a functionality of three, being the functional groups allyl or epoxide. As thiol monomers, we selected three different compounds derived from renewable resources: commercially available PETMP, derived from pentaerythritol that can be obtained from biosynthetic procedures<sup>35</sup> and two thiols synthesized from squalene<sup>36</sup> and eugenol, by a clean methodology consisting in the thiol-ene addition of thioacetic acid and further saponification. From the combination of the different monomers shown in Scheme 1, we have prepared new bio-based materials with different characteristics that have been evaluated.



**Scheme 1.** Chemical structures of the allyl and epoxy eugenol derivatives and the thiols selected as monomers



As far as we know, the work reported in the present paper is the first one addressing the preparation of renewable thermosets from bio-based compounds using an efficient environmentally friendly dual click curing methodology.

## **2. Experimental part**

### **2.1. Materials**

Eugenol (EU), allyl bromide, thioacetic acid (TAA), 2,2-dimethoxy-2-phenylacetophenone (DMPA), pentaerythritol tetrakis (3-mercaptopropionate) (PETMP), squalene (SQ), 1-methylimidazole (1-MI), Irgacure 184 (1-hydroxycyclohexyl phenyl ketone), benzyl triethylammonium chloride (TEBAC) and epichlorohydrin (EPC) were purchased from Sigma-Aldrich and were used without further purification. Irgacure 819 (phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide) was supplied by BASF. Inorganic salts and bases were purchased from Scharlab. Methanol (Carlo Erba) has been used as received. N,N-dimethylformamide (DMF) from VWR was dried by standard procedures.

### **2.2. Preparation of starting products**

#### **2.2.1. Synthesis of the triallyl compound from eugenol (3A-EU)**

Triallyl eugenol was prepared following a previously reported procedure.<sup>32</sup> The synthesis includes the allylation of eugenol in basic medium to obtain O-allyl eugenol (2A-EU) and then a Claisen rearrangement on heating to obtain 6-allyleugenol (r2A-UE). This product was allylated and the triallyl eugenol (3A-EU) was obtained (see supporting information).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  in ppm): 6.7 s (Ar, 2H), 6.05 m (-CH=, 1H), 5.90 m (-CH=, 2H), 5.34 dd ( $\text{CH}_2$ =, 1H), 5.19 dd ( $\text{CH}_2$ =, 1H), 5.15-5.0 m ( $\text{CH}_2$ =, 4H), 4.46 d (- $\text{CH}_2$ -O-, 2H), 3.87 s ( $\text{CH}_3$ -O-, 3H), 3.38 d (- $\text{CH}_2$ -Ar, 2H), 3.31 d (- $\text{CH}_2$ -Ar, 2H) (see Figure A in supporting information).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  in ppm): 152.6, 144.1, 137.5, 137.3, 135.7, 134.5, 133.7, 121.7, 117.0, 115.8, 115.5, 110.5, 73.7, 55.7, 40.1 and 34.3.

FT-IR (ATR): 3072, 3018, 2901, 2825, 1637, 1583, 1510, 1451, 1418, 1256, 1230, 1141, 1026, 986, 907, 804 and  $752\text{ cm}^{-1}$ .

### 2.2.2. Synthesis of diallylglycidyl derivative of eugenol (2AG-EU)

10.49 g (51.4 mmol) of r2A-EU, 30.76 g (332.4 mmol) of epichlorohydrin and 0.84 g (3 mmol) of benzyltriethylammonium chloride (TEBAC) were stirred in a 250 mL flask at  $100^\circ\text{C}$  for one hour. The mixture was cooled down to  $30^\circ\text{C}$  and then 30 mL of an aqueous solution of 20 % NaOH and 0.84 gr of TEBAC were added and maintained under stirring for 90 min. Once finished 20 mL of ethyl acetate was added to the mixture for dilution. The phases were separated and the organic layer was washed twice with water and dried with magnesium sulphate. The solvent and excess epichlorohydrin were eliminated in a rotary evaporator at  $60^\circ\text{C}$ . The product obtained, with 97 % yield, was purified by silica-gel chromatography using hexane/ethyl acetate 7/3. The product is a pale yellow liquid.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  in ppm): 6.6 s (Ar, 2H), 5.95 m (-CH=, 2H), 5.06 m ( $\text{CH}_2$ =, 4H), 4.15 dd (- $\text{CH}_2$ -O-, 1H), 3.93 dd (- $\text{CH}_2$ -O-, 1H), 3.83 s ( $\text{CH}_3$ -O-, 3H), 3.42 d (- $\text{CH}_2$ -Ar, 1H), 3.33 m (CH epoxy ring, 1H), 3.28 d (- $\text{CH}_2$ -Ar, 1H), 2.85 dd and 2.68 dd ( $\text{CH}_2$  epoxy ring, 2H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  in ppm): 152.2, 143.8, 137.3, 137.2, 135.8, 133.5, 121.8, 115.7, 115.4, 110.6, 73.6, 55.5, 50.5, 44.4, 39.9 and 34.0.

FT-IR (ATR): 3072, 3050, 3018, 2901, 2825, 1583, 1451, 1418, 1256, 1230, 1141, 1110, 1026, 986, 915, 907, 804 and  $752\text{ cm}^{-1}$ .

### 2.2.3. Synthesis of the trithiol derivative of eugenol (3SH-EU)

#### Photochemical thiol-ene reaction (3STA-EU)

A mixture of 5 g (20.5 mmol) of triallyl eugenol derivative (3A-EU), 22.2 g (291.6 mmol) of TAA and 0.1290 g (0.50 mmol) of DMPA were photoirradiated with a UV lamp at 356 nm for 1 h. The product obtained was dissolved in  $\text{CHCl}_3$ , extracted with a saturated NaOH solution, washed with water, and dried over anhydrous  $\text{MgSO}_4$ . The solvent was removed on a rotary evaporator. The product obtained was a viscous liquid with 96 % yield.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  in ppm): 6.52 s and 6.50 s (Ar, 2H), 3.91 t ( $-\text{CH}_2\text{-O-}$ , 2H), 3.80 s ( $\text{CH}_3\text{-O-}$ , 3H), 3.10 ( $-\text{CH}_2\text{-S-}$ , 2H), 2.85 m ( $-\text{CH}_2\text{-Ar}$ , 4H), 2.56 m ( $-\text{CH}_2\text{-S-}$ , 4H), 2.31 s ( $\text{CH}_3\text{-CO-S-}$ , 9H), 1.99 m ( $-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-O-}$ , 2H), 1.8 m ( $-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-Ar}$ , 4H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  in ppm): 195.7, 195.6, 195.5, 152.3, 143.9, 136.6, 134.5, 121.4, 110.3, 70.0, 55.5, 34.5, 31.0, 30.5, 30.3, 30.2, 29.1, 28.7, 28.4 and 25.8.

FT-IR (ATR): 2930, 2825, 1680, 1587, 1505, 1460, 1424, 1355, 1260, 1232, 1135, 1010, 950, 800 and  $607\text{ cm}^{-1}$ .

#### Hydrolysis of 3STA-EU (3SH-EU)

9.31 g (19.7 mmol) of 3STA-EU were added to 100 mL of methanol in a flask equipped with magnetic stirrer. 1.70 g (42.5 mmol) of pulverized NaOH

were added and the mixture was heated to reflux temperature under inert atmosphere for 5.5 h. The solution was allowed to cool down and the solvent was removed. The product obtained was dissolved in water and acidified with 0.1 M HCl solution and then extracted with CHCl<sub>3</sub>. The organic phase was washed with distilled water and then dried over anhydrous MgSO<sub>4</sub>. The product obtained was a pale-yellow viscous liquid. 84 % yield.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, δ in ppm): 6.56 s (Ar, 2H), 3.98 t (-CH<sub>2</sub>-O-, 2H), 3.82 s (CH<sub>3</sub>-O, 3H), 2.77 q (-CH<sub>2</sub>-S-, 2H), 2.61 m (-CH<sub>2</sub>-S-, 4H), 2.51 q (-CH<sub>2</sub>-Ar, 4H), 2.1 m (-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-, 2H), 1.85 m (-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Ar, 4H), 1.5 t (-SH, 1H), 1.35 t (-SH, 1H) and 1.33 t (-SH, 1H). (Figure B in supporting information)

<sup>13</sup>C NMR (CDCl<sub>3</sub>, δ in ppm): 152.2, 143.9, 136.7, 134.6, 121.5, 110.2, 70.3, 55.5, 35.3, 34.6, 34.3, 34.0, 28.5, 24.1, 23.8 and 21.2.

FT-IR (ATR): 2930, 2825, 2580, 1587, 1503, 1460, 1430, 1260, 1230, 1150, 1090, 1010, 950 and 830 cm<sup>-1</sup>.

