

# Self-healing polymers based on eugenol via combination of thiol-ene and thiol oxidation reactions

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**Abstract** Eugenol, a relatively cheap and abundant renewable resource, is used to design terminal diene compounds. Thiol-ene click reactions between the terminal diene intermediates and 1,6-hexanedithiol afford the corresponding oligomers with molecular mass of about 1.3 kDa. Finally, the oligomers and tricapto compound trimethylolpropane tris(3-mercaptopropionate) undergo thiol-oxidation reactions to form disulfide-crosslinked polymers. The brown polymers indicate self-healable behavior under UV light irradiation, presumably due to reversible reshuffling of weak disulfide bonds and/or reversible addition-dissociation reaction between benzoxazine and thiol groups.

**Keywords** Eugenol · Self-healing · Thiol-ene · Renewable resource

## Introduction

Resource and energy crisis has been a global problem due to strong dependence of human life on fossil resources that become more and more deficient. Therefore, importance of renewable natural resources is emphasized in recent years by both scientists and engineers [1–8]. Eugenol (i.e., 4-allyl-2-methoxy phenol), a major component of clove essential oil, is a relatively cheap natural feedstock [9]. This compound has been successfully used in flavoring and pharmaceutical

industry because of its pleasant odor. Besides, applications of eugenol in preparing polymer materials also draw great attention in recent years, because this renewably unique compound and its derivatives can be used as aromatic monomers [10–13]. Polymers from eugenol can usually endure high temperatures. For example, Muthusamy's research group reported preparation of bio-based benzoxazine monomers by reactions between eugenol and different diamines [14]. After thermal curing of the benzoxazine monomers, the resulting polymers showed high thermal stability (340 °C) as well as good flame retardance. More recently, Deng and coworkers prepared polymeric microspheres with diameters ranging 500–800 μm from eugenol derived methacrylate monomer by using suspension polymerization in aqueous media [15]. The reusable microspheres possess remarkably large oil absorbency in a relatively high speed.

Self-healing or self-repairing phenomena are common in nature. For example, lost or injured tissues and organs can be regenerated or remended in most living organisms. Inspired by these phenomena, studies on artificial self-healing materials have attracted much interest in the past two decades [16–19]. Intrinsic and extrinsic self-healing materials are the two main types of the matter, and the former is more promising as these materials can be self-healed for many times under certain stimuli or even without external stimuli [20]. Among various intrinsic self-healing polymers, sulfur-containing materials such as sulfides, disulfides and trithiocarbonates are intensively researched due to relatively easy accessibility to weak sulfur-sulfur and carbon-sulfur bonds, and these bonds can be reversibly formed and cleaved under light, heating or redox stimuli [21–24]. Well known routes to carbon-sulfur and sulfur-sulfur bonds are thiol-ene and thiol-oxidation reactions [25, 26]. A typical example is the work of Canadell and his colleagues reported in 2011 [27]. They utilized a disulfide-bond-containing epoxy compound and a four-thiol-group species

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to undergo ring-opening reactions between thiol and epoxy groups. The resulting crosslinked material, after being cut, showed self-healing behavior at 60 °C for 1 h. This self-healing property may originate from reversible exchange of disulfide groups in the polymer. Recently, our research group designed a photo-active trithiocarbonate that can be a crosslinker of multi-hydroxyl polymer, and the crosslinked polymer indicated self-healing property under UV irradiation because of weak C-S bonds in the polymer can be reversibly reshuffled under light stimulus [28].

Herein, we report preparation of self-healing polymers from the renewable eugenol by combining thiol-ene and thiol-oxidation reactions. Thiol-ene/yne click reactions have been extensively studied in recent years [29, 30]. To the best of our knowledge, there are no reports on preparation of self-healing functional polymers based on the cheap and renewable eugenol resource.

## Experimental

### Materials

1,4-Phenylenediamine, allylic bromide, 1,6-hexanedithiol, benzophenone, potassium carbonate, sodium carbonate, sodium thiosulfate, sodium iodide, trimethylolpropane tris(3-mercaptopropionate), acetone, dichloromethane (DCM), tetrahydrofuran (THF), 37 % aqueous HCHO, chloroform, *iso*-propanol and 30 % H<sub>2</sub>O<sub>2</sub> were all AR grade and were used straightly as received from Shanghai Aladdin Co. Ltd. Eugenol (industrial grade) was purified on silica gel column prior to use.

### Characterization

Gel permeation chromatography (GPC) was conducted on an HP 1100 HPLC, equipped with a Waters 2414 refractive index detector and three Styragel HR 2, HR 4, HR 5 of 300 × 7.5 mm columns (packed with 5 mm particles of different pore sizes). The column packing allowed the separation of polymers over a wide molecular weight range of 500–1,000,000. THF was used as the eluent at a flow rate of 1 mL·min<sup>-1</sup> at 40 °C. PMMA standards were used as the reference. IR measurement was completed with FTIR-650 spectrometer by using KBr pellet pressing method. Structures of trithiocarbonate and the copolymer poly(MMA-co-HEA) were characterized by <sup>1</sup>H NMR spectroscopy on a Bruker AV 400 MHz spectrometer. CDCl<sub>3</sub> was used as the solvent. Thiol-ene reactions and self-healing experiments were conducted under 365 nm of UV irradiation by using a UV lamp (power 2500 mW·cm<sup>-2</sup>). The glass transition temperature (T<sub>g</sub>) was tested by a differential scanning calorimeter DSC 2910 (Modulated DSC, TA Instruments Corporation, USA). Tensile strength analysis was conducted with an electronic universal testing machine

according to National standard GB/T1040.2-2006. Impact strength was performed on an impact testing machine with the type of X CJ-40. SEM images were given from a Hitachi scanning electron microscope.

### Synthesis of *O*-allylic eugenol (2)

To a 250 mL of flask were added sequentially eugenol (1.642 g, 10 mmol), allylic bromide (1.331 g, 11 mmol), potassium carbonate (1.382 g, 10 mmol), and acetone (20 mL). The mixture was stirred at room temperature for 24 h. After the reaction was completed, water was added to the mixture, followed by adding dichloromethane to extract product. The organic phase was dried with anhydrous sodium sulfate, and crude product was obtained after removal of solvent. Further purification of the crude product on silica gel chromatography with petroleum ether/ethyl acetate (5 : 1, v : v) as eluant gave oily **2** (1.14 g, 56 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.83–6.68 (m, 3H), 6.16–5.83 (m, 2H), 5.49–5.24 (m, 2H), 5.12–5.03 (m, 2H), 4.63–4.55 (m, 2H), 3.86 (s, 3H), 3.44–3.36 (m, 2H).

