Synthesis and Characterization of Multifunctional Secondary Thiol Hardeners Using 3-Mercaptobutanoic Acid and Their Thiol–Epoxy Curing Behavior

Seung-Mo Hong and Seok-Ho Hwang*

ABSTRACT: 3-Mercaptobutanoic acid (3-MBA) was synthesized by the less odorous Michael addition pathway using an isothiouronium salt intermediate. Using the synthesized 3-MBA, multifunctional secondary thiol (sec-thiol) compounds were obtained and applied to thiol–epoxy curing systems as hardeners. As the functionality of the sec-thiol hardeners increased, the purity of the product obtained after distillation decreased. The equivalent hardeners were evaluated on their impact on the curing behavior in thiol–epoxy click reactions by differential scanning calorimetry. The thermal features of sec-thiol–epoxy click reactions in the presence of a base catalyst were assessed according to the functionality of the sec-thiol hardeners. Our results showed that sec-thiol hardeners with less reactivity to the epoxy group provide long-term storage stability for the formulated epoxy resin, promising for industrial applications.

INTRODUCTION

Click chemistry is one of the widely used technologies in academic and industrial fields because of the unique characteristics induced by highly controllable reactions and cleaning mechanisms. Base-catalyzed thiol–epoxy click polymerization has attracted a growing interest due to numerous advantages, including fast curing rates, excellent regioselectivity, versatility, and high conversion, making it suitable for the preparation of cross-linked polymeric thermosets. This addition reaction involves the nucleophilic ring-opening reaction of strained epoxide electrophiles yielding β-hydroxythioether, and the formation of the hydroxy group provides enhanced adhesion to metallic surfaces and broad applicability to the synthesis and modification of polymers. Furthermore, the reaction can take place at elevated temperatures without the use of a catalyst, but the addition reaction with a base catalyst can proceed at a relatively low temperature within a short reaction time. An anionic nucleophilic polymerization mechanism makes the process less sensitive to oxygen and impurities, except for acidic compounds. After thermal curing with a thiol-based hardener, the cross-linked epoxy resin shows excellent properties, such as lower shrinkage, better adhesion, and superior chemical resistance.

Unfortunately, despite its potential utility and widespread use, this system has major drawbacks in the industrial field. It is well known that commonly used thiols are often accompanied by a foul smell, making them difficult to work with in certain cases. Furthermore, the stability of the thiol–epoxy system, which is operated by the nucleophilic attack of commonly applied base catalysts, is limited due to fast initial curing rates. To overcome their short shelf life, weak bases such as amine compounds or a latent catalyst activated by an external stimulus (e.g., elevated temperature and/or UV light) has been employed.

In this study, we report an alternative synthetic pathway using a building block, 3-mercaptobutanoic acid, based on crotonic acid and thiourea salt reagent to produce a multifunctional secondary thiol (sec-thiol). We prepared and characterized multifunctional sec-thiol hardeners (di-, tri-, and tetra-functional sec-thiols) using the synthesized 3-mercaptobutanoic acid. In previous reports, sec-thiols used in the thiol–ene system provided a slow reaction rate as well as a less offensive odor. Despite these positive results for the thiol–ene system, little information has been provided about thiol–epoxy systems. Thus, we describe how the multifunctionality of sec-thiols affects the curing behavior of a diglycidyl ether of bisphenol-A (DGEBA). Subsequent utility for the functionality of sec-thiols was demonstrated by the characterization of the epoxy resins cross-linked with multifunctional sec-thiol hardeners using 3 mercaptobutanoic acid and their thiol–epoxy curing behavior.

Received: April 22, 2022
Accepted: June 1, 2022
Published: June 10, 2022
eners, fabricated by the 2,4,6-tris(dimethylaminomethyl)-phenol-catalyzed curing reaction using calorimetry and thermogravimetry.