#### **2.2.4. Synthesis of the hexathiol derived from squalene (6SH-SQ)**

The product was obtained following a two-step procedure previously reported,<sup>36</sup> which includes a thiol-ene photochemical reaction of squalene with thioacetic acid followed by a saponification of the thioester groups (see supporting information).

#### **2.3. Preparation of the curing mixtures**

Two different types of formulations were prepared. Thiol-ene formulations named as 3A-EU/thiol and dual formulations named as 2AG-EU/thiol. The mixtures were prepared by mixing with a spatula stoichiometric

amounts of allyl/S<sub>H</sub> and allyl-epoxy/S<sub>H</sub> groups until reaching homogenous mixtures.

Four different thiol-ene formulations were prepared from 3A-EU as allyl monomer and three different thiols: PETMP, 3SH-EU, 6SH-SQ and PETMP/3SH-EU in equimolecular proportion. The photochemical reaction was catalyzed by adding a 0.2 or 4% of a mixture of Irgacure 184 and Irgacure 819 in weight ratio 3:1 in some drops of acetone to obtain a homogenous mixture. Then, acetone was eliminated in a vacuum oven for 30 minutes.

Four different dual formulations were prepared similarly from 2AG-EU with three thiols: PETMP, 3SH-EU, 6SH-SQ and an equimolecular thiol mixture PETMP/3SH-EU. The formulations contained a 0.2 or 4% of a mixture of Irgacure 184 and Irgacure 819 in weight ratio 3:1 to activate thiol-ene reaction and 1 phr (part per hundred of total mixture) of 1-MI as a basic catalyst for the activation of thiol-epoxy thermal process.

### **2.3. Characterization techniques**

<sup>1</sup>H and <sup>13</sup>C NMR spectra were registered in a Varian Gemini 400 spectrometer. CDCl<sub>3</sub> was used as the solvent. For internal calibration the solvent signal corresponding to CDCl<sub>3</sub> was used:  $\delta$  (<sup>1</sup>H) = 7.26 ppm,  $\delta$  (<sup>13</sup>C) = 77.16 ppm.

Samples of the different compositions were photocured at 35 °C, in a Mettler DSC-821e calorimeter appropriately modified with a Hamamatsu Lightning cure LC5 (Hg–Xe lamp) with two beams, one for the sample side and the other for the reference side. 5 mg samples were cured in open aluminium pans in nitrogen atmosphere. Two scans were performed on each sample, the

second one needed to subtract the thermal effect of the radiation. The method consisted of 1 min without irradiation for temperature stabilization, followed by 12 min irradiation and finally 0.50 min without irradiation. The light intensity used was 35.6 mW/cm<sup>2</sup>, measured at 365 nm using a radiometer.

Studies of the thermal reaction were performed by differential scanning calorimetry (DSC) in a Mettler DSC-821e apparatus. For dynamic studies a flow of N<sub>2</sub> at 100 mL/min was used and the weight of the samples for the analysis was 10 mg. The calorimeter was calibrated using an indium standard (heat flow calibration) and an indium-lead-zinc standard (temperature calibration). The studies were performed in the temperature range of 30-250 °C, with a heating rate of 10 K/min.

The glass transition temperatures ( $T_g$ s) of the samples after irradiation were determined in dynamic scans at 20°C/min from -100 °C to 100 °C. The  $T_g$ s of the final thermosets were determined after two consecutive dynamic scans at 20 °C/min starting at -100 °C in a Mettler DSC-822e device to delete the thermal history. The  $T_g$  value was taken as the middle point in the heat capacity step of the glass transition.

A Bruker Vertex 70 FTIR spectrometer equipped with an attenuated total reflection accessory (ATR) (Golden Gate, Specac Ltd. Teknokroma) which is temperature controlled (heated single-reflection diamond ATR crystal) equipped with a liquid nitrogen-cooled mercury-cadmium-telluride (MCT) detector was used to register the FTIR spectra of the mixtures during UV irradiation and fully cured samples. The spectra were registered in the wave number range between 4000 and 600 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> and averaged over 20 scans. UV-

curing was performed using a Hamamatsu Lightning cure LC5 (Hg-Xe lamp) with one beam conveniently adapted to the ATR accessory. A wire-wound rod was used to set a sample thickness of 50  $\mu\text{m}$ . OPUS software was used for the analysis of the spectra. The spectra were corrected for the dependence of the penetration depth on the wavelength and normalized with respect to the absorbance of C=C aromatic peaks at  $1587\text{ cm}^{-1}$  (neglecting the contribution of the overlapping tiny signal associated with the allyl group). The normalized thiol band at  $2576\text{ cm}^{-1}$  and the allyl band at  $1639\text{ cm}^{-1}$  were integrated and the thiol and allyl conversions after the photocuring ( $x_{UV}$ ) and after thermal curing ( $x_{final}$ ) were determined as:

$$x_{UV} = 1 - \frac{A'_{UV}}{A'_0} \quad (1)$$

$$x_{final} = 1 - \frac{A'_{final}}{A'_0} \quad (2)$$

where  $A'_{UV}$ ,  $A'_{final}$  and  $A'_0$  are the normalized area of thiol or allyl bands after photocuring and thermal curing and at the beginning of the curing, respectively.

The thermal stability of the cured samples was studied by thermogravimetric analysis (TGA), using a Mettler TGA/SDTA 851e thermobalance. All the experiments were performed under inert atmosphere ( $\text{N}_2$  at  $100\text{ mL/min}$ ). Pieces of the cured samples with an approximate mass of  $8\text{ mg}$  were degraded between  $30$  and  $600\text{ }^\circ\text{C}$  at a heating rate of  $10\text{ K/min}$ .

Dynamic mechanical thermal analyses (DMTA) were carried out with a TA Instruments DMA Q800 analyser. Cured rectangular samples ( $40\text{ mm} \times 7.7\text{ mm} \times 1.6\text{ mm}$ ) from the different formulations based on 3A-EU were obtained in

silicon moulds irradiated in an ultraviolet chamber (320-390 nm), DymaxECE 2000 UV model systems. The samples were irradiated with an intensity of 105 mW/cm<sup>2</sup> for a period of 60 seconds each face 14 times, waiting 60 s minimum between irradiations, to control the temperature of the sample. The dual cured samples with the selected formulations based on 2AG-EU were photocured as described before and then isothermally cured without mould at 120°C for 1 h with a post curing at 150 °C for 30 min. Three point bending clamp was used on the prismatic rectangular samples. The apparatus operated dynamically at 5 K/min from 30 to 150 °C to delete the thermal history and then dynamically at 3 K/min from -20 to 120°C at a frequency of 1 Hz with an oscillation amplitude of 10 µm. Young's modulus was determined under flexural conditions at 30 °C, with the same clamp and geometry samples, applying a force ramp at constant load rate of 3 N/min, from 0.001 N to 18 N. Three samples of each material were analyzed and the results were averaged. Stress strain at break tests were performed with the film-tension clamp in force controlled mode. Dogbone samples were used at a force rate of 1 N/min and the averaged values of at least three different samples were reported.

Microindentation hardness was measured with a Wilson Wolpert 401 MAV device following the ASTM E384-16 standard procedure. For each material 10 determinations were made with a confidence level of 95%. The Vickers hardness number (HV) was calculated from the following equation:

$$HV = \frac{1.8544 \cdot F}{d^2} \quad (3)$$

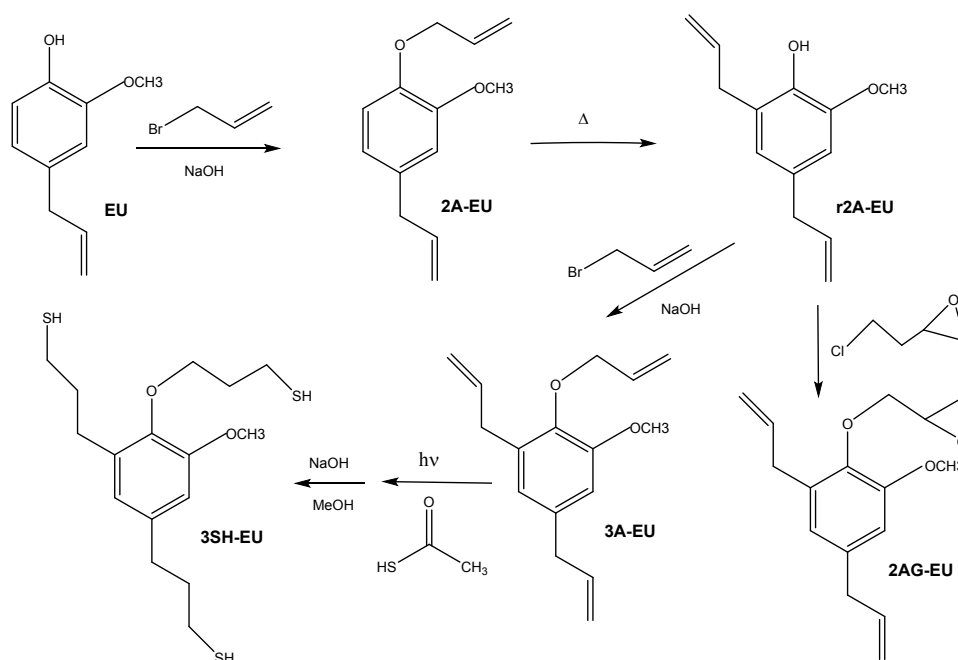


where,  $F$  is the load applied to the indenter in kgf and  $d$  is the arithmetic mean of the length of the two diagonals of the surface area of the indentation measured after load removal in mm.