### Synthesis of eugenol-based oligomer (3) via thiol-ene reaction

The allylic eugenol **2** (1.02 g, 5 mmol), 1,6-hexanedithiol (1.127 g, 7.5 mmol), and benzophenone (0.01 g) were dissolved in dichloromethane (10 mL). The solution was irradiated under UV light for 3 h. Solvent and excess monomers were removed under reduced pressure, and the residue was crude oligomer **3** as a viscous liquid (0.785 g, 77 % conversion based on eugenol).

### Preparation of eugenol-derived crosslinked polymer (5)

The oligomer **3** (4.0 g), crosslinker trimethylolpropane tris(3-mercaptopropionate) (**4**) (20 mg), NaI (10 mg) and 30 % H<sub>2</sub>O<sub>2</sub> (2 mL) were dissolved in THF (40 mL). The resulting solution was stirred at room temperature till gel appeared, then aqueous 5 % Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (10 mL) was poured into the mixture, and stirring was continued. When yellow color disappeared, the system was stirred for another 1 h. After filtration and drying, the polymer **5** was obtained as a light brown gel-like semi-solid, which can form a sticky film on glass substrates.

### Synthesis of eugenol-derived benzoxazine (6)

To a 250 mL of flask were added sequentially eugenol (3.28 g, 20 mmol), 1,4-phenylenediamine (1.08 g, 10 mmol) and 37 % aqueous formaldehyde (3.25 g, 40 mmol). The mixture was stirred at 120 °C for 40 min. When the reaction was completed, chloroform (20 mL) was added, and the mixture was washed twice with saturated aqueous Na<sub>2</sub>CO<sub>3</sub>. The organic

phase was dried with anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and the filtrate was concentrated to afford crude product (4.0 g), which was recrystallized in iso-propanol gave benzoxazine product **6** (3.05 g, 63 %). M.p. 89–91 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.14 (s, 4H), 6.60 (s, 2H), 6.46 (s, 2H), 5.95–5.85 (m, 2H), 5.42 (s, 4H), 5.20–5.15 (m, 2H), 4.56 (s, 4H), 3.98 (s, 6H), 3.31–3.26 (m, 4H).

### Synthesis of eugenol-derived benzoxazine polymer via thiol-ene

The eugenol-derived benzoxazine monomer **6** (0.242 g, 0.5 mmol), 1,6-hexanedithiol (0.078 g, 0.52 mmol) and benzophenone (0.001 g) were dissolved in dichloromethane (10 mL). The solution was irradiated under UV for 3 h. Excess cold methanol was then poured into the reaction mixture to precipitate polymer product (0.21 g, 62 %). Molecular weight of the oligomer was  $M_n$ ,  $\text{GPC}$  = 1307 from GPC.

### Preparation of eugenol-derived benzoxazine crosslinked polymer (**8**)

In a similar method as preparation of the polymer **5**, eugenol-derived benzoxazine crosslinked polymer **8** was obtained. Note that the precipitated **8** is at swell state and can form a film on glass substrates. But, compared with polymer **5**, the film of **8** becomes relatively “hard” after being dried.

### Measurement of chemical resistance of the eugenol-derived crosslinked polymer

The crosslinked polymer was formed a film on a glass substrate (mass of the film was weighed  $m_1$ ), which was then dipped into the corresponding media under ambient conditions. One week later, the sample was taken out of the media, dried, weighed (mass of the film was weighed  $m_2$ ) and observed the appearance as well as changes. Relative loss of mass of the film was calculated as  $\Delta m\% = [(m_1 - m_2)/m_1] \times 100\%$ . The smaller  $\Delta m\%$  is, the better chemical resistance of the polymer is.

### Self-healing behavior of the eugenol-derived crosslinked polymer

The film of the crosslinked polymer was scratched by a razor. Then, the “injured” sample was exposed to UV ( $\lambda = 365$  nm) light. After a period of time, changes of the sample are observed.

## Results and discussion

### Synthesis of *O*-allylic eugenol (**2**)

There exists an allylic group in eugenol molecule. It will become a diene if another allylic group is introduced. Thus, by using Williamson method for ether synthesis, eugenol reacts with allylic bromide under basic conditions to afford *O*-allylic eugenol (**2**) in moderate yield (Scheme 1). Structure of compound **2** is confirmed by  $^1\text{H}$  NMR spectrum shown in Fig. 1. Note that peaks at 0–2 ppm in Fig. 1 may be residues of water (c.a. 1.6 ppm) and petroleum ether, which have no negative effect on subsequent reactions such as thiol-ene.