**EXPERIMENTAL SECTION**

**Materials.** The starting materials (crotonic acid, thiourea, 1,4-butanediol, trimethylolpropane, and pentaerythritol) and the curing base catalyst [2,4,6-tris(dimethylaminomethyl)-phenol] were purchased from Sigma-Aldrich (Milwaukee, WI, USA). p-Toluenesulfonic acid monohydrate (p-TSA) was purchased from TCI Co., Ltd. (Tokyo, Japan). Other organic solvents and chemicals were purchased from Daeyeung Chemical (Goyeong-gun, Korea). Epoxy resin based on diglycidylether bisphenol-A (DGEBA; YD-128) with an epoxide equivalent weight of 184−190 g/equiv was donated from Kulko Chemical Co., Ltd. (Seoul, Korea).

**Synthesis of 1,4-Butanediol.** Thiourea (152.24 g, 2.0 mol) and H2O (152 mL) were added to a three-necked flask equipped with a mechanical stir, a cooling condenser, and a thermocouple. 4.0 mol of HCl (36% aqueous solution) was dropped into the mixture at 25 °C while stirring and then refluxed for an additional 6 h. The reaction was monitored by thin-layer chromatography (TLC) to determine thiourea consumption. After this step, crotonic acid (86.09 g, 1.0 mol) was added, and the mixture was refluxed for an additional 5 h. The reaction mixture was cooled, and 8.0 mol of NaOH (50% aqueous solution) was dropped into the mixture and then refluxed for 5 h. The mixture was cooled to 25 °C and acidified with H2SO4 (40% aqueous solution) until obtaining pH 1. The reaction mixture was extracted with methylene chloride, and the combined organic phase was washed with brine, dried with MgSO4, and then further annealed at 130 °C for 12 h.

**Synthesis of Trimethylolpropane (3-Mercaptobutanol).** A mixture of trimethylolpropane (110.00 g, 0.82 mol), 1,4-butanediol, and pentaerythritol) and then rehydrolyzed, and the mixture samples were cured at room temperature for 24 h and then further annealed at 130 °C for 12 h.

**Sample Preparation for Curing Behavior Measurement.** The samples were prepared by the equivalent blending of DGEBA with multifunctional sec-thiol hardeners without any catalyst. The samples for obtaining the gel time data using a house-designed digital temperature recording device equipped with a temperature sensor were prepared by mixing the 0.5 phr of 2,4,6-tris(dimethylaminomethyl)phenol with an equivalent mixture of DGEBA and a hardener.

**Preparation of Cured Epoxy Sample.** The cross-linked samples were obtained from the curing of an equivalent mixture of DGEBA and multifunctional sec-thiol hardeners with 0.5 phr of 2,4,6-tris(dimethylaminomethyl)phenol. The mixture samples were cured at room temperature for 24 h and then further annealed at 130 °C for 12 h.

**Equipment and Experiments.** Fourier-transform infrared (FT-IR) spectra were recorded on an FT/IR-4100 spectrophotometer (Jasco Co., Tokyo, Japan) in the transmittance mode under the air conditions. Nuclear magnetic resonance (NMR) for chemical structure analysis was performed on a VNM400 400 MHz NMR spectrometer (Agilent Technologies Inc., Santa Clara, CA, USA), using chloroform-d1 (CDCl3) as a solvent. Liquid chromatography (LC)—mass spectra (MS) were recorded on an LC−MS-2020 spectrometer equipped with a Shim-pack FC-ODS column (Shimazu, Japan) under acetoniitrite and H2O as the eluent, and the gradient ranged from 40% acetoniitrite at 0 min to 70% acetoniitrite at 20 min. The purity characterization was performed on an Agilent 1220 Infinity HPLC system equipped with a Hектор C18 column (Agilent, USA) under acetoniitrite and H2O as the eluent and the gradient ranged from 40% acetoniitrite at 0 min to 70% acetoniitrite at 18 min. The thermal curing behavior was studied using a DSC 1 differential scanning calorimeter (Mettler Toledo Co., Greifensee, Switzerland). The scans were performed at a heating rate of 10 °C/min under an N2 atmosphere. Thermogravimetric analysis (TGA) measurements were performed on a TGA/SDTA 85e thermobalance (Mettler Toledo Co., Greifensee, Switzerland) from 30 to 600 °C with a heating rate of 20 °C/min under an N2 atmosphere. The dynamic viscosities of all liquid samples were measured at 25 °C using a viscometer (model DV-II+, Brookfield Engineering Labs Inc., Middleboro, MA, USA) equipped with an LV-5 (51) spindle.