### 3. Results and discussion

#### 3.1. Synthesis and characterization of monomers

The synthetic procedure applied to the preparation of eugenol derivatives used as monomers in the present study is depicted in Scheme 2.



**Scheme 2.** Synthetic procedure used in the preparation of the triallyl derivative (3A-EU), the glycidyl derivative (2AG-EU) and the trithiol (3SH-EU) from eugenol

This synthetic procedure is based on the preparation of the diallyl derivative (r2A-EU), previously reported by Yoshimura et al.<sup>32</sup> They described that the allylation of the phenol group of eugenol followed by a Claisen rearrangement allows the preparation of the diallyl compound r2A-EU, from which the triallyl (3A-EU) or the glycidyl derivative (2AG-EU) can be, alternatively

obtained. This glycidic compound has not been previously described but the synthesis is quite conventional and based in the reaction of phenols with epichlorohydrin in excess in the presence of a quaternary ammonium salt. The triallyl derivative was converted into the trithiol (3SH-EU) following the synthetic procedure consisting in a photochemical thiol-ene addition of thioacetic acid and further saponification with a base, as previously reported.<sup>37</sup>

The synthesized compounds did not required further purification with the exception of 2AG-EU, which was purified by column chromatography. The characterization of the previously reported compounds was performed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and they perfectly agree with those previously published and confirmed their high purity (see spectra in supporting information).

Figure 1 and 2 show the <sup>1</sup>H and <sup>13</sup>C NMR spectra of 2AG-EU with the corresponding assignments. As we can see, and in spite of the complexity due to the lack of symmetry, the <sup>1</sup>H NMR spectrum of 2AG-EU shows the typical pattern expected for both allyl groups, partially overlapped among them, and the five signals expected for the five unequivalent protons of glycidyl group. Aromatic protons and methoxy group appear as singlets. The <sup>13</sup>C-NMR spectrum of this compound also shows its high purity and confirms the expected structure of the compound. The assignments have been performed based on similar compounds previously reported.<sup>27,32</sup>

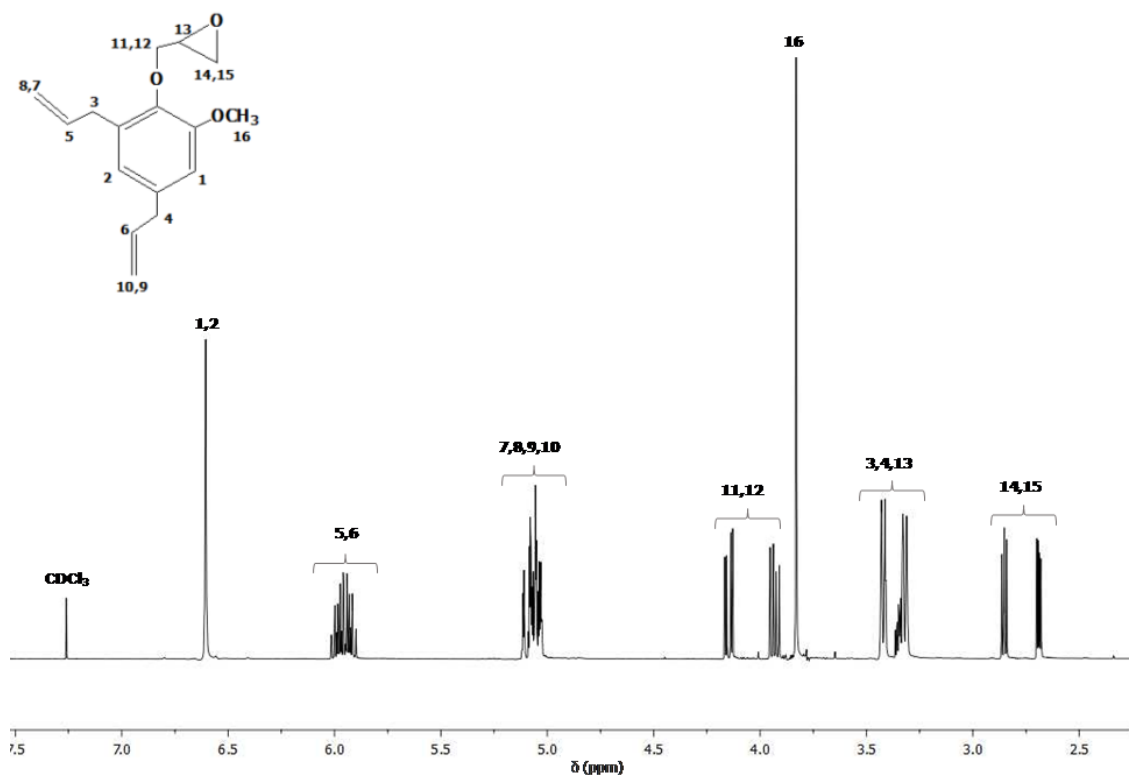


Figure 1. <sup>1</sup>H-NMR spectrum of the 2AG-EU in CDCl<sub>3</sub>

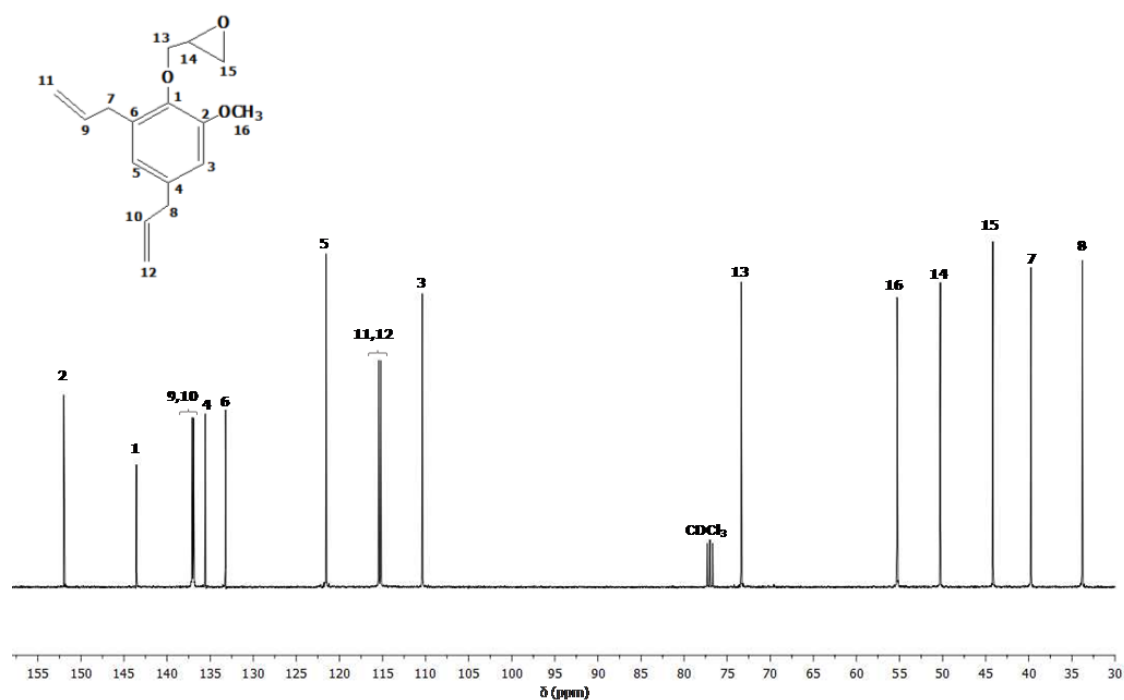


Figure 2. <sup>13</sup>C-NMR spectrum of the 2AG-EU in CDCl<sub>3</sub>

In the FTIR spectra the most typical signals could be observed, as for 2A-EU and r2A-Eu, the vinyl stretching signals at 1637 and 1630 cm<sup>-1</sup> respectively