### Synthesis of eugenol-derived oligomer (**3**) via thiol-ene reaction

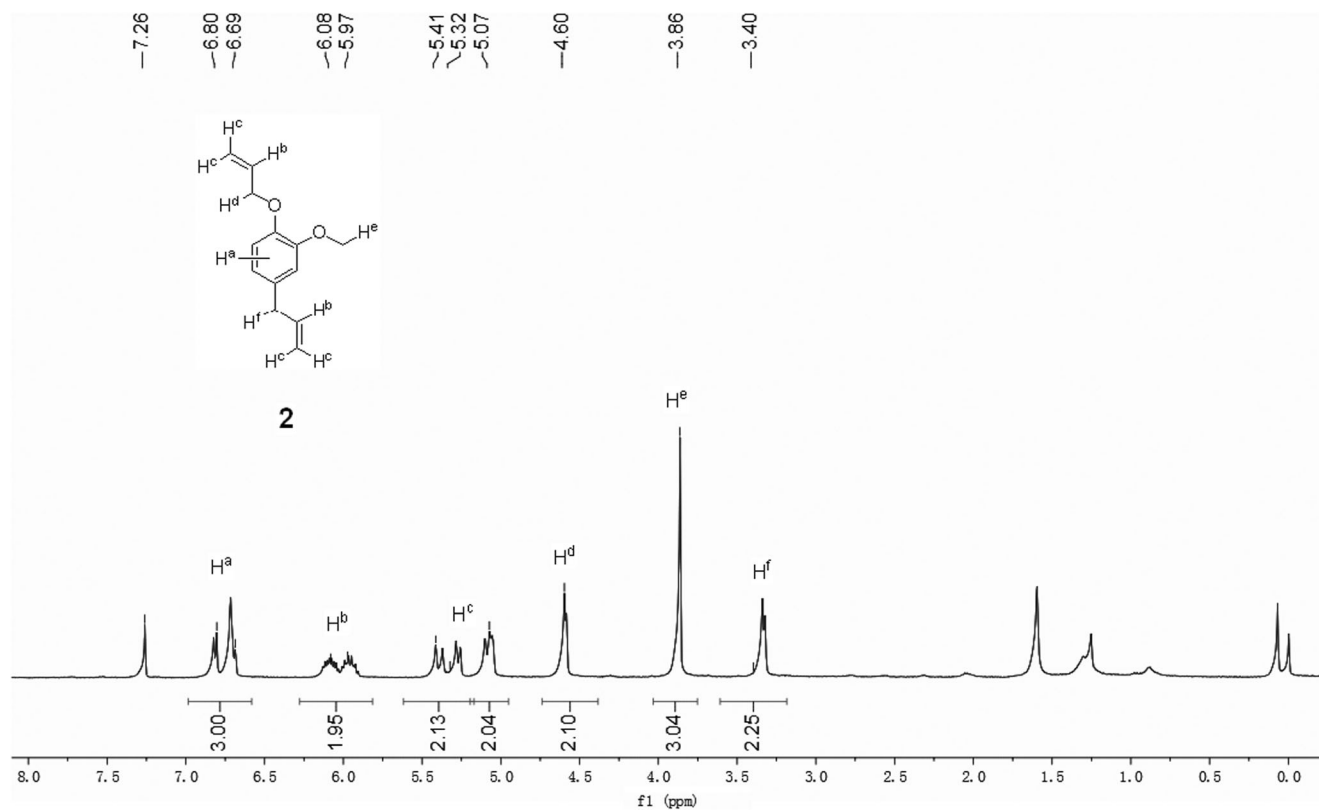
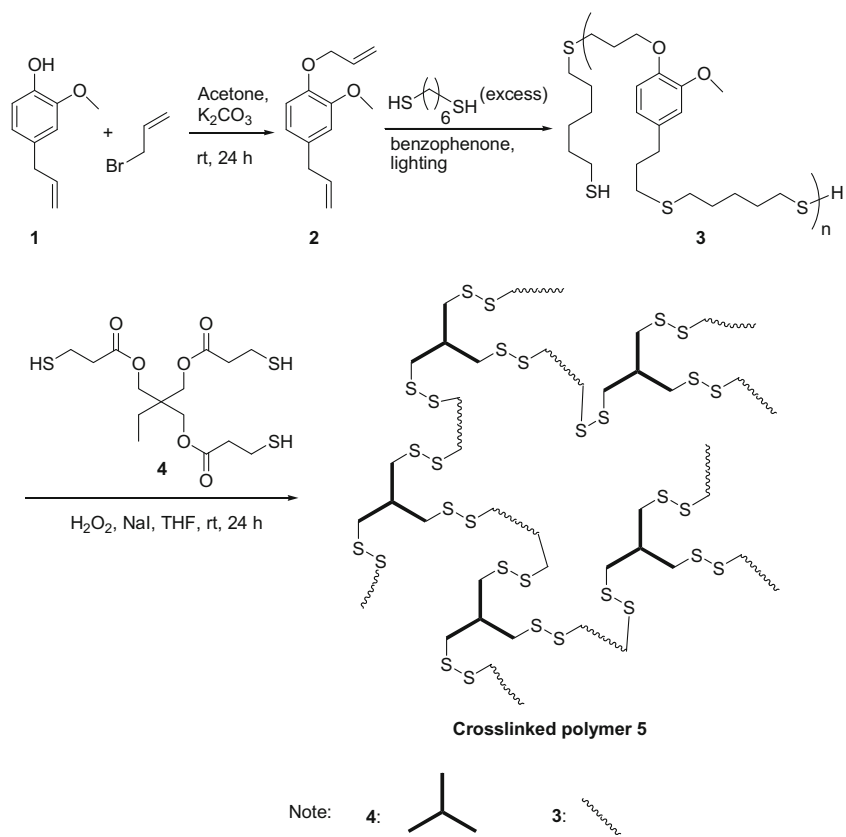
Thiol-ene reaction can proceed through radical or ionic route. For example, thia-Michael addition is usually through sulfur anion's attack on an electron-deficient double bond [31]. On the other hand, in the presence of a radical initiator, thiol-ene reaction will proceed via radical species, a frequently utilized route to varieties of polymers and oligomers [32]. For our system, the eugenol-derived diene compound **2** can undergo thiol-ene reaction with 1,6-hexanedithiol in the presence of a benzophenone photo-initiator under UV irradiation conditions. After reaction for 3 h, the corresponding oligomer was obtained.  $^1\text{H}$  NMR spectrum indicates that vinyl signal (chemical shift of 5–6 ppm) almost disappear completely, meaning that the “ene” part of compound **2** is converted to saturated one (Fig. 2). To keep terminal groups to be mercapto ones, excess 1,6-hexanedithiol is added in the reaction system.

According to Fig. 2, the weak peak at chemical shift of 2.26 is signal of mercapto protons ( $\text{H}^a$ ), and the number of these terminal protons is designated as two, which is base of other peaks. Thus, the number of aryl protons ( $\text{H}^b$ ) is about 18, indicating that there are around six phenyl units ( $18 \div 3 = 6$ ) in the oligomer. The number of  $\text{H}^c$  (c.a. 12) and  $\text{H}^d$  (c.a. 18) further prove that about six units exist in the oligomer. Therefore, molecular weight of the oligomer **3** can be estimated as  $M_{n,\text{NMR}} = 340 \times 6 + 150 = 2190$  Da. The molecular weight of **3** measured by GPC is  $M_{n,\text{GPC}} = 2280$  Da, which is consistent with  $M_{n,\text{NMR}}$ . Molecular weight distribution of **3** is 1.66.

