

## A novel method for preparation of epoxy resins using thiol-ene click reaction

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**ABSTRACT:** Epoxy resins (EPs) have a wide range of applications due to their remarkable performances. A major issue about them is the associated serious environmental pollution and high manufacturing cost because of the tedious synthetic procedure and the large amount of organic solvents used in production. Here, we report a facile, highly efficient approach to addressing these challenges using thiol-ene click reaction. The new synthesis process is based on mass-produced materials including triols, diols, mercaptopropionic acid and glycidyl methacrylate and involves only two steps, that is, esterification and thiol-ene click reaction. Three types of high purity sulfur-containing EPs are synthesized at high yields. The chemical structures and molecular weights of the newly synthesized EPs were characterized by Fourier transformation infrared spectroscopy, <sup>1</sup>H-NMR and matrix-assisted laser desorption/ionization time of flight mass spectrometry. Using the methyl nadic anhydride as crosslinker, these resins have shown excellent heat-resistance due to the absence of hydroxyl groups. They demonstrate high thermal decomposition temperatures, showing no dehydration decomposition at 260°C and therefore are suitable for applications as solvent-free resins. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42316.

**KEYWORDS:** click reaction; epoxy resin; synthesis; thiol-ene

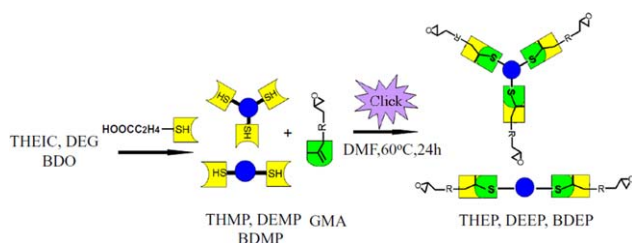
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### INTRODUCTION

Epoxy resins (EPs) as a uniquely versatile material<sup>1</sup> have a broad range of applications, including coatings, paintings, adhesives, electrical insulating materials, laminates and encapsulants based on their excellent electrical insulation, mechanical and adhesion properties. The most popular class of EPs, diglycidyl ether of bisphenol-A (DGEBA), is prepared by a tedious synthetic process. DGEBA has high viscosity (8–16 Pa·S) due to the hydrogen bond interaction between molecular chains and requires a large amount of poisonous organic solvents or reactive thinners to reduce its viscosity to facilitate processing. To overcome the low impact strength of DGEBA, many solid tougheners, such as rubbers,<sup>2</sup> thermoplastic PEI,<sup>3</sup> core-shell particles,<sup>3</sup> are used, introducing even more poisonous solvents and thinners into the system. Considerable efforts have been devoted to preparation and design of low viscosity EPs.<sup>4</sup> Although hydroxyl-free DGEBA produced by tedious chromatographic column separation has excellent stability, the product shows low impact strength and high viscosity, both of which hamper its

wide application. A few years ago, we reported that several hyperbranched EPs (HERs) with low viscosity in the range of 350–5000 mPa·S, including hyperbranched poly (trimellitic anhydride diethylene glycol) ester epoxy resin, hyperbranched poly (trimellitic anhydride ethylene glycol) ester epoxy resin, hyperbranched poly (trimellitic anhydride butanediol glycol) ester epoxy resin<sup>5</sup> and hyperbranched epoxy resin containing nitrogen heterocycle,<sup>6</sup> and the HERs, could be used to reinforce DGEBA, leading to several folds of increase in toughness and 20–30% reinforcement,<sup>7,8</sup> compared with DGEBA. Because HERs has good solubility and a large number of functional groups, which are significant advantages, they are usually used as toughening and reinforcing agent. A great deal of pioneering work to synthesize HERs has been reported, including proton transfer polymerization,<sup>9–11</sup> atom transfer radical polymerization,<sup>12</sup> grafting epoxy<sup>5,6,13–21</sup> group on hyperbranched polymers using epichlorohydrin esterification.<sup>22</sup> These synthesis HER techniques not only require large quantities of organic solvents<sup>22</sup> during reaction and water to wash and remove the



**Scheme 1.** Synthesis scheme of epoxy resins by thiol-ene click reaction. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

byproduct from NaCl,<sup>6,7,14–22</sup> but also involve tedious processes.<sup>9–11</sup> Most HERs are high viscosity liquid<sup>9–11</sup> or solid<sup>23</sup> and cannot be used in solvent-free applications. In order to prepare HERs in a manner that is solvent-free, we prepared hyperbranched EPs with silicone skeleton (HERSS)<sup>24,25</sup> having viscosity in the range of 103.5–697.4 mPa·S using hydrosilylation. This is the lowest viscosity value for HERs reported so far. Because the multi-step reactions and expensive platinum catalyst used during the preparation of HERSS, the process was difficult to up-scale. Therefore, a highly efficient and environmentally-friendly process for preparation of epoxy resin remains to be a major challenge.