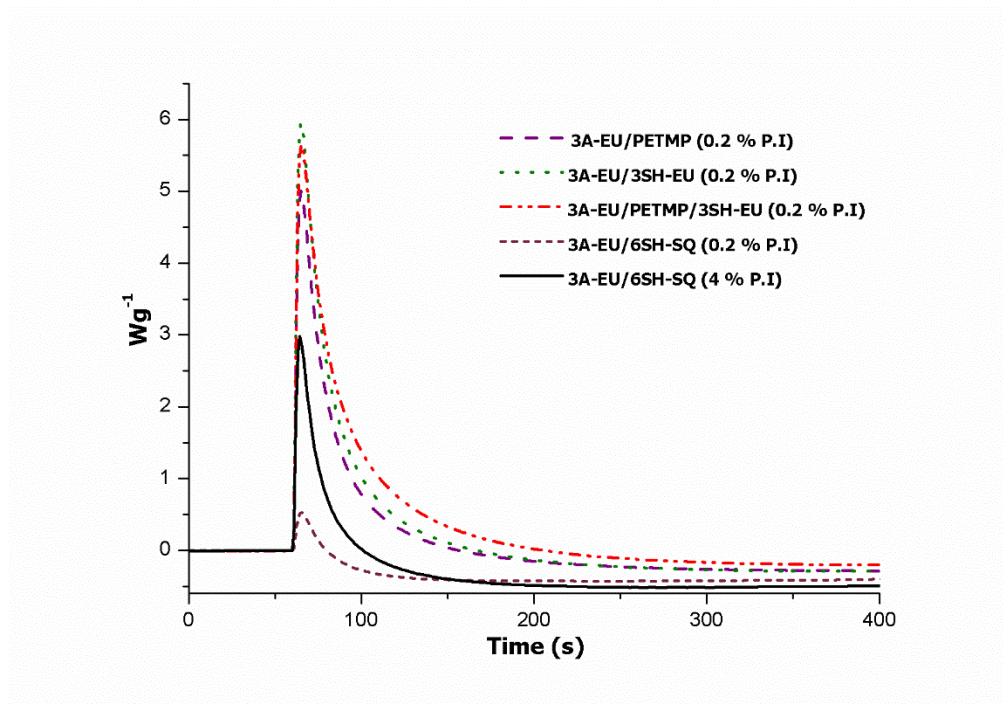
and the absorptions at  $1637\text{ cm}^{-1}$  for vinyl and  $907\text{ cm}^{-1}$  for epoxy groups for the compound 2AG-EU. The spectrum of the thiol 3SH-EU shows a weak band at  $2570\text{ cm}^{-1}$  corresponding to the S-H stretching.

In addition to eugenol derivatives, a biobased thiol derived from squalene (6SH-SQ) was synthesized following a reported procedure.<sup>36</sup> Its characterization was done by  $^1\text{H-NMR}$  and FTIR spectroscopy, which were coincident with the reported data. The structure of 6SH-SQ, although aliphatic and therefore quite flexible, allowed to reach high  $T_g$ s in thiol-epoxy formulations because of the six thiol reactive groups per molecule, as it was proved in the curing of cycloaliphatic resins.<sup>37</sup> According to that, it has been selected in the present study to help to increase the  $T_g$ s of the thermosets prepared.

### **3.2. Preparation and characterization of materials based on 3A-EU by thiol-ene reaction**

First of all, we studied the preparation of thermosets by thiol-ene reaction triggered by photoirradiation and in the presence of a radical photoinitiator. This was already done by Yoshimura et al.<sup>32</sup> using 3A-EU, but using in our case, different thiols as comonomers. First, we tried DMPA as radical initiator, since it catalysed thiol-ene reactions even in low proportion (0.1 phr).<sup>34</sup> However, in the case of eugenol derivatives this reaction did not occur even when proportions of 3 phr of DMPA were added to the formulation. Thus, we tried with a 0.2% wt% of a mixture of Irgacure 184/Irgacure 819 in 3:1 weight ratio as used by Yoshimura.<sup>32</sup>

Photocalorimetric studies were done to see the evolution of the curing process. Figure 3 shows the exothermic curing curves for the various formulations studied.



**Figure 3.** DSC thermograms corresponding to the photocuring at 30°C of the mixtures of 3A-EU with different thiols

As we can see in the photocalorimetric curves, the reaction seems to proceed quite well for all the mixtures with the exception of the formulation prepared from 6SH-SQ. However, on increasing the proportion of photoinitiator in this formulation up to 4 %wt the heat evolved increased, but it does not reach the maximum observed in the other formulations. This seems to indicate a lower reactivity of this thiol that can be explained by its structure with a high functionality and thiols attached to methine carbons.

In the mixture of PETMP/3SH-EU as thiol, the system appears to be more reactive than formulations with each one of the thiols (PETMP or 3SH-EU) separately. The shape of these curves made the evaluation of heat quite

unreliable but values around 50 kJ/thiol eq could be calculated. In a previous study we could determine similar enthalpies for thiol-ene process.<sup>34</sup>

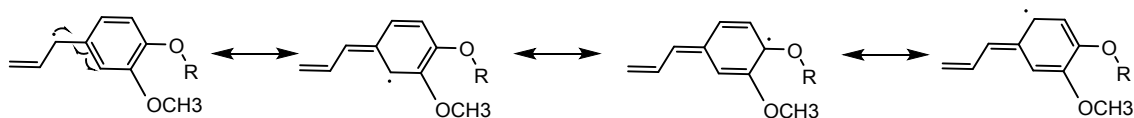
Although calorimetric studies give valuable insight to the curing process, the evolution of the reactions contributing to the curing must be evaluated from the point of view of the chemical transformations. Thus, the evolution of the most significant bands of the monomers was followed by FTIR spectroscopy during irradiation of a film of the sample on the ATR. Thiol groups evolution was monitored by the band at 2576  $\text{cm}^{-1}$  corresponding to S-H st and the reduction of allyl groups by the band at 1639  $\text{cm}^{-1}$  attributable to C=C st. As reference band we selected the absorption at 1587  $\text{cm}^{-1}$  of the aromatic ring. Table 1 shows the final conversion of allyl and thiol groups reached in the cured material.

**Table 1.** Conversions of the reactive species after thiol-ene process calculated by FTIR/ATR

Sample	Photoinitiator (wt%)	Allyl conversion (%)	Thiol conversion (%)
3A-EU/3SH-EU	0.2	71	100
3A-EU/PETMP	0.2	60	67
3A-EU/PETMP/3SH-EU	0.2	65	87
3A-EU/6SH-SQ	4	54	55

It should be commented that if the reaction was complete and occurred by an only thiol-ene process, the conversion of allyl and thiol groups should approach both to 100%. However, the values in Table 1 evidence the lower reactivity of 6SH-SQ, with parallel conversions of thiol and allyl eugenol during the photoirradiation, but reaching only partial conversion, even when a high amount of photoinitiator was added to the formulation. The mixture 3A-EU/PETMP does not react completely either, but the conversion of thiol and allyl moieties are quite similar. In contrast, the use of 3SH-EU as thiol crosslinker leads

to a surprising difference in conversions of thiol and allyl moieties. In the case of the 3A-EU/3SH-EU mixture, the thiol disappears completely but allyl is converted in only 71%. A similar behaviour is observed in the case of the 3A-EU/PETMP/3SH-EU mixture, although the difference between thiol and allyl conversion is not as high and there are still thiol groups remaining. Several authors reported on the limitations of thiol-ene processes due to the possibility of thiol-thiol coupling and carbon-carbon radical coupling.<sup>38</sup> The thiol-thiol coupling should be the responsible of the thiol exhaustion when 3SH-EU is selected. The run out of thiol leads to the prompt termination in the crosslinking process. Yoshimura et al.<sup>32</sup> also reported there was a different evolution of allyl and thiol groups, leading to remaining unreacted allyl, when 3A-EU was cured with thiols of different structure, and they attributed the difference to thiol-thiol coupling reactions. It seems that the structure of eugenol monomers could also make difficult the quantitative thiol-ene reaction. Given that thiol-ene reactions involve the formation of radical intermediates, it can be hypothesized that these unexpected results can be related to the possible formation and stabilization of radical species in the methylene carbon of the allyl group directly attached to the aromatic ring by resonance as represented in Scheme 3. The formation of such species would contribute to the slow and incomplete thiol-ene reaction, leading to the presence of unreacted allyl or -ene groups.



**Scheme 3.** Stabilization of eugenol radical species by resonance

Different samples were obtained from the various formulations by irradiation in a UV chamber during the adequate time to reach the ultimate properties. However, the amount of photoinitiator was raised to 4%wt in all the formulations to get the maximum curing degree, because of the size of the samples made difficult reaching the complete and homogenous curing and lower amounts of initiator led to sticky samples. The results of the thermal analysis of the cured samples are collected in Table 2.