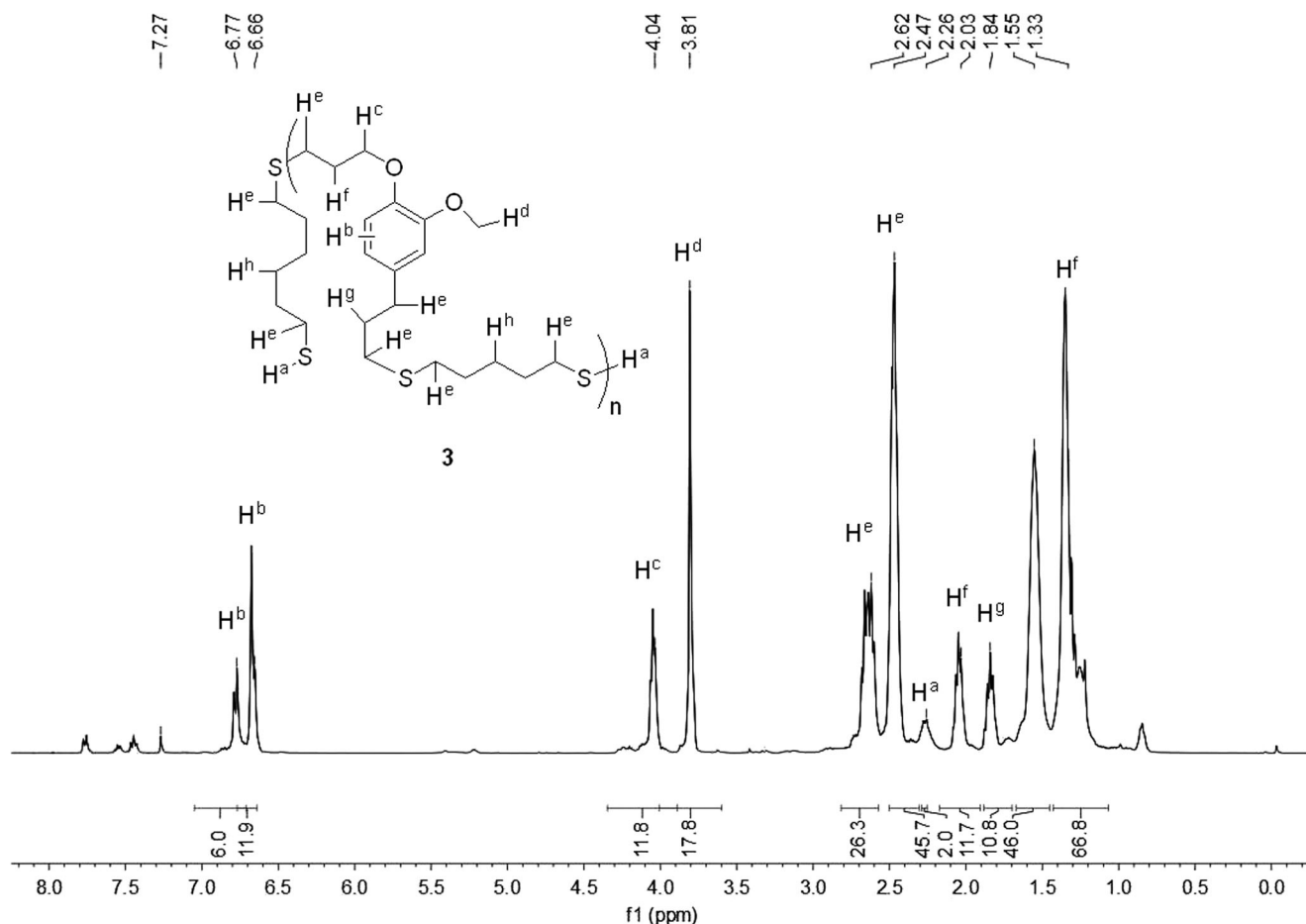
### Preparation and characterization of eugenol-derived crosslinked polymer (**5**)

With oligomer **3** in hand, we then investigate crosslinking of **3** with trimethylolpropane tris(3-mercaptopropionate) (**4**) under oxidation conditions. It is known that thiol compounds can be oxidized by iodine or hydrogen peroxide to form the corresponding disulfide products [33]. Herein, reactions between **3**

**Scheme 1** Preparation of eugenol-derived disulfide-bonds-containing polymer **5**



**Fig. 1** <sup>1</sup>H NMR spectrum of *O*-allylic eugenol (**2**)



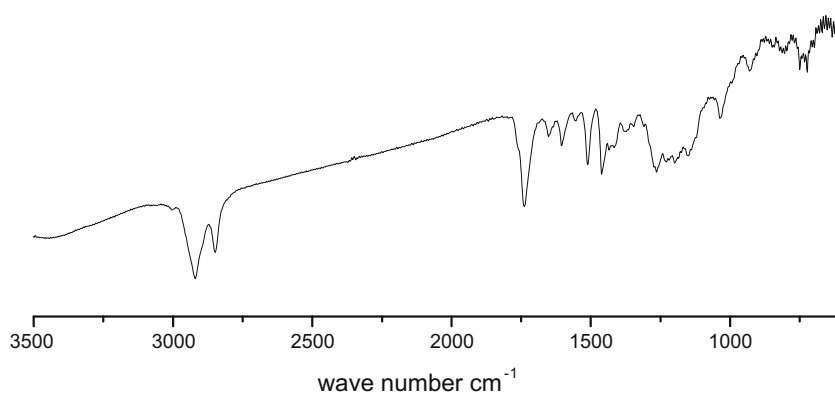
**Fig. 2**  $^1\text{H}$  NMR spectrum of eugenol-derived oligomer (**3**)

and **4** are conducted under hydrogen peroxide-NaI oxidation conditions, in which in situ formed iodine acts as an oxidant (Scheme 1). After reaction, the oligomer **3** is transformed into crosslinked polymer **5**. IR spectrum of **5** is shown in Fig. 3. Absence of peaks at  $2500\text{--}2600\text{ cm}^{-1}$  indicates that mercapto groups ( $-\text{SH}$ ) in oligomer **3** has been consumed and transformed in to double sulfide groups ( $-\text{S}-\text{S}-$ ). Furthermore,

weak peaks at  $400\text{--}500\text{ cm}^{-1}$  may prove the presence of double sulfide groups ( $-\text{S}-\text{S}-$ ).

From IR spectrum of polymer **5**, crosslinking is confirmed. What's more, medium resistance of **5** is measured to estimate qualitatively crosslinking density. The results are shown in Table 1. The polymer shows good resistance to strong acid, a certain resistance to ethanol and toluene, and poor resistance

**Fig. 3** IR spectrum of the crosslinked polymer **5**

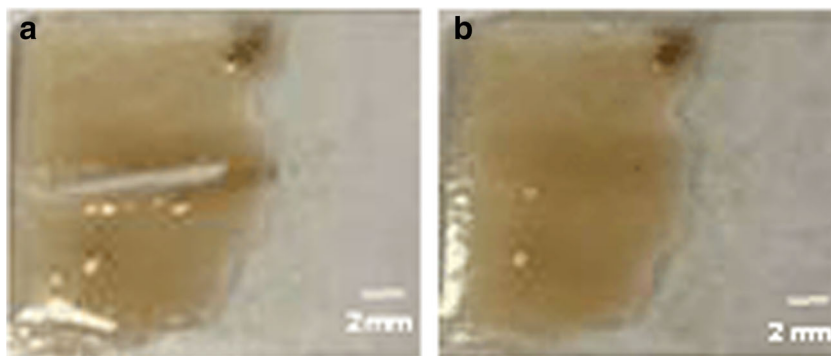




**Table 1** Medium resistance of the polymer **5**<sup>a</sup>

Medium	$m_1/g^b$	$m_2/g^b$	Relative mass loss (%) <sup>b</sup>	Whiteness	Chapped	Breaking off
HCl <sup>c</sup>	1.9634	1.9634	0	no	no	no
NaOH <sup>d</sup>	2.2032	2.1814	0.99	yes	yes	yes
THF	2.0878	2.0831	0.23	yes	yes	yes
ethanol	2.3748	2.3748	0	no	yes	no
toluene	2.1292	2.1241	0.24	no	yes	yes