**Determination of SH Value for Synthesized Multi-Functional sec-Thiol Hardeners.** After adding 0.1 g of multi-functional sec-thiol hardener sample in a beaker, 40 mL

---

**Synthesis of 3-Mercaptobutylate.** A mixture of pentaerythritol (152.24 g, 2.0 mol) and H2O (152 mL) was charged in a three-necked flask equipped with a mechanical stir, a cooling condenser, and a Dean–Stark trap. Then, the same procedure described above was followed to obtain 344.52 g TMPMB as colorless oil (95.5%): SH value = 140 g/equiv; 1H NMR (CDCl3, 400 MHz): δ 0.86 (t, 3H, CH2CH3), 1.32 (d, 3H, CH2CH3), 1.45 (m, 2H, CH2CH3), 1.75 (d, 1H, CHSH), 2.55 (m, 2H, CH2C==O), 3.38 (m, 1H, CHSH), 4.06 (s, 2H, CH2O); 13C NMR (CDCl3, 100 MHz): δ 7.8, 23.1, 56.1, 54.9, 64.1, 170.8.

**Synthesis of Pentamethylenetriol tetra(3-Mercaptobutylate).** A mixture of pentaerythritol (111.62 g, 0.82 mol), 3-mercaptopentane-1,1,1-triol (3-Mercaptobutanol) (433.57 g, 3.61 mol), and p-TSA (4.68 g, 25 mmol) in toluene (250 mL) was charged in a three-necked flask equipped with a mechanical stir, a cooling condenser, and a Dean–Stark trap. Then, the same procedure described above was followed to obtain 426.91 g of PETMB as colorless oil (94.9%): SH value = 130 g/equiv; 1H NMR (CDCl3, 400 MHz): δ 1.38 (d, 3H, CH2CH3), 1.74 (d, 1H, CHSH), 2.62 (m, 2H, CH2C==O), 3.34 (m, 1H, CHSH), 4.18 (s, 2H, CH2O); 13C NMR (CDCl3, 100 MHz): δ 25.6, 31.8, 41.9, 45.8, 62.1, 171.1.

**Sample Preparation for Curing Behavior Measurement.** The samples were prepared by the equivalent blending of DGEBA with multifunctional sec-thiol hardeners without any catalyst. The samples for obtaining the gel time data using a house-designed digital temperature recording device equipped with a temperature sensor were prepared by mixing the 0.5 phr of 2,4,6-tris(dimethylaminomethyl)phenol with an equivalent mixture of DGEBA and a hardener.

**Preparation of Cured Epoxy Sample.** The cross-linked samples were obtained from the curing of an equivalent mixture of DGEBA and multifunctional sec-thiol hardeners with 0.5 phr of 2,4,6-tris(dimethylaminomethyl)phenol. The mixture samples were cured at room temperature for 24 h and then further annealed at 130 °C for 12 h.