**Table 2.** Thermal data of the materials obtained by thiol-ene reaction

Sample	TGA			DSC	DMTA		
	$T_{5\%}^a$ (°C)	$T_{max}^b$ (°C)	Res. <sup>c</sup> (%)	$T_g^d$ (°C)	$T_{tan\delta}^e$ (°C)	$E_r^f$ (MPa)	$E_g^g$ (MPa)
3A-EU/3SH-EU	249	386	16	1	14	2.7	6.7
3A-EU/PETMP	237	369	16	9	18	6.7	23.9
3A-EU/PETMP/3SH-EU	241	373	16	8	16	3.7	18.2
3A-EU/6SH-SQ	252	356	3	14	30	2.2	20.6

- Temperature of 5% of weight loss in  $N_2$  atmosphere
- Temperature of the maximum rate of degradation in  $N_2$  atmosphere
- Residue after thermal degradation in  $N_2$  atmosphere
- Glass transition temperature determined by DSC
- Glass transition temperature determined by DMTA
- Storage modulus in the rubbery state determined at  $\tan \delta + 50^\circ C$
- Young modulus at 30 °C under flexural conditions

As we can see, the results from TGA analysis do not show large differences between the different materials but the presence of ester groups in the PETMP structure slightly decreases the temperature of initial degradation.



By DSC and DMTA the  $T_g$  of these materials was determined. The maximum value reached was 14 °C (by DSC) or 30 °C (by DMTA) for the material obtained from the squalene thiol derivative, because of its high functionality, although the reaction was not complete. The  $T_g$ s of the other materials were lower than the one obtained from 6SH-SQ material. Yoshimura et al.<sup>32</sup> reached a maximum  $T_g$  value of 9.1 °C for the material obtained from PETMP as the thiol which is coincident with the value reached by us. The moduli measured reflect not only the degree of curing achieved but also the structure of the thiol used and therefore the rationalization of the values measured is not an easy task. The Young's moduli were measured at 30 °C and the low values agree with their rubbery state, according to the low  $T_g$ s of these materials. Moreover, from the values of the table we can conclude that the use of 3SH-EU is highly detrimental for the quality of the thiol-ene cured formulations and only improves when a mixture of 3SH-EU and PETMP was used as crosslinker agent.

The results obtained lead to the conclusion that the applicability of the materials derived from 3A-EU by thiol-ene curing is quite limited because of their low thermomechanical characteristics. The structure and functionality of the thiol crosslinker usually have a significant influence on the thermal-mechanical properties of the materials, but the tailoring of the properties of these materials is negatively affected by the incomplete reaction and the occurrence of undesired side-reactions that occurs in a greater extent in eugenol monomers, according to the results reported by Yoshimura.<sup>32</sup>

### **3.3. Preparation and characterization of the materials derived from 2AG-EU by thiol-ene/thiol-epoxy dual curing process**

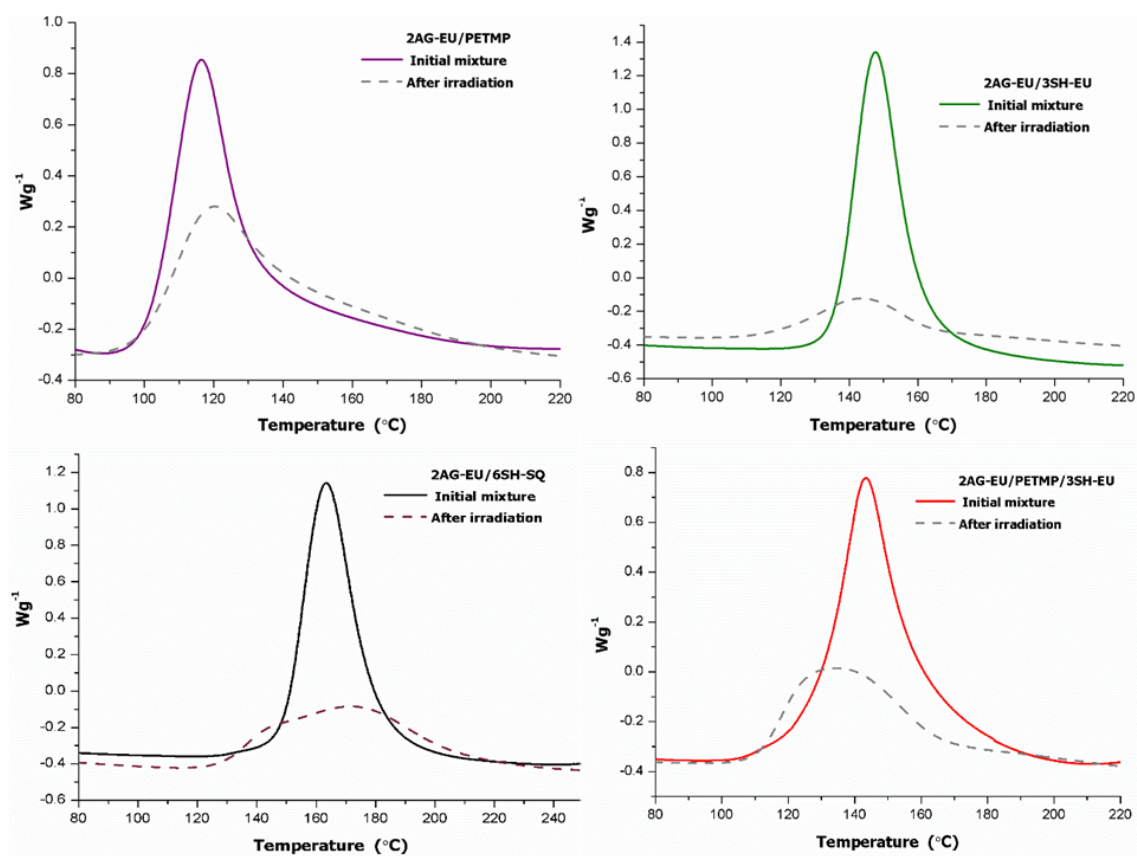
To improve the performance of eugenol-derived materials we proposed the combination of thiol-ene with thiol-epoxy reactions, following a dual curing procedure. Once studied the thiol-ene stage and characterized the materials obtained from 3A-EU, the study of this dual curing process was attempted starting from 2AG-EU formulations with 3SH-EU, PETMP, 6SH-EU and the mixture of PETMP and 3SH-EU. In addition to the photoinitiator, a base must be included in the formulation to catalyse the thermal thiol-epoxy reaction. In the present study 1-MI was selected as the base.<sup>39</sup>

Sequential thiol-ene/thiol-epoxy dual curing systems were developed in our group for formulations of DGEBA/TAIC/PETMP.<sup>34</sup> Thiol epoxy reaction requires an amine to convert the thiol groups into thiolates, which are more nucleophilic and able to attack epoxy rings, forming networks through thioether bonds. The use of latent amine precursors allowed the second step to be triggered at will. This fact opens the possibility of irradiating the initial formulation to complete the thiol-ene reaction obtaining an intermediate material able to be stored, manipulated or transformed safely. On heating this material at the required temperature the second reaction can be activated and the material can be further crosslink until it achieves the ultimate network structure and properties. However, dual systems are in general quite complex and the structure of the monomers has an enormous influence in the reactivity and can lead to a partial overlapping between processes or even limit the conversion in one of the

steps. Therefore, it is necessary to adjust the curing conditions for each reactive system.<sup>40</sup>

The implementation of a new dual curing process requires a previous study to find out the right proportion of initiator or catalyst, the reaction times required and the best reaction conditions to get the maximum degree of curing in each stage. After that, it is important to determine if both processes overlap in the conditions selected.

Figure 4 shows the calorimetric curves of the thermal stage in irradiated and non-irradiated samples.



**Figure 4.** Calorimetric curves of irradiated and non-irradiated 2AG-EU formulations with the thiols tested.

In clean sequential dual curing processes, irradiation should not affect the second thermal process. As we can see in the figure, in the present case the initial irradiation step has a notable influence on the second thermal stage, both in the shape of the curve and especially in the heat evolved, reported in Table 3 for all the formulations studied. In that table, the enthalpies released during the first photochemical step and during the second thermal thiol-epoxy stage are given separately. In addition, the enthalpies released by thermal curing of non-irradiated mixtures (initial mixture) are also given. The values of enthalpy are expressed by gram and by reactive equivalent (allyl groups in the photochemical step and epoxides in the thermal). The  $T_g$ s of the materials in the intermediate stage and after curing completion are also detailed.