<sup>a</sup> the polymer is dipped into the medium for 7 days under ambient conditions. <sup>b</sup>  $m_1$ : mass of sample before dipping,  $m_2$ : mass of sample after dipping in medium for 7 days; relative mass loss (%) =  $[(m_1 - m_2) / m_1] \times 100$  %.  
<sup>c</sup> 1 mol.L<sup>-1</sup> aqueous HCl. <sup>d</sup> 1 mol.L<sup>-1</sup> aqueous NaOH

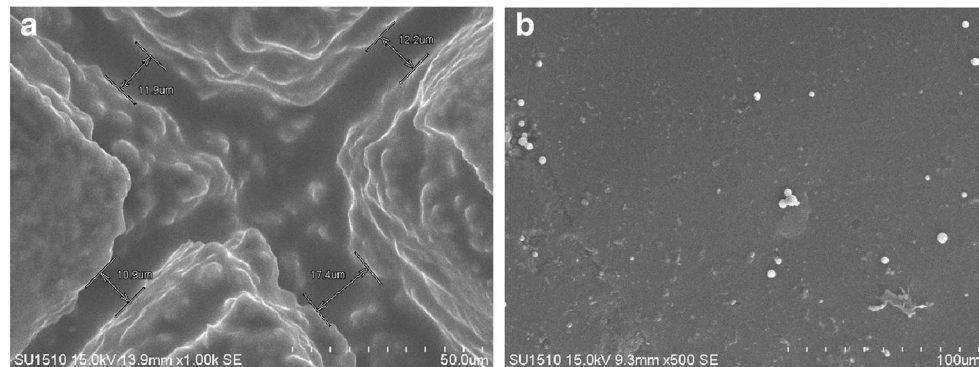
**Fig. 4** Self-healing images of the eugenol-derived crosslinked polymer **5** as films. **(a)** scratched film; **(b)** self-healed film after being irradiated under UV for 10 min

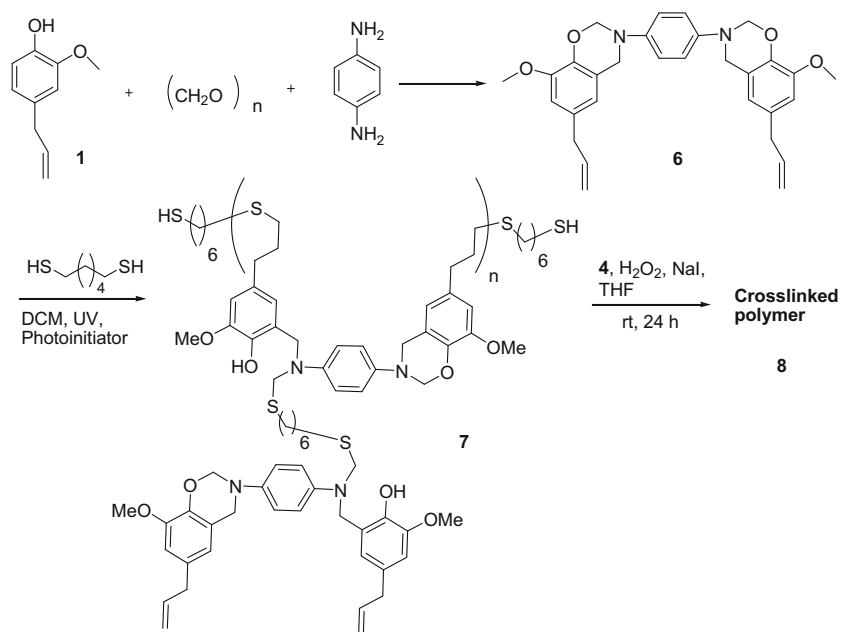
to strong base and good solvent THF. These results indicate that crosslinking density is not high for the polymer **5**.

Mechanical properties are important for materials. Thus, tensile strength of the polymer **5** is measured as 0.93 Mpa, elongation rate of rupture is 89 %, impact strength is 26 kJ.m<sup>-2</sup>. Hardness of the polymer film is lower than 2B from pencil method. Besides, glass transition temperature of the polymer **5** is -44.2 °C.

Next, we test self-healing behavior of the polymer under UV irradiation. The light brown film of polymer **5** is scratched by a razor to form the “injured” film as indicated in Fig. 4a.

Then, the “injured” film is under 365 nm of UV irradiation. Ten minutes later, the “injured” film restore to its original state (Fig. 4b). The self-healing property may result from two aspects: one is that the “injured” part of the polymer becomes soft under thermal condition (heat from UV) to make the two sides (surfaces) of the scratch close to and reach each other; the other is that weak S-S bonds reversibly cleave and reform under UV irradiation conditions. To further observe self-healing behavior of the polymer, SEM image is given in Fig. 5. Similar changes are observed in Fig. 5, i.e., the scratched film was restored after 10 min of UV irradiation.