Thiol-ene click reaction as a typical click reaction has many advantages,<sup>26–28</sup> including (near) quantitative yields, harmless byproducts, high selectivity and rapid reaction rate. Its exceptional versatility and propensity for near quantitative conversion under even the mildest conditions make thiol-ene chemistry amenable to applications in optical, biomedical, sensing, and bioorganic modifications. Especially the radical step-growth polymerization of thiol-ene click reaction can easily be used to control the degree of polymerization.<sup>29</sup> From a practical standpoint, thiol-ene click reaction may be accomplished with readily available starting materials and reagents, and performed under solventless conditions or in environmentally benign media, such as water so as to facilitate simple product isolation. We have explored synthesis of an epoxy resin containing sulfur by thiol-ene reaction between trimethylolpropane tri(3-mercaptopropionate) and glycidyl methacrylate<sup>30</sup>, however the unique reaction condition consuming much time could not be used to synthesize other structural EPs. Sulfur-containing EPs have been used as dental materials<sup>31</sup> for their low shrinkage and optical materials for their high refractive index.<sup>32,33</sup> Their preparation involves mainly a reaction between EPs and thiourea<sup>31</sup> and a thiol-epoxy click reaction.<sup>34</sup> The thiol-epoxy click reaction is an efficient method due to rapid reaction rate and high yield, but the resultant products need to be functionalized by crosslinkable groups or crosslinking additives to improve their mechanical performance.<sup>34</sup> Therefore the direct synthesis of sulfur-containing EPs by thiol-ene click, rather than the thiol-epoxy click reaction, is worth studying.

In this article, we report a facile process for preparing EPs based on thiol-ene click reaction. The method is shown in Scheme 1. First, a series of mercaptopropionates, including 1,3,5-tris(2-hydroxyethyl)isocyanurate-tris(3-mercaptopropionate) (THMP),

diethylene glycol dimercapto propanoate (DEMP), and 1,4-butanediol dimercapto propanoate (BDMP), are prepared by esterification between diols (or triols) and 3-mercaptopropionic acid (MPA), such as 1,3,5-tris(2-hydroxyethyl)isocyanurate (THEIC), diethylene glycol (DEG), and 1,4-butanediol (BDO). The mercaptopropionates react with glycidyl methacrylate (GMA) through a thiol-ene click process to produce three types of EPs, 1,3,5-tris(glycidyl 2-methylpropionate ethyl propionate)thioether isocyanurate epoxy resin (THEP), diethylene glycol di(glycidyl 2-methylpropionate propionate)thioether ester epoxy resin (DEEP), and butanediol di(glycidyl 2-methylpropionate-propionate)-thioether ester epoxy resin (BDEP).

## EXPERIMENTAL

### Materials

THEIC, DEG, BDO, MPA, *p*-toluenesulfonic acid, GMA, dimethylsulfoxide (DMSO), methylbenzene, dichloromethane, *n*-hexane, *N,N*-dimethylbenzylamine, methyl nadic anhydride (MNA), NaOH, and Na<sub>2</sub>SO<sub>4</sub> were all of analytical grade and were sourced from Shanghai Chemical Reagent Co., Ltd. They were used in this study without further purification unless noted.

### Synthesis of Mercaptopropionates

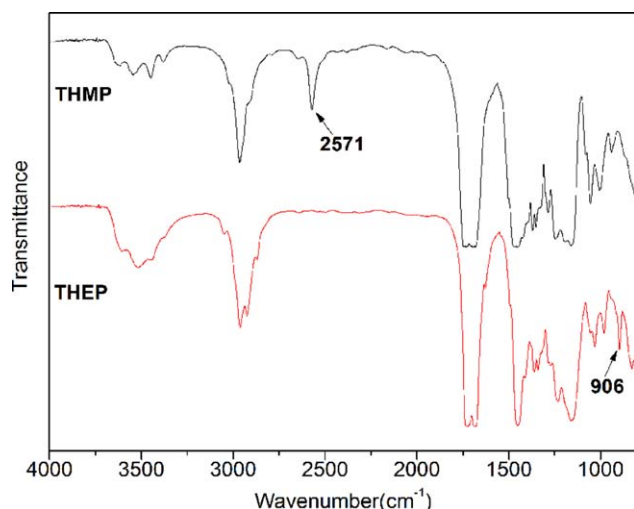
**Preparation of THMP.** THEIC (7.84 g, 0.03 mol), MPA (14.35 g, 0.135 mol), toluene (50 ml), and *p*-toluenesulfonic acid (1.10 g) as a catalyst were added into a four-necked flask equipped with stirrer, cooler, nitrogen inlet and water-trap (Dean-Stark) to react for about 10 h at reflux temperature about 80°C under mechanical stirring. The resulting solution was washed for three times using 5 ml NaOH solution (5 wt %). The organic layer was dried by Na<sub>2</sub>SO<sub>4</sub> over a night. After the solvent was removed under reduced pressure, a colorless liquid of 15.45 g was obtained, which proved to be THMP.