**Table 3.** Reaction enthalpies and  $T_g$ s of the different formulations determined by DSC

Sample	Initial mixture		1 <sup>st</sup> stage			2 <sup>nd</sup> stage		
	$\Delta h^a$ (J/g)	$\Delta h^b$ (kJ/eq)	$\Delta h^c$ (J/g)	$\Delta h^d$ (kJ/eq)	$T_g^e$ (°C)	$\Delta h^f$ (J/g)	$\Delta h^g$ (kJ/eq)	$T_g^h$ (°C)
2AG-EU/3SH-EU	197.1	121.9	154.0	30.0	-	57.3	35.4	-
2AG-EU/PETMP	192.4	124.1	138.0	28.2	-12	171.0	110.8	36
2AG-EU/PETMP/3SH-EU	184.8	117.4	183.9	36.9	-6	106.9	68.0	28
2AG-EU/6SH-SQ	203.6	123.2	86.5	24.8	1	129.0	78.6	57

- Enthalpy released per gram on heating the initial mixture
- Enthalpy released per epoxy equivalent on heating the initial mixture
- Enthalpy released per gram during the irradiation of the mixture
- Enthalpy released per allyl equivalent during the irradiation of the mixture
- Glass transition temperature of the intermediate material
- Enthalpy released per gram of previously irradiated samples during the thermal step
- Enthalpy released per epoxy equivalent of previously irradiated samples during the thermal step
- Glass transition temperature of the final cured material

The difference between the reaction enthalpy in the epoxy-thiol thermal reaction in previously irradiated and virgin formulations gives information about the overlapping among photochemical and thermal processes. In the case of completely controlled sequential curing, both enthalpies must be similar.<sup>34</sup>

However, from the values of the table we can see that the heat released in the second curing stage, after irradiation, is lower in all the formulations than that of the non-irradiated mixtures. This result can be related to the occurrence of two different undesired processes during photoirradiation: a) thiol-epoxy reaction can start because of the increased temperature caused by the thiol-ene process and b) the remaining amount of thiol groups can be lower than expected due to thiol-thiol coupling, as previously detected in the curing of 3A-EU formulations. The difference between enthalpies in irradiated and non-irradiated samples is minimal for 2AG-EU/PETMP formulations (89% of conversion in epoxide during the second step) and maximal for 3SH-EU formulations (29 and 58% of conversion in epoxide during the thermal step for 3SH-EU and PETMP/3SH-EU, respectively). In the case of 6SH-SQ mixture, a 64% of the epoxide conversion occurs during the thermal process.

To investigate the evolution of the different reactive groups during the photochemical stage, FTIR spectra were taken during irradiation. Table 4 shows the conversion of allyl and thiol groups and the values of the theoretical conversion of thiol have been added to the table, since thiol groups also participates in the thermal thiol-epoxy process and therefore should be in excess in reference to the ally groups. The measured conversion in allyl groups has been included in these calculations for every mixture. The evaluation of epoxide, although very interesting to determine the real conversion of epoxy groups in this step, was not possible because the overlapping of the  $907\text{ cm}^{-1}$  band of the oxirane ring with other absorptions in this zone.

**Table 4.** Conversion of allyl and thiol groups in the photochemical stage of the dual curing of 2AG-EU formulations calculated by FTIR spectroscopy

Sample	Allyl conversion (%)	Thiol conversion (%)	Theoretical thiol conversion (%)
2AG-EU/3SH-EU	99	100	66
2AG-EU/PETMP	76	53	51
2AG-EU/PETMP/3SH-EU	99	76	66
2AG-EU/6SH-SQ	93	64	62

As we can see in the table, allyl groups disappear completely during photoirradiation when 3SH-EU is in the formulation, but in both cases, thiol reacts much more than the theoretically calculated, confirming that undesired thiol-thiol coupling takes place. This reaction leads to the exhaustion of thiol in the 2AG-EU/3SH-EU mixture, which implies that the second thermal thiol-epoxy process will not occur. However, some enthalpy is released in this process (see Table 3) which can be related to the homopolymerization of epoxide by the 1-MI acting as a thermal anionic initiator.<sup>39</sup>

The conversion of allyl groups in the 2AG-EU/PETMP formulation is quite low, but the conversion of thiol barely exceed the theoretical one and confirms that PETMP has not the tendency to thiol-thiol coupling as observed previously by us.<sup>34</sup> In addition, the enthalpy released in the thermal step is quite high (see Table 3) and only slightly lower than the obtained from the non-irradiated samples. Thus, the curing of this mixture is the more controlled and could be considered as a sequential dual curing, although some allyl groups might not react completely because of the special features of the eugenol structure.

Finally, 6SH-SQ seems to have the best structure to reach a practically quantitative conversion in thiol-ene process when the proportion of thiol is higher than the stoichiometric, because of the thiol excess required to react with epoxide

in the second step. It must be remembered that the 3A-EU/6SH-SQ formulation reached an only 54-55% of conversion in stoichiometric thiol-ene formulations previously studied. However, the enthalpy released in the thermal stage by epoxy equivalent is lower than expected (78.6 kJ/ee that corresponds to a 64% of epoxy reaction). Both results suggest the existence of topological restrictions in 6SH-SQ due to the high functionality of its structure that prevents completion of the reaction.

As expected, the  $T_g$ s of the intermediate materials are low (see Table 3), but the highest value corresponds to the material cured with the squalene derivative, because of its high functionality. On comparing the  $T_g$ s of the cured materials derived from 2AG-EU with the corresponding materials prepared from 3A-EU we can see a notable increase by the occurrence of the second thermal process that leads to a tighter network structure. In case of 6SH-SQ cured materials an increase in more than 50°C are achieved by the contribution of the epoxy thermal step that leads to a final  $T_g$  of 57°C that impart rigid characteristics to this material at room temperature. The  $T_g$ s of the materials prepared in the present study were higher than others reported in the literature for eugenol derivatives.<sup>31, 32</sup>

The materials prepared were characterized by TGA and DMTA and the main data obtained are collected in Table 5. The material prepared from 2AG-EU/3SH-EU formulation has not been included in this characterization because of the non-comparable structure of the network, coming from different unexpected reactions taken place.

**Table 5.** Thermal data of the materials obtained after dual curing process from 2AG-EU

Sample	TGA			DMTA		
	T <sub>5%</sub> <sup>a</sup> (°C)	T <sub>max</sub> <sup>b</sup> (°C)	Residue <sup>c</sup> (%)	T <sub>tanδ</sub> <sup>d</sup> (°C)	E <sub>r</sub> <sup>e</sup> (MPa)	E <sup>f</sup> (MPa)
2AG-EU/PETMP	329	364	19	52	10.1	184.7
2AG-EU/PETMP/3SH-EU	317	372	17	41	3.7	44.2
2AG-EU/6SH-SQ	298	366	4	76	10.2	935.7

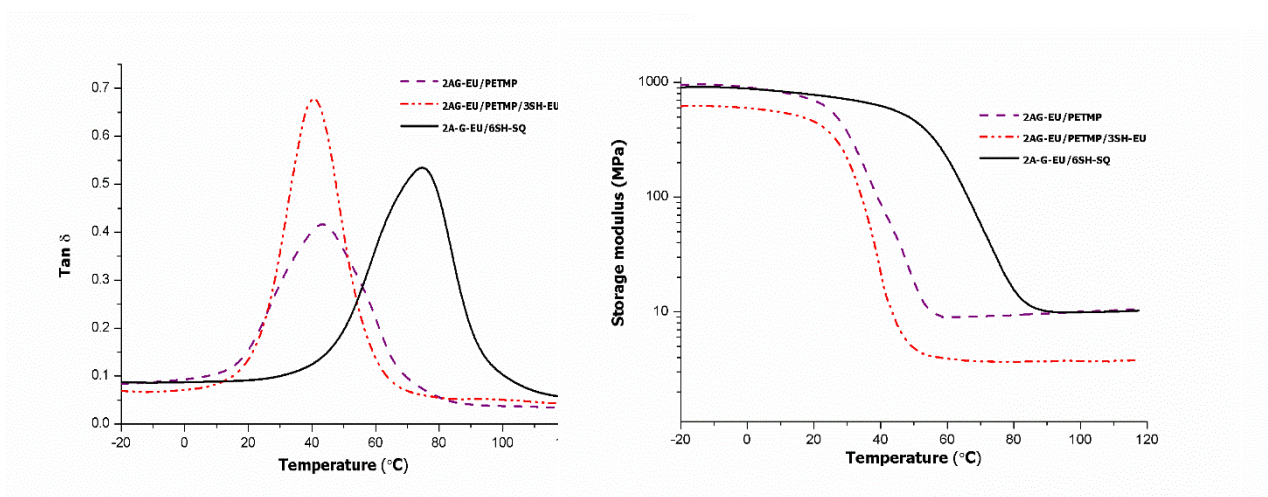
- Temperature of 5% of weight loss in N<sub>2</sub> atmosphere
- Temperature of the maximum rate of degradation in N<sub>2</sub> atmosphere
- Residue after thermal degradation in N<sub>2</sub> atmosphere
- Glass transition temperature determined by DMTA
- Storage modulus in the rubbery state determined at tan δ + 50°C
- Young's modulus at 30 °C under flexural conditions

The dual cured materials show higher temperature of initial degradation, but similar temperature of the maximum rate of weight loss and char yield in comparison with the materials obtained by thiol-ene photochemical curing from 3A-EU (see Table 2). This is related to the more densely crosslinked structure of the dual thermosets and the absence of uncrosslinked fraction, leading to a delay in the apparent start of the degradation process.