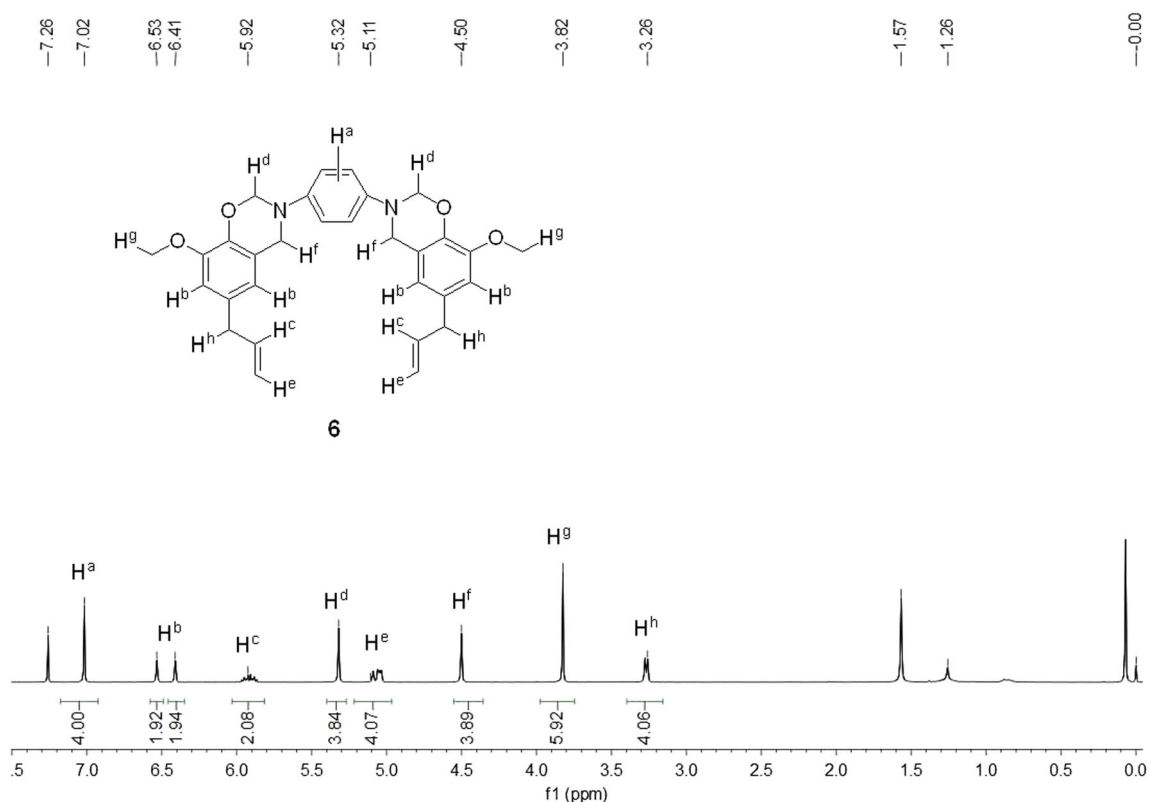
**Fig. 5** Self-healing images of the eugenol-derived crosslinked polymer **5** as films. **(a)** scratched film; **(b)** self-healed film after being irradiated under UV for 10 min (white particles on the image is gold particles needed for performing SEM)

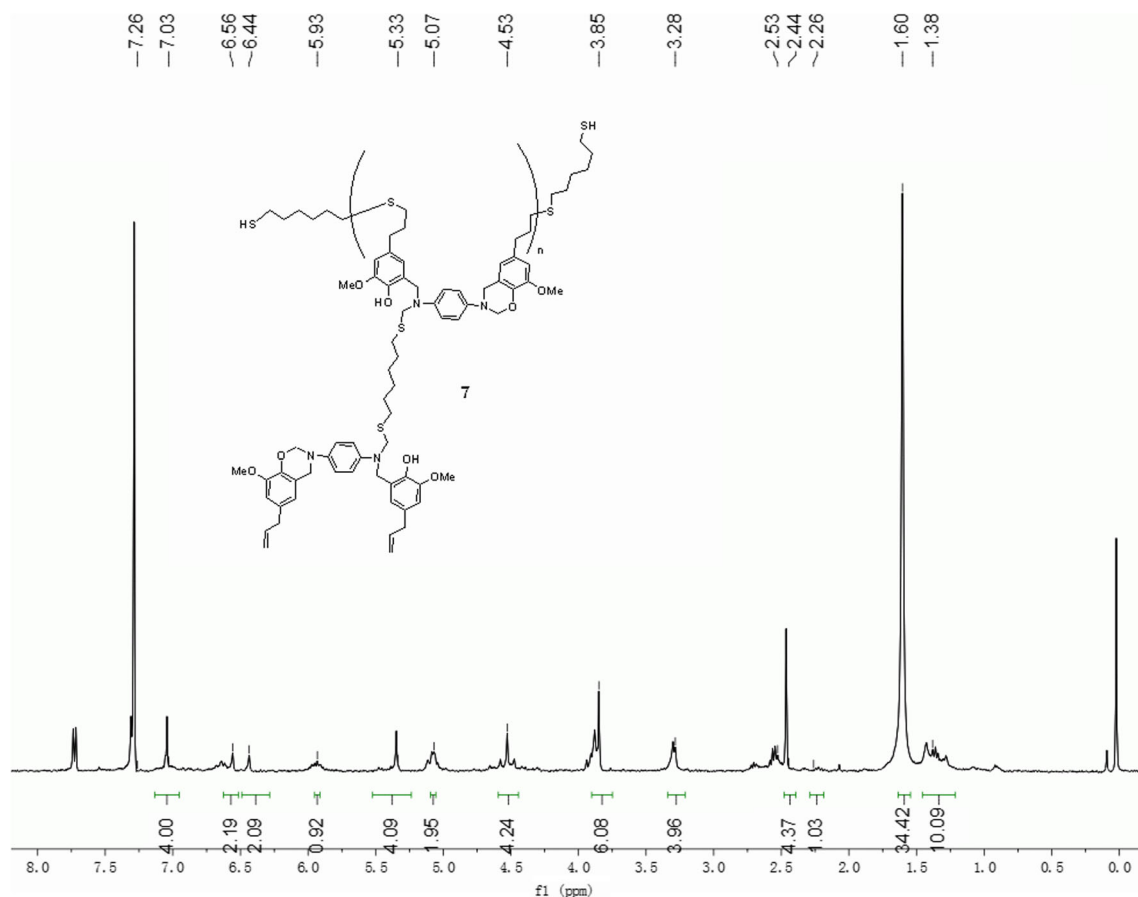
**Scheme 2** Synthesis of eugenol-derived benzoxazine polymer

### Preparation and characterization of eugenol-derived crosslinked polymer (8)

Benzoxazine polymers as novel phenolic resin have attracted considerable attention in recent years due to their

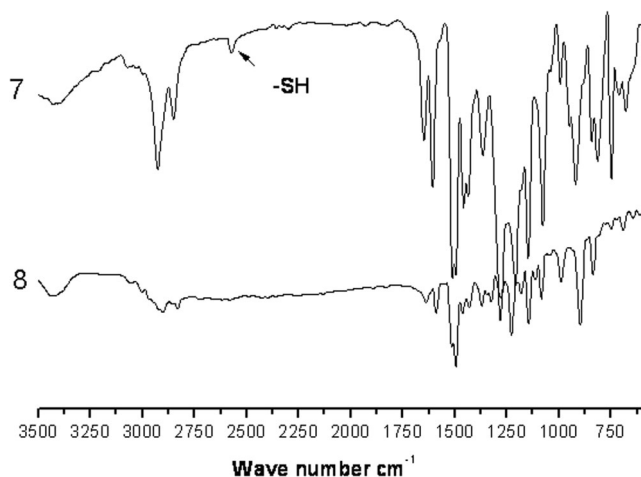
advantages such as excellent heat resistance, flame retardance, high modulus and strength [34–36]. To extend application of eugenol and to improve performance of eugenol-derived polymers, the corresponding benzoxazine from eugenol is designed and synthesized as shown in