**Preparation of DEMP.** DEG (3.18 g, 0.03 mol), MPA (9.55 g, 0.09 mol), toluene (50 ml), and *p*-toluenesulfonic acid (0.64 g) were added into a flask using a similar process as the preparation of THMP. The resulting product was a colorless liquid of 8.23 g, which proved to be DEMP.

**Preparation of BDMP.** BDO (2.70 g, 0.03 mol), MPA (9.55 g, 0.09 mol), toluene (50 ml), and *p*-toluenesulfonic acid (0.61 g), were added into a flask using a similar process as the preparation of THMP, resulting in a colorless liquid of 7.39 g, which proved to be BDMP.

### Synthesis of Epoxy Resins

**Preparation of THEP.** THMP (5.27 g, 0.01 mol), GMA (5.12 g, 0.036 mol), and DMSO (4 ml) were added into a flask to react for about 4 h at 60°C when the absorption peak of –SH group at about 2571 cm<sup>–1</sup> disappeared by FT-IR measurement. The resulting solution was put in a separation funnel for delamination after both dichloromethane (50 ml) and brine (50 ml) were added into the solution. The organic layer was washed using *n*-hexane (5 ml) about five times for removing the excessive GMA. The resulting organic phase was dried with magnesium sulfate (5.0 g). After dichloromethane was removed under reduced pressure, a colorless liquid was obtained, which proved to be THEP with viscosity of about 16,960 mPa·S and epoxy



**Figure 1.** FT-IR spectra of 1,3,5-tris(2-hydroxyethyl)isocyanurate-tris(3-mercaptopropionate) (THMP) and 1,3,5-tri(glycidyl 2-methylpropionate ethyl propionate)thioether isocyanurate epoxy resin (THEP). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

epoxy equivalent weight of 328 g/mol, being close its theoretical value of 317 g/mol.

**Preparation of DEEP.** DEMP (2.83 g, 0.01 mol), GMA (3.41 g, 0.024 mol), and DMSO (4 ml) were added into a flask, following a similar process as the preparation of THEP. The reaction time was about 2 h at 60°C when the absorption peak of -SH group at about 2567  $\text{cm}^{-1}$  disappeared in the FT-IR measurement. This gave a colorless liquid, which proved to be DEEP with a viscosity of about 320 mPa·S and epoxy equivalent weight of 310 g/mol, being close its theoretical value of 284 g/mol.

**Preparation of BDEP.** BDMP (2.66 g, 0.01 mol), GMA (3.41 g, 0.024 mol), and DMSO (4 ml) were added into a flask, following a similar process as the preparation of THEP. The reaction was allowed for about 2 h at 60°C when the absorption peak of -SH group at about 2569  $\text{cm}^{-1}$  disappeared in the FT-IR spectra. Then a colorless liquid was obtained, which proved to be BDEP with a viscosity of about 640 mPa·S and epoxy equivalent weight of 288 g/mol, being close its theoretical value of 275 g/mol.

THEP, DEEP, and BDEP EPs were cured by using stoichiometric MAN as curing agent, and using tris(dimethylaminomethyl)phenol as accelerator, following the curing process: 80°C for 2 h, 120°C for 2 h, 180°C for 2 h, 200°C for 2 h. The cured samples were cooled gradually to room temperature and then placed for about 12 h before their thermal performances were measured using the following methods.

Statistic heat-resistant index ( $T_s$ ) was used to evaluate the thermal stability of the cured resins.  $T_s$  was calculated from  $T_{d5}$  and  $T_{d30}$  of the samples obtained from thermogravimetric analysis (TGA) using the equation:<sup>35</sup>

$$T_s = 0.49 [T_{d5} + 0.6 (T_{d30} - T_{d5})] \quad (1)$$

Here,  $T_{d5}$  and  $T_{d30}$  refer to the thermal decomposition temperatures for 5% and 30% weight loss of cured sample, respectively.