Figure 5 shows the storage modulus and tan δ variations against temperature for the materials prepared obtained by the DMTA technique. The plots of tan δ are unimodal according to the homogeneity of these materials because of the participation of thiol structures in both reactive processes that hinders phase separation of the two types of network structures. The tan δ maximum shifts to higher temperature for the squalene-derived material because of the tight network formed. Similarly, the decrease in storage modulus associated with the network relaxation takes place at higher temperature than the other materials. The values of relaxed modulus are similar for the materials obtained from 6SH-SQ and PETMP, in spite of having very different structures.



This may be caused by the different final conversion of the cured materials and the coexistence of side-reactions producing a network structure different from the one expected. It is noticeable the low thermomechanical characteristics of the material containing 3SH-EU structures.



**Figure 5.** Plots of  $\tan \delta$  and storage modulus against temperature for the various materials prepared.

Young's moduli, determined at 30 °C (see Table 5), show notable differences on comparing the three materials, being the more rigid the thermoset obtained from 6SH-SQ.

The comparison of the thermomechanical data of the materials obtained from 2A-EU and 3A-EU (Tables 5 and 2, respectively) allows to see the valuable contribution of the thiol-epoxy reaction in the enhancement of the characteristics of the cured materials. Although from the point of view of the structure, thiol-ene and thiol-epoxy processes should lead to similar thermomechanical properties, the undesired side-reactions of thiol-ene process and incomplete conversion in these eugenol monomers justify the observed differences.

Dogbone samples of dual cured materials were prepared to perform stress-strain at break tests in DMTA at 30 °C. Table 6 shows the values obtained, together with the values of microindentation hardness measured from the prismatic samples prepared for DMTA studies.

**Table 6.** Mechanical data of the materials obtained by dual curing by stress-strain at break and microindentation hardness testing. Coefficients of variation less than 8% for stress, strain and tensile modulus, and less than 5% for microindentation hardness.

Sample	Strain at break (%)	Stress at break (MPa)	Tensile elastic modulus <sup>a</sup> (MPa)	Microindentation hardness <sup>b</sup> (HV)
2AG-EU/PETMP	20.5	11.7	315.9	7.6
2AG-EU /PETMP/3SH-EU	27.5	13.8	152.2	2.0
2AG-EU /6SH-SQ	3.7	39.1	1814.9	11.0

<sup>a</sup> The tensile elastic modulus was determined as the slope of the curve at the initial and proportional part of the curve.

<sup>b</sup> Indentation test load of 10 g for 2AG-EU /PETMP/3SH-EU and 50 g for the others.

From the mechanical point of view, it can be confirmed that the material derived from 6SH-SQ shows the highest stress at break, stiffness and microindentation hardness because of the multifunctionality and smaller size of the structure between thiol groups, leading to stiffer materials and a higher crosslinking density. The worst mechanical performance in the same terms (stress at break, stiffness and microindentation hardness) was obtained for the material prepared from the PETMP/3SH-EU formulation, which also presents higher ductility because of the smaller difference between  $T_g$  and measurement temperature (room temperature).

#### 4. Conclusions

The monomer 2AG-EU, derived from eugenol, has been synthesized by a three-step procedure that includes a first allylation of eugenol, a Claisen rearrangement a glycidation of the phenol obtained with epichlorohydrin in basic medium. The other eugenol derivatives, 3A-EU, with three allyl groups in the structure, and 3SH-EU, with three thiol groups were successfully prepared according to previous descriptions.

The photoinduced thiol-ene polymerization of 3A-EU with three different thiols was studied by photocalorimetry and FTIR spectroscopy. The curing was incomplete in all cases by the low reactivity of thiol and eugenol allyl derivatives, and in some cases, undesired side-reactions took place, leading to materials with low  $T_g$  and poor thermomechanical performance.

The curing of the allyl-glycidyl eugenol derivative, 2AG-EU, with different thiols by means of a combination of photoinduced thiol-ene and thermally-activated thiol-epoxy polymerization reactions was studied. Calorimetric and spectroscopic measurements showed, however, that the dual-curing procedure applied in this work did not have a clean sequential character, since the first thiol-ene process did not reach completion and photochemical and thermal process partially overlapped. This was rationalized in terms of the structure of the eugenol derivatives, which had a negative effect on the photochemical thiol-ene processes.

The dual-cured materials obtained from the eugenol derivative 2AG-EU had enhanced thermal and mechanical properties in comparison with those obtained from 3A-EU. A  $T_g$  of 57 °C (by DSC) and 76 °C (by DMTA) could be

obtained for the material obtained from the combination of 2AG-EU with a hexathiol derived from squalene (6SH-SQ). This material also had higher stiffness, microindentation hardness and tensile strength values. In contrast, dual-cured materials obtained from the combination of 2AG-EU with the trithiol derived from eugenol, 3SH-EU, had a very low thermal and mechanical performance.

The contribution of thermal thiol-epoxy reactions to thiol-ene cured eugenol materials improves thermal and thermomechanical characteristics of the thermosets in comparison to purely photocrosslinked materials.

### **Acknowledgments**

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## Supporting information

### Synthesis of the triallyl compound from eugenol (3A-EU):

#### *Synthesis of 1-allyl-4-allyloxy-3-methoxybenzene (2A-EU)*

16.4 g of eugenol (100 mmol) and 4.40 g of pulverized NaOH (110 mmol) were dissolved in 120 mL of dry DMF in a 500 mL three necked round bottomed flask under inert atmosphere. The mixture was stirred for 10 min and then allyl bromide (13.30 g, 110 mmol) was added dropwise over 1 h at 40°C, once the addition was finished the solution was maintained at 40°C for 3 h and then half an hour at 70°C. The solvent was eliminated in the rotavap and the oil was dissolved in CHCl<sub>3</sub> and filtered to eliminate the precipitate of inorganic salts. The organic phase was washed twice with distilled water, dried over anhydrous MgSO<sub>4</sub> and the solvent eliminated to obtain 96% yield of *2A-EU* as a yellowish oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ in ppm): 6.7 d (Ar, 1H), 6.6 m (Ar, 2H), 6.1 m (-CH=,1H), 5.9 m (-CH=,1H), 5.3 dd (CH<sub>2</sub>=, 1H), 5.2 dd (CH<sub>2</sub>=, 1H), 5.0 m (CH<sub>2</sub>=, 2H), 4.50 d (-CH<sub>2</sub>-O-, 2H), 3.8 s (CH<sub>3</sub>-O-, 3H) and 3.3 d (-CH<sub>2</sub>-Ar, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ in ppm): 149.2 (Ar), 146.2 (Ar), 137.8 (-CH=CH<sub>2</sub>), 133.7 (-CH=CH<sub>2</sub>), 133.0 (Ar), 120.2 (Ar), 118.0 (=CH<sub>2</sub>), 115.8 (=CH<sub>2</sub>), 113.5 (Ar), 112.0 (Ar), 70.0 (-CH<sub>2</sub>-O), 56.0 (CH<sub>3</sub>-O-) and 40.0 (-CH<sub>2</sub>-). FT-IR (ATR): 3070, 3015, 2970, 2830, 1680, 1630, 1592, 1505, 1460, 1423, 1250, 1225, 1145, 1023, 997, 910, 850, 803 and 749 cm<sup>-1</sup>.

#### *Pyrolysis of 1-allyl-4-allyloxy-3-methoxybenzene (r2A-EU)*

In a glass tube provided with a gas outlet 19.48 g (95.5 mmol) of *2A-EU* were stirred at 200 °C for 3 h to obtain a 98% yield of a yellowish oil. <sup>1</sup>H NMR

(CDCl<sub>3</sub>, δ in ppm): 6.59 s (Ar, 2H), 5.91 m (-CH=, 2H), 5.6 s (-OH, 1H), 5.1 m (CH<sub>2</sub>=, 4H), 3.9 s (CH<sub>3</sub>-O-, 3H), 3.4 dd (-CH<sub>2</sub>-Ar, 2H) and 3.3 dd (-CH<sub>2</sub>-Ar, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ in ppm): 146.4 (Ar), 141.6 (Ar), 138.0 (-CH=CH<sub>2</sub>) 136.8 (-CH=CH<sub>2</sub>, 131.1 (Ar), 125.5 (Ar), 122.0 (Ar), 115.5 (=CH<sub>2</sub>), 115.4 (=CH<sub>2</sub>), 108.9 (Ar), 56.0 (CH<sub>3</sub>-O-), 40.0 (-CH<sub>2</sub>-) and 34.0 (-CH<sub>2</sub>-). FT-IR (ATR) 3540, 3075, 3012, 2970, 2900, 2845, 1630, 1605, 1442, 1498, 1293, 1227, 1205, 1146, 1070, 993, 910, 848 and 750 cm<sup>-1</sup>.