**Fig. 6**  $^1\text{H}$  NMR spectrum of eugenol-derived benzoxazine compound 6



**Fig. 7**  $^1\text{H}$  NMR spectrum of eugenol-derived benzoxazine oligomer **7**

Scheme 2. Firstly, eugenol, formaldehyde, and 1,4-phenylene diamine react to form benzoxazine compound **6**. The structure of compound **6** is well characterized by  $^1\text{H}$  NMR spectrum as demonstrated in Fig. 6. Note that the peak at 1.57 ppm in Fig. 6 is the residue of water, and that



**Fig. 8** IR spectra of the oligomer **7** and the crosslinked polymer **8**

at 1.26 ppm may be the residue of petroleum ether. These impurities will not affect subsequent reactions. Then, the benzoxazine compound **6** reacts with 1,6-hexanedithiol under photo-initiated radical polymerization conditions to produce the oligomer **7**. Note that in oligomer **7**, there still exists a certain amount of carbon-carbon double bonds according to  $^1\text{H}$  NMR spectrum (Fig. 7), which may origin from ring opening of benzoxazine ring by 1,6-hexanedithiol [37]. The weak peak at 2.26 ppm proves that there are mercapto groups in the oligomer **7**. Molecular weight of **7** is measured as 1370 Da with polydispersity of 1.22. Finally, the oligomer **7** and trimethylolpropane tris(3-mercaptopropionate) (**4**) are oxidized to disulfide-bond-linked deep-brown polymer **8**.

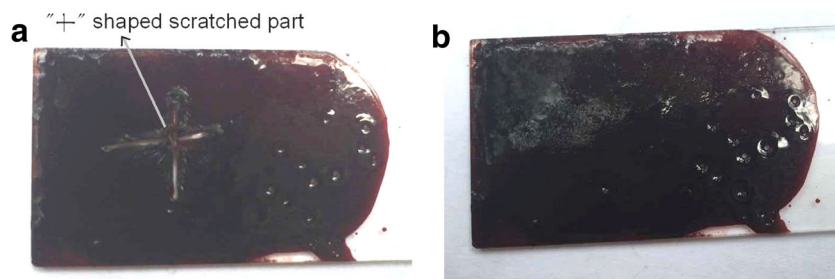
To prove the formation of **8** from **7**, IR analysis are conducted as demonstrated in Fig. 8. There is a weak peak at  $2570\text{ cm}^{-1}$  for IR spectrum of the oligomer **7**, meaning the presence of mercapto groups ( $-\text{SH}$ ). After oxidation reaction, the disappearance of the weak peak at  $2570\text{ cm}^{-1}$  indicates mercapto groups are transformed into double sulfide groups.



**Table 2** Medium resistance of the polymer **8**<sup>a</sup>

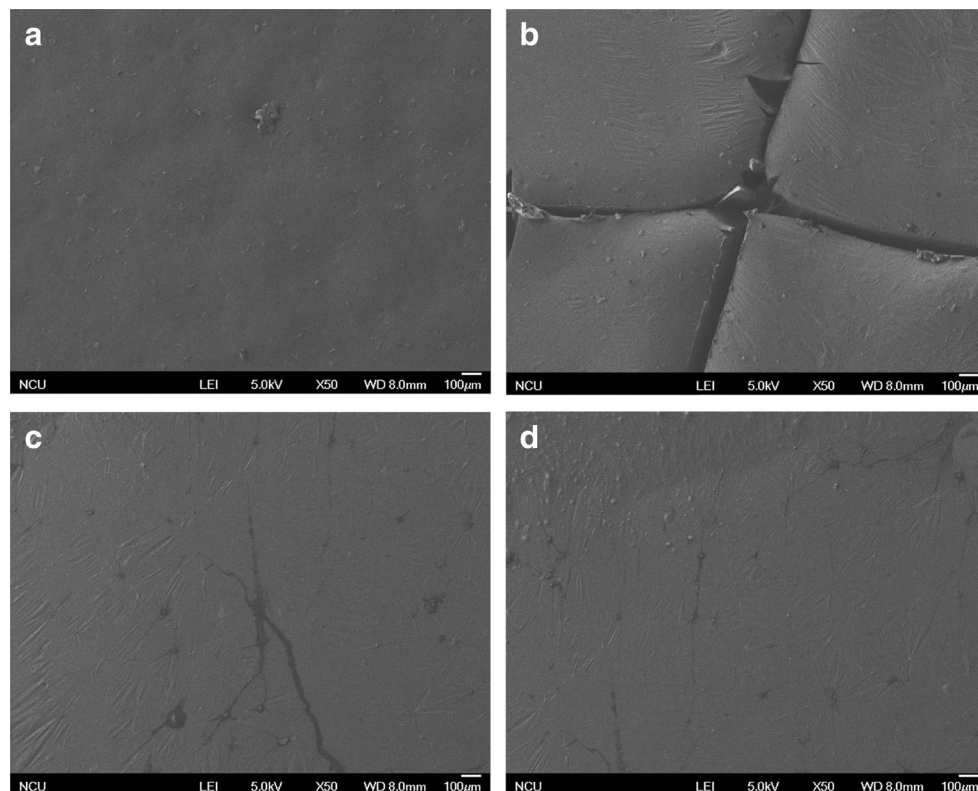
Medium	$m_1/g^b$	$m_2/g^b$	Relative mass loss (%) <sup>b</sup>	Whiteness	Chapped	Breaking off
HCl <sup>c</sup>	0.2237	0.2230	0.31	no	no	no
NaOH <sup>d</sup>	0.2406	0.2370	1.40	yes	yes	no
THF	0.2257	0.2235	0.97	yes	yes	yes
ethanol	0.2344	0.2334	0.42	yes	no	no
toluene	0.2183	0.2156	1.20	yes	no	no

<sup>a</sup> the polymer is dipped into the medium for 7 days under ambient conditions. <sup>b</sup>  $m_1$ : mass of sample before dipping,  $m_2$ : mass of sample after dipping in medium for 7 days; relative mass loss (%) =  $[(m_1 - m_2) / m_1] \times 100$  %.  
<sup>c</sup> 1 mol.L<sup>-1</sup> aqueous HCl. <sup>d</sup> 1 mol.L<sup>-1</sup> aqueous NaOH