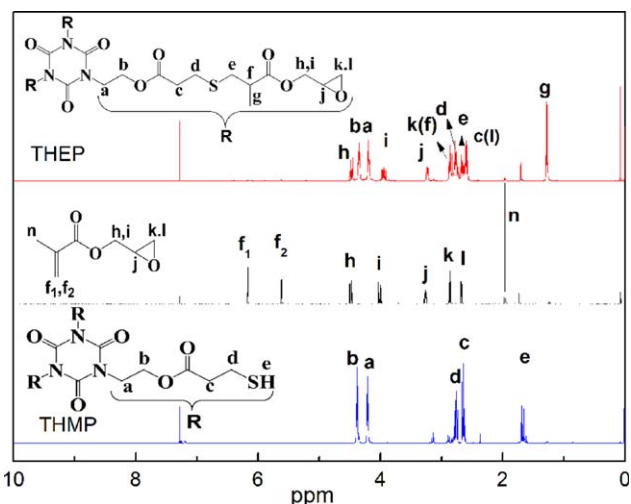
### Characterization

FT-IR measurements were performed on a Bruker Vector 33 spectrometer using sealed cell (KBr 0.5mm) with a scanning number of 32.  $^1\text{H}$  NMR measurements were conducted on an AVANCE III-400 (Bruker) nuclear magnetic resonance spectrometer using DMSO- $d_6$  as solvent. Mass spectra were recorded on a Matrix-assisted laser-desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS, US Applied Biosystems 4800) using alpha-cyano-4-hydroxycinnamic acid as the matrix. Viscosity of EPs was determined by a DV-III+Ultra viscometer (Brookfield) using a 07 rotor at rotational speed of 100g and temperature 25°C. Differential scanning calorimetry (DSC) was performed at a heating rate of 10°C/min on a NETZSCH DSC204 F1 differential scanning calorimeter using 1.8–3.0 mg samples placed in standard aluminum pans with a temperature range from 10°C to 200°C. TGA were performed with a NETZSCH TG209 thermogravimetric analyzer at a heating rate of 20 K/min and at a flow rate of 20 ml/min nitrogen with a temperature range from 20 to 800°C.

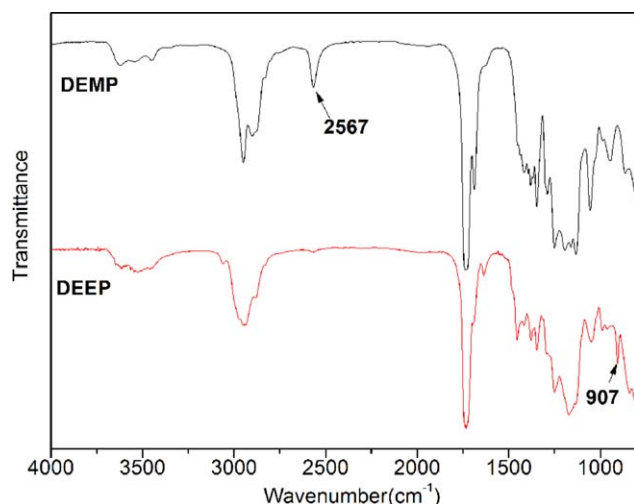
## RESULTS AND DISCUSSION

### FT-IR and $^1\text{H}$ -NMR Spectra of Mercaptopropionates and EPs

FT-IR and  $^1\text{H}$  NMR spectra of THMP and THEP are shown in Figures 1 and 2. FT-IR (KCl,  $\text{cm}^{-1}$ ) about THMP: 2955 (s,  $\text{CH}_3$ ), 2571 (s, S-H), 1738 (s, C=O), 1682 (s, C=O), 1460 (s, C-N) 1246 (s, C-O-C).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ) about THMP:  $\delta$  ppm 4.36–4.39 (b, 2H), 4.19–4.22 (a, 2H), 2.73–2.77 (d, 2H), 2.62–2.66 (c, 2H), 1.64–1.69 (e, 1H). FT-IR (KCl,  $\text{cm}^{-1}$ ) about THEP: 2973 (s,  $\text{CH}_3$ ), 1732 (s, C=O), 1697 (s, C=O), 1462 (s, C-N), 1241 (s, C-O-C), 906 (s, epoxy group).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ) about THEP:  $\delta$  ppm 4.43–4.45 (h, 1H), 4.33–4.35 (b, 2H), 4.17–4.20 (a, 2H), 3.91–3.98 (i, 1H), 3.20–3.26 (j, 1H), 2.66–2.87 (k,l,c,d,e,m, 9H), 1.26–1.28 (g, 3H). FT-IR and  $^1\text{H}$  NMR spectra of DEMP and DEEP are



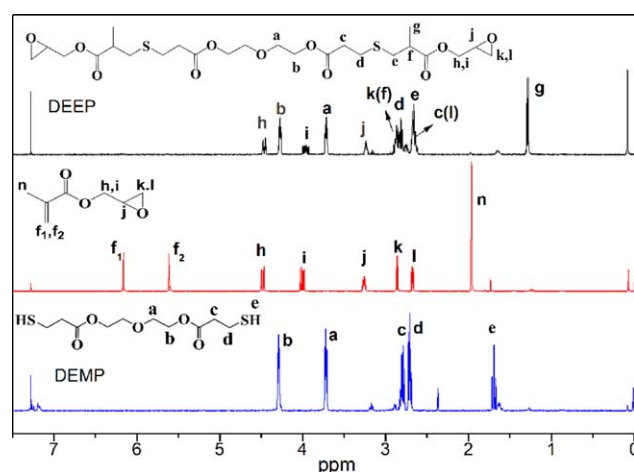
**Figure 2.**  $^1\text{H}$ -NMR spectra of THMP and THEP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