#### *Synthesis of 1,3-diallyl-4-allyloxy-5-methoxybenzene (3A-EU)*

19.14 g of the previously obtained r2A-EU (94 mmol), 4.13 g (103 mmol) of pulverized NaOH and 120 mL of DMF were placed in a three necked round bottomed flask under inert atmosphere. The mixture was stirred for 10 min and then allyl bromide (12.49 g, 105 mmol) was added dropwise over 1 h at 40°C. Once the addition was completed the mixture was kept at 40°C for 3 h and then half an hour at 70°C. The reaction product was treated with distilled water to dissolve the NaBr formed and extracted with chloroform. The organic phase was washed twice with distilled water, dried with anhydrous MgSO<sub>4</sub> and concentrated on a rotary evaporator to obtain 97% yield of 3A-EU as a yellowish oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ in ppm): 6.7 s (Ar, 2H), 6.05 m (-CH=, 1H), 5.90 m (-CH=, 2H), 5.34 dd (CH<sub>2</sub>=, 1H), 5.19 dd (CH<sub>2</sub>=, 1H), 5.15-5.0 m (CH<sub>2</sub>=, 4H), 4.46 d (-CH<sub>2</sub>-O-, 2H), 3.87 s (CH<sub>3</sub>-O-, 3H), 3.38 d (-CH<sub>2</sub>-Ar, 2H), 3.31 d (-CH<sub>2</sub>-Ar, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ in ppm): 152.6 (Ar), 144.1 (Ar), 137.5 (-CH=CH<sub>2</sub>), 137.3 (-CH=CH<sub>2</sub>), 135.7 (Ar), 134.5 (Ar), 133.7 (-CH=CH<sub>2</sub>), 121.7 (Ar), 117.0 (=CH<sub>2</sub>), 115.8 (=CH<sub>2</sub>), 115.5 (=CH<sub>2</sub>), 110.5 (Ar), 73.7 (-CH<sub>2</sub>-O-), 55.7 (CH<sub>3</sub>-O-), 40.1 (-CH<sub>2</sub>-)

and 34.3 (-CH<sub>2</sub>-). FT-IR (ATR) 3072, 3018, 2901, 2825, 1637, 1583, 1510, 1451, 1418, 1256, 1230, 1141, 1026, 986, 907, 804 and 752 cm<sup>-1</sup>

### **Synthesis of the hexathiol derived from squalene (6SH-SQ)**

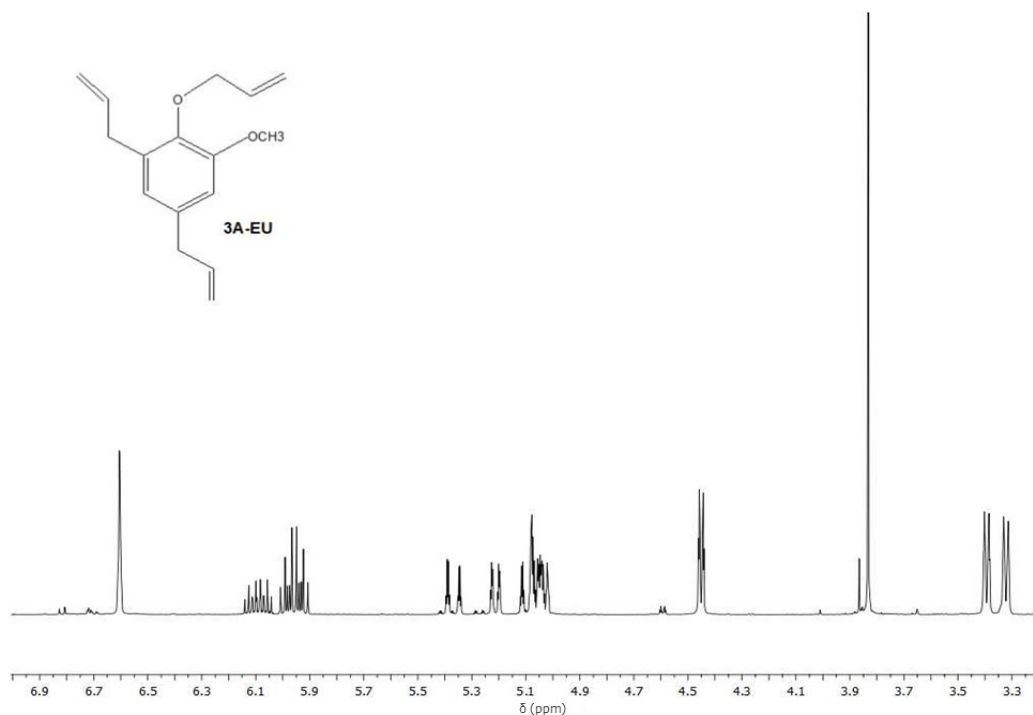
#### *Photochemical thiol-ene reaction (6STA-SQ)*

A mixture of 5 g (12.2 mmol) of SQ, 11.1 g (146 mmol) of TAA and 0.062 g (0.24 mmol) of DMPA were photoirradiated with a UV lamp at 356 nm for 30 min. The product was dissolved in CHCl<sub>3</sub> and extracted with a 10% NaOH solution and then washed with water and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed on a rotary evaporator. A clear viscous liquid was obtained with 87% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ in ppm), 3.3 broad (CH-S, 6H), 2.3 s (CH<sub>3</sub>-CO-, 18H), 1.1-2.0 broad (-CH<sub>2</sub>- and -CH-, 26H) and 0.8-0.9 broad (CH<sub>3</sub>-, 24H). FT-IR (ATR): 2960, 2925, 1680, 1450, 1380, 1365, 1110, 1140, 950, 752 and 620 cm<sup>-1</sup>

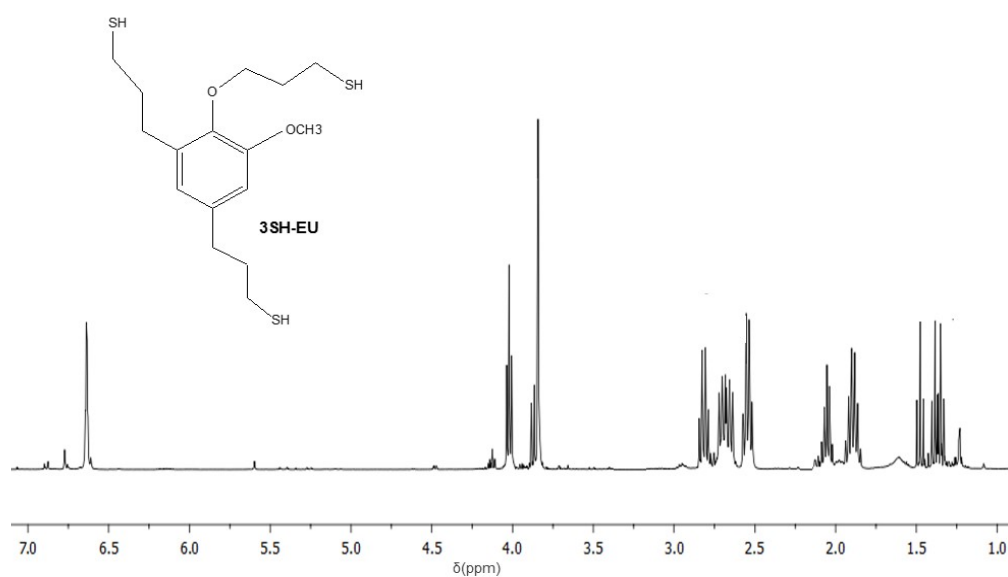
#### *Hydrolysis of 6STA-SQ (6SH-SQ)*

9 g (10.4 mmol) of the 6STA-SQ were put in a round-bottomed flask with 60 mL of methanol and 1.8 g (45 mmol) of pulverized NaOH and vigorously stirred for 5.5 h at reflux temperature and inert atmosphere. The solution was allowed to cool and the solvent was removed. The product obtained was dissolved in water and acidified with 0.1 M HCl solution and then extracted with CHCl<sub>3</sub>. The organic phase was washed with distilled water and dried over anhydrous MgSO<sub>4</sub>. After solvent evaporation the purification of 6SH-SQ was carried out by silica gel column chromatography using hexane/ethyl acetate 8/2 mixture as eluent. The purified product was a pale yellow viscous liquid with a 71 % yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ in ppm), 2.60 broad (-CH-S-, 6H), 1.10-1.95

unresolved broad signals (-CH<sub>2</sub>-, -CH- and -SH, 32H) and 0.8-1.05 broad (CH<sub>3</sub>-, 24H). FT-IR (ATR): 2955, 2923, 2570, 1450, 1378, 1350 and 752 cm<sup>-1</sup>. Spectra are fully coincident to those reported in the literature.<sup>22</sup>



**Figure A.** <sup>1</sup>H NMR spectrum of the triallyl (3A-EU) derived from eugenol registered in CDCl<sub>3</sub>



**Figure B.** <sup>1</sup>H NMR spectrum of the trithiol (3SH-EU) derived from eugenol registered in CDCl<sub>3</sub>