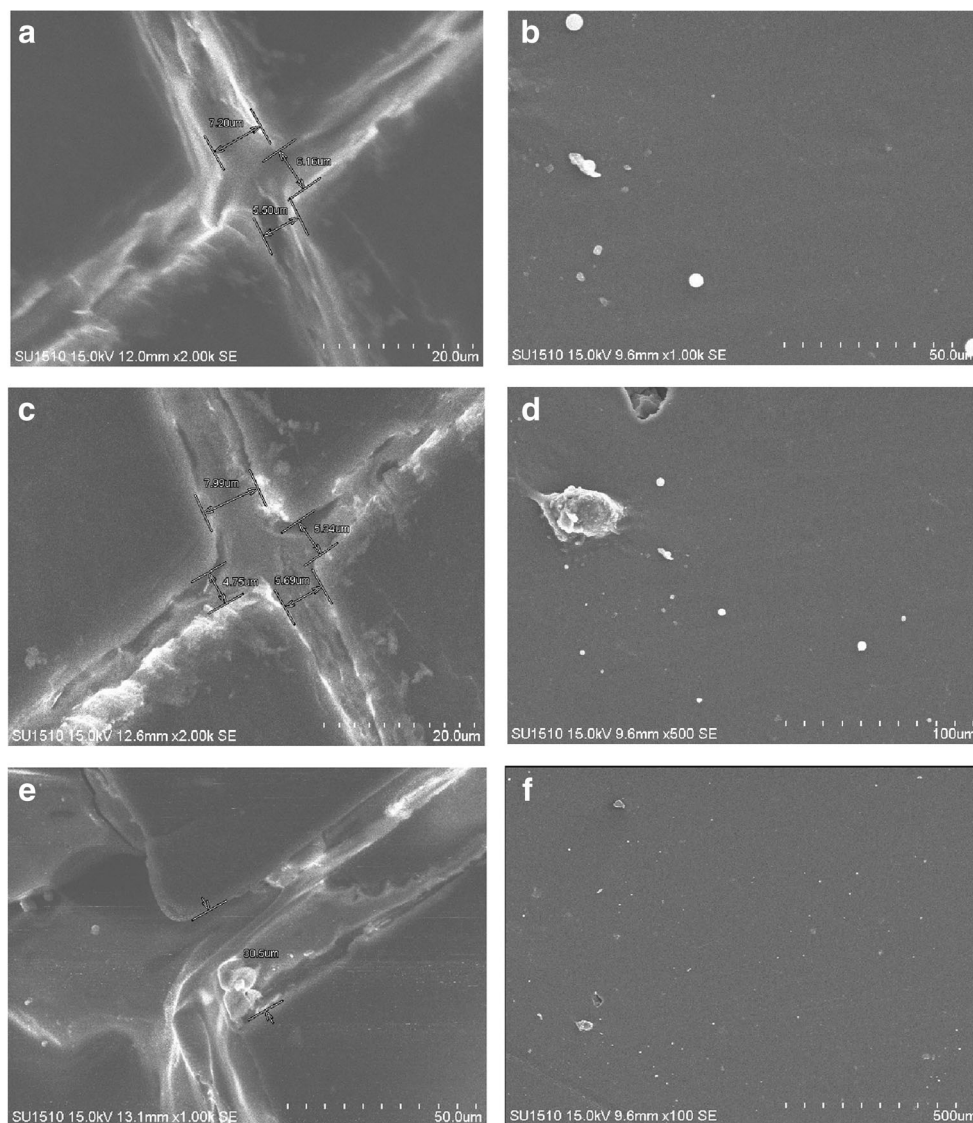
**Fig. 9** Self-healing behavior of eugenol-derived benzoxazine polymer **8**. (a) the film with a “+”-shaped scratched part; (b) self-healed film after being irradiated under UV for 10 min

Crosslinking density of the polymer **8** is estimated by measuring medium resistance as shown in Table 2. Similar to the

results of polymer **5**, the polymer **8** has good resistance to strong acid, a certain resistance to ethanol and toluene, and

**Fig. 10** SEM images showing self-healing process of eugenol-derived benzoxazine polymer **8**. (a) the original polymer sample; (b) the cut sample with a “+” shape; (c) the cut sample after being irradiated for 5 min; (d) the cut sample after being irradiated for 10 min

**Fig. 11** SEM images showing recyclable self-healing process of eugenol-derived benzoxazine polymer **8**. (a) the cut sample with a “+” shape; (b) the cut sample after being irradiated for 10 min; (c) the sample was cut again at the same site; (d) the cut sample after being irradiated for 10 min; (e) the sample was cut for the 3rd time at the same site; (f) the cut sample after being irradiated for 10 min



poor resistance to aqueous solution of strong base and good solvent THF. Thus, crosslinking density of **8** is not high.

Mechanical properties of the polymer **8** are also determined. Tensile strength of **8** is 0.76 Mpa, elongation rate of rupture is 78 %, and impact strength is  $23 \text{ kJ}\cdot\text{m}^{-2}$ . In comparison, mechanical properties of **8** are weaker than that of **5**, which may be ascribed to the smaller molecular weight of the oligomer **7** than that of **3**. For the thermal property of **8**, its glass temperature is  $-48 \text{ }^\circ\text{C}$ .

Self-healing properties of **8** is studied in a similar manner as that of polymer **5**. The film of polymer **8** is scratched with a razor to form “injured” polymer sample as shown in Fig. 9a. Then the “injured” sample is placed under UV irradiation. Ten minutes later, the scratched part of the polymer disappears, indicating that the polymer possesses self-healable properties.

This behavior is also ascribed to reshuffling of weak S-S bonds in the polymer under light irradiation.

To further observe microscopic self-healing process of the eugenol-derived benzoxazine polymer **8**, images from scanning electron microscope (SEM) are shown in Fig. 10. Figure 10a is an original film of polymer **8**, which is then cut by a razor to for a “+” shape as indicated in Fig. 10b. Width of the crack is about  $50\text{--}80 \text{ }\mu\text{m}$ . The injured film is irradiated under UV light for 5 min, and the crack is almost self-healed (Fig. 10c). After UV irradiation for another 5 min, the film almost restore to its original state (Fig. 10d). One of advantages of reversible chemical bonds-induced self-healing is that self-healing behavior can be cycled for many times. Figure 11 shows three self-healing cycles of polymer **8**. The polymer can be well healed under UV irradiation even after three cycles.

## Conclusions

Terminal diene intermediates are synthesized from renewable resource eugenol by using etherification and benzoxazine formation reactions, respectively. Then the intermediates undergo thiol-ene click reaction with 1,6-hexanedithiol under UV irradiation conditions. Molecular weights of the resulting oligomers are about 1300 Da, and hardness of the film is lower than 2B. The oligomers further react with tri-mercapto compound trimethylolpropane tris(3-mercaptopropionate) under oxidation conditions to form disulfide-bonds-crosslinked polymers. The brown crosslinked polymers show self-healing properties under UV light irradiation for 10 min, which may origin from reversible reshuffling of disulfide-bonds. This work is expected to extend applications of eugenol in designing functional materials.

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