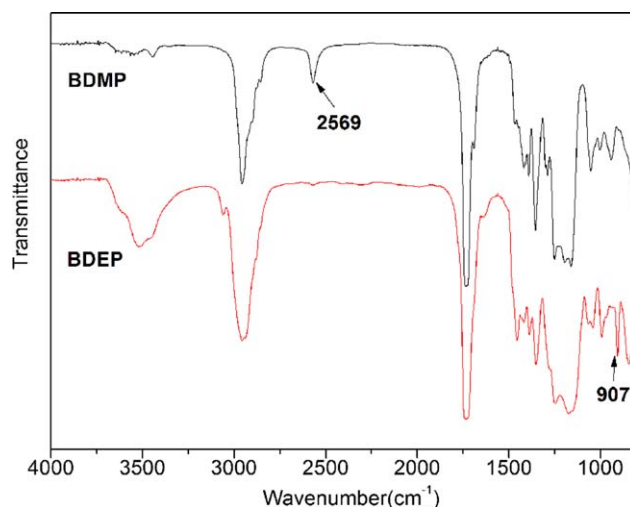
**Figure 3.** FT-IR spectra of diethylene glycol dimercapto propanoate (DEMP) and diethylene glycol di(glycidyl 2-methylpropionate propionate)thioether ester epoxy resin (DEEP). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shown in Figures 3 and 4. FT-IR (KCl,  $\text{cm}^{-1}$ ) about DEMP: 2949 (s,  $\text{CH}_3$ ), 2567 (s, S—H), 1732 (s, C=O), 1246 (s, C—O—C).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ) about DEMP:  $\delta$  ppm 4.28–4.30 (b, 2H), 3.71–3.73 (a, 2H), 2.77–2.83 (c, 2H), 2.69–2.73 (d, 2H), 1.67–1.72 (e, 1H). FT-IR (KCl,  $\text{cm}^{-1}$ ) about DEEP: 2937 (s,  $\text{CH}_3$ ), 1732 (s, C=O), 1251 (s, C—O—C), 907 (s, epoxy group).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ) about DEEP:  $\delta$  ppm 4.45–4.48 (h, 1H), 4.26–4.29 (b, 2H), 3.93–4.00 (i, 1H), 3.70–3.73 (a, 2H), 3.24 (j, 1H), 2.64–2.88 (k,f,d,e,c,l, 9H).

FT-IR and  $^1\text{H NMR}$  spectra of BDMP and BDEP are shown in Figures 5 and 6. FT-IR (KCl,  $\text{cm}^{-1}$ ) about BDMP: 2957 (s,  $\text{CH}_3$ ), 2569 (s, S—H), 1728 (s, C=O), 1251 (s, C—O—C).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ) about BDMP:  $\delta$  ppm 4.13–4.18 (b, 2H), 2.76–2.80 (d, 2H), 2.64–2.68 (c, 2H), 1.73–1.76 (a, 2H), 1.61–1.67 (e, 1H). FT-IR (KCl,  $\text{cm}^{-1}$ ) about BDEP: 2956 (s,  $\text{CH}_3$ ), 1732 (s, S—H), 1255 (s, C—O—C), 907 (s, epoxy group).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ) about BDEP:  $\delta$  ppm 4.36–4.43



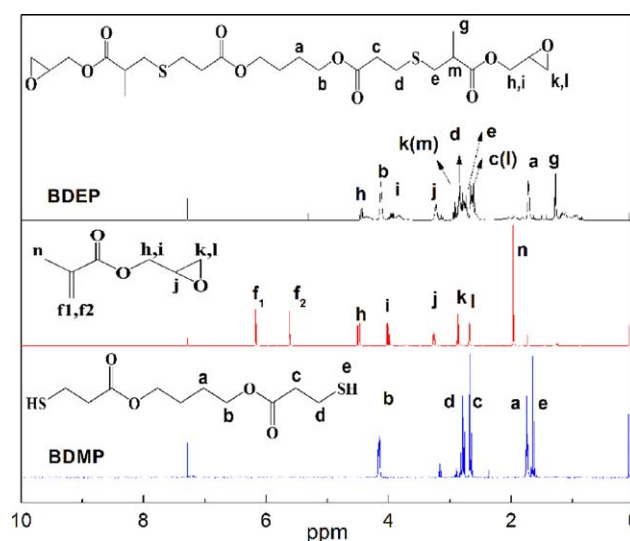
**Figure 4.**  $^1\text{H-NMR}$  spectra of DEMP and DEEP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 5.** FT-IR spectra of 1,4-butanediol dimercapto propanoate (BDMP) and butanediol di(glycidyl 2-methylpropionate-propionate)thioether ester epoxy resin (BDEP). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(h, 1H), 4.13 (b, 2H), 3.83–3.98 (i, 1H), 3.22–3.24 (j, 1H), 2.56–2.94 (c,d,e,m,k,l, 9H), 1.71–1.72 (a, 2H), 1.26–1.28 (g, 3H).

Appearance of an absorption peak at about 2567–2571  $\text{cm}^{-1}$  indicates the formation of —SH group in mercapto propanoate (THMP, DEMP, and BDMP), and disappearance of the absorption peak of the —SH group indicates the complete reaction between mercapto propanoate (THEP, DEMP, and BDMP) and GMA in Figures 1, 3, and 5, respectively. Appearance of an absorption peak at 906–907  $\text{cm}^{-1}$  confirms existence of epoxy group in mercapto propanoate (THEP, DEMP, and BDMP). Disappearance of characteristic peaks of double bonds at  $\delta$  4.7 ppm and 6.2 ppm and existence of peaks of epoxy groups at  $\delta$  3.2 ppm, 2.8 ppm and 2.7 ppm illuminate complete conversion of double bonds in GMA via click reaction and formation of epoxy resin. All the above FT-IR



**Figure 6.**  $^1\text{H-NMR}$  spectra of BDMP and BDEP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

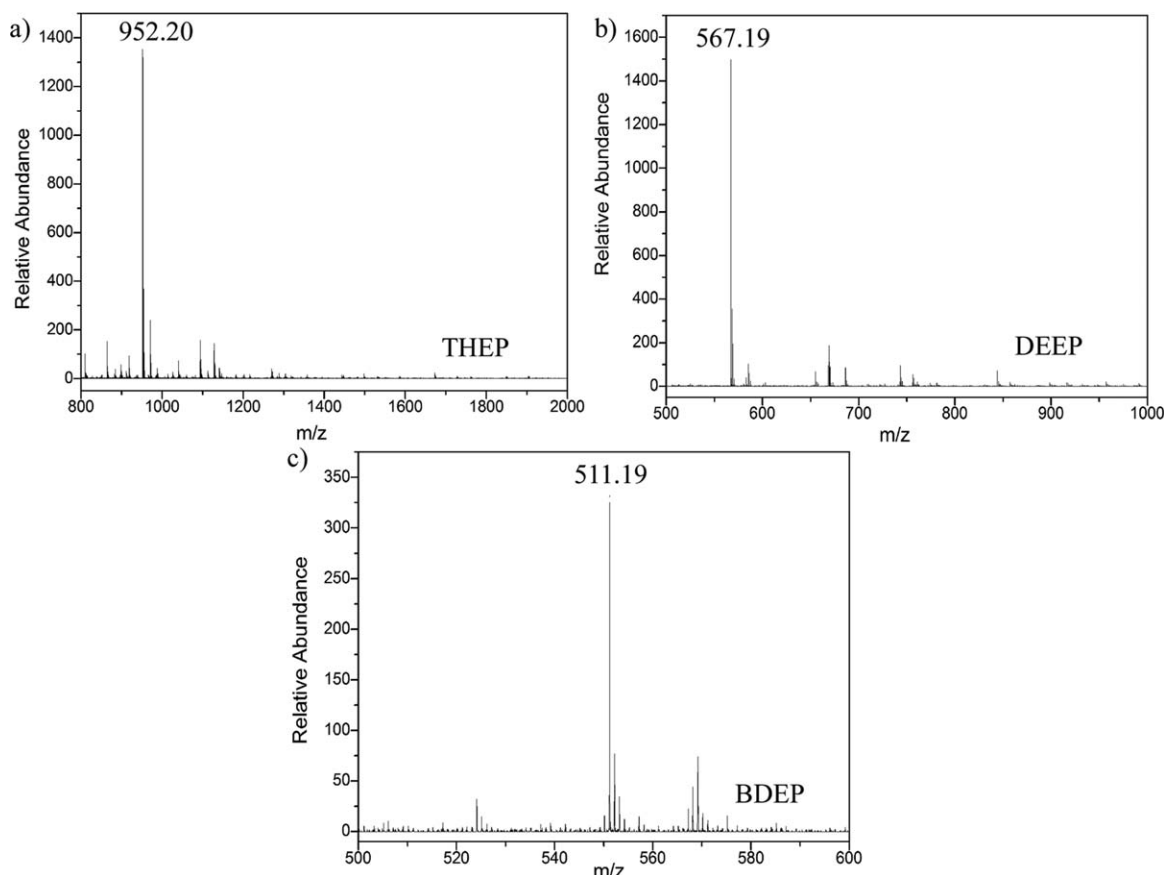


Figure 7. MALDI-TOF mass spectra of THEP, DEEP, and BDEP.

and  $^1\text{H-NMR}$  data have confirmed their chemical structures. In the click reaction between mercaptopropionate and glycidyl methacrylate reported here, thiol-ene reaction and the thiol-epoxy click reaction compete with each other.<sup>36</sup> Bowman<sup>36</sup> has demonstrated that thiol-epoxy click reaction has a much higher rate than thiol-ene reaction using amine catalyst. Without any catalysts, we achieved complete conversion of thiol and ene from the reaction

between mercaptopropionate and glycidyl methacrylate. In comparison to the conditions used in synthesizing EPs,<sup>6,7,14–22</sup> the reaction used for preparing THEP, DEEP, and BDEP has a much higher efficiency because of the much shorter reaction time (about 2–4 h) and the much lower reaction temperature. The benign synthetic conditions for EPs will also be conducive for production scale-up. The prepared EPs without hydroxyl groups can potentially be used in solvent-free materials. The crosslinkable THEP, DEEP, and BDEP may also be used in optical materials due to their high refractive indexes of 1.5145, 1.4975, and 1.5032, respectively, measured by Abbe refractometer at room temperature.

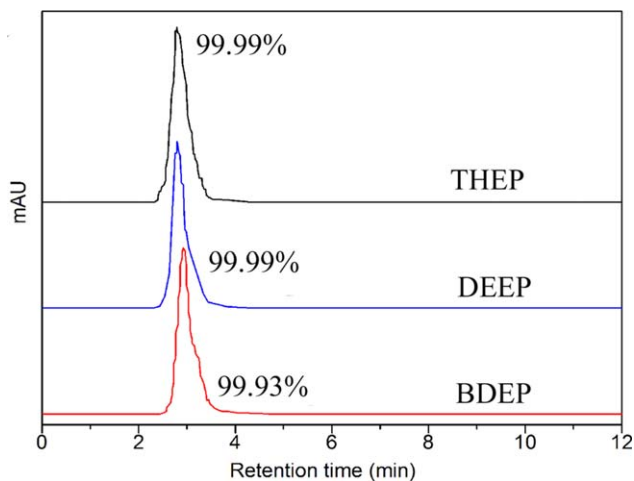
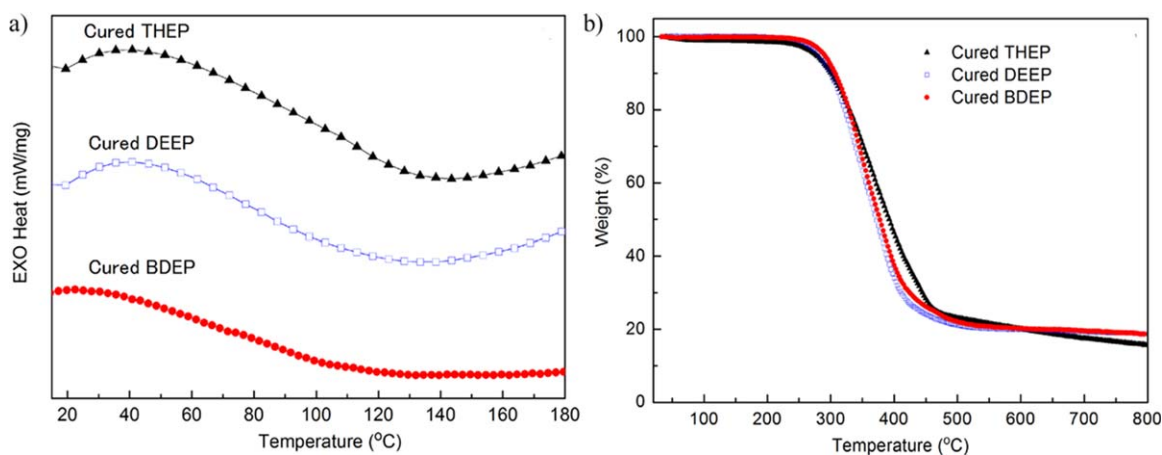


Figure 8. High efficiency liquid chromatographs of THEP, DEEP, and BDEP. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

#### MALDI-TOF Mass Spectra and HPLC Spectra of EPs

Figures 7 and 8 show MALDI-TOF mass spectra and high efficiency liquid chromatographs of THEP, DEEP, and BDEP. The strong peak at  $m/z$  952.20 observed in Figure 7a closely matches the theoretical value for THEP ( $\text{C}_{39}\text{H}_{57}\text{N}_4\text{O}_{18}\text{S}_3$ ) of  $m/z$  952.07. The measured values of  $m/z$  567.19 and 551.19 also match closely the calculated values for DEEP ( $\text{C}_{24}\text{H}_{38}\text{O}_{11}\text{S}_2$ ) of  $m/z$  566.68 and for BDEP ( $\text{C}_{24}\text{H}_{38}\text{O}_{10}\text{S}_2$ ) of  $m/z$  550.68, respectively, as shown in Figure 7b–c. The purity levels of THEP, DEEP, and BDEP are all more than 99.93% (Figure 8), indicating excellent quality. The viscosities of THEP, DEEP, and BDEP at room temperature are 16,960, 320, and 640 mPa·S, respectively. The viscosities of DEEP and BDEP are much lower than that of DGEBA (15,600 mPa·S) most industrial epoxy resin thickeners.



**Figure 9.** Differential scanning calorimetry and thermogravimetric analysis curves of cured THEP, DEEP, and BDEP. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

This low hydromechanical volume points to potential applications in solvent-free resins.

#### Thermal Performance of Cured EPs

Traditional EPs as active thinners also have low viscosity in range of 300–800 mPa·S, such as 1,2,3-tris(2,3-epoxypropoxy)propane, 1,4-butanediol diglycidyl ether. But they cannot be used on their own because of their poor mechanical and thermal performances. Both glass temperature ( $T_g$ ) and thermal decomposition temperature ( $T_d$ ) are considered to be important indicators of thermal performance for EPs. Because of its high-temperature resistance, MNA is regarded as a primary curing agent in preparing solvent-free insulation materials for wind power rotors.<sup>24,25</sup> Glass temperature ( $T_g$ ) and thermal decomposition temperature ( $T_d$ ) of the cured samples could be obtained by differential scanning calorimetry (DSC) and TGA measurements. The  $T_{gs}$  of the cured THEP, DEEP, and BDEP are 108.4, 96.6, and 95.6°C, respectively (Figure 9a and Table I). The disappearance of an absorption peak at 906–907  $\text{cm}^{-1}$  in Figure 10 indicates that their epoxy groups of all the three kinds of epoxy group were cured completely with methyl nadic anhydride. Therefore, their lower glass temperature than that of cured DGEBA may be attributed to their flexible thioether structure.<sup>25</sup> The initial thermal decomposition temperatures for 5% weight loss ( $T_{d5}$ ) of cured THEP, DEEP and BDEP are 277.3, 281.3, and 290.4°C, respectively (Figure 9b and Table I), indicating remarkable increases in comparison with that of cured DGEBA-MNA of about 99.1°C.<sup>24,25</sup>

**Table I.** Thermal Properties of the Cured Epoxy Resins

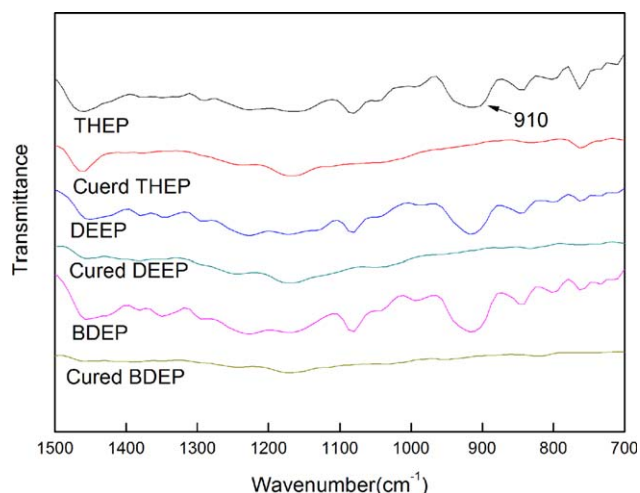
Samples	$T_g$ (°C)	$T_{d5}$ (°C)	$T_{d30}$ (°C)	$T_s$ (°C)
THEP-MNA	108.4	277.3	352.3	157.9
DEEP-MNA	96.6	281.3	340.3	155.2
BDEP-MNA	95.6	290.4	345.4	158.5

BDEP, butanediol di(glycidyl 2-methylpropionate-propionate)thioether ester epoxy resin; DEEP, diethylene glycol di(glycidyl 2-methylpropionate propionate)thioether ester epoxy resin; MNA, methyl nadic anhydride; THEP, 1,3,5-tri(glycidyl 2-methylpropionate ethyl propionate)thioether isocyanurate epoxy resin

The statistic heat-resistant indices ( $T_s$ ) for the three cured EPs in Table I are all higher than 155°C and thus meet the heat resistance requirement for F-class insulating materials. Their outstanding thermal performance may be attributed to two factors. First, because of the absence of hydroxyl group in the prepared EPs, dehydration does not occur during decomposition. Second, the incorporation of sulfur atom in the EPs promotes curing reaction, and these EPs may be used as insulation materials.

#### CONCLUSIONS

In conclusion, we investigated a novel synthetic strategy for the preparation of EPs by thiol–ene click reaction between mercaptopropionates and glycidyl methacrylate. Three high-yielding products were obtained as proof-of-concept examples. The click reactions ensure that all the thiol groups can completely react with double bond while retaining the epoxy groups. This novel synthetic method of EPs eliminates the tedious purification process in existing methods and may open a new avenue for the



**Figure 10.** FT-IR spectra of cured THEP, DEEP, and BDEP. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

design and synthesis of functional EPs. The products may be used as solvent-free resins because of their low viscosity and good processability owing to the absence of hydroxyl groups.

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