**Equipment and Experiments.** Fourier-transform infrared (FT-IR) spectra were recorded on an FT/IR-4100 spectrophotometer (Jasco Co., Tokyo, Japan) in the transmittance mode under the air conditions. Nuclear magnetic resonance (NMR) for chemical structure analysis was performed on a VNM400 400 MHz NMR spectrometer (Agilent Technologies Inc., Santa Clara, CA, USA), using chloroform-d1 (CDCl3) as a solvent. Liquid chromatography (LC)—mass spectra (MS) were recorded on an LC−MS-2020 spectrometer equipped with a Shim-pack FC-ODS column (Shimazu, Japan) under acetoniitrite and H2O as the eluent, and the gradient ranged from 40% acetoniitrite at 0 min to 70% acetoniitrite at 20 min. The purity characterization was performed on an Agilent 1220 Infinity HPLC system equipped with a Hектор C18 column (Agilent, USA) under acetoniitrite and H2O as the eluent, and the gradient ranged from 40% acetoniitrite at 0 min to 70% acetoniitrite at 18 min. The thermal curing behavior was studied using a DSC 1 differential scanning calorimeter (Mettler Toledo Co., Greifensee, Switzerland). The scans were performed at a heating rate of 10 °C/min under an N2 atmosphere. Thermogravimetric analysis (TGA) measurements were performed on a TGA/SDTA 85e thermobalance (Mettler Toledo Co., Greifensee, Switzerland) from 30 to 600 °C with a heating rate of 20 °C/min under an N2 atmosphere. The dynamic viscosities of all liquid samples were measured at 25 °C using a viscometer (model DV-II+, Brookfield Engineering Labs Inc., Middleboro, MA, USA) equipped with an LV-5 (51) spindle.

**Determination of SH Value for Synthesized Multi-Functional sec-Thiol Hardeners.** After adding 0.1 g of multi-functional sec-thiol hardener sample in a beaker, 40 mL
of CH₃Cl was added with stirring for 10 min, and then added 20 mL of isopropyl alcohol. The solution was titrated using a 0.1 N iodine standard solution with determining that the end point is the color of the titrated solution changing from white to dark red. The SH value (g/equiv) was calculated by the following equation

\[
\text{SH value (g/equiv) = \frac{\text{sample weight (g)}}{0.1 \times \text{0.1 N iodine consumed (L)}}}
\]

RESULTS AND DISCUSSION

A thiol compound is commonly synthesized using an indirect but versatile process involving an alkyl halide with thiourea to give an isothiouronium salt, followed by the subsequent treatment of this salt with a base, which generates the thiol group.²⁴,²⁵ By modifying this method, 3-mercaptobutanoic acid (2; 3-MBA) as the building block was synthesized from \(\alpha,\beta\)-unsaturated carboxylic acid, crotonic acid, via a two-step reaction process (Scheme 1). The first step involved the Michael addition of the isothiouronium salt (1) as the Michael donor to crotonic acid as the Michael acceptor. Thiourea was protonated to maximize its reactivity in the Michael addition reaction.²⁶,²⁷ To ensure the formation of the isothiouronium salt in the first step, the completed reaction mixture was characterized by TLC using a ninhydrin spray reagent.²⁸ The intermediate salt was formed from crotonic acid and then underwent a nucleophilic attack using protonated thiourea, resulting in the formation of the isothiouronium salt with excellent yield. The isothiouronium salt was then deprotected under basic conditions to give the desired 3-MBA (68.1%). The structure of this building block was confirmed \(^{13}\text{C NMR}\) by the resonance at 30.8 ppm for tertiary carbon (CHSH) as well as a mass peak (ESI-MS) at \(m/z\) 143 \([\text{M + Na}]^+\) (Calcld \(m/z\) 120.02) (Supporting Information, Figure S1).

The esterification reaction of 3-MBA with multiarmed alcoholic compounds was promoted using the previously reported synthetic parameters.¹⁷ The synthetic pathway is briefly shown in Scheme 2. BDMB was synthesized and characterized by \(^1\text{H}\) and \(^{13}\text{C NMR}\) (Supporting Information, Figure S2). On the \(^{13}\text{C NMR}\) spectrum, all resonances for the corresponding nuclei in the expected product were observed without any other peaks. However, the \(^1\text{H NMR}\) signals of the methylene proton adjacent to the carbonyl group and the methine proton adjacent to the thiol group were multiplets, not doublets, indicating the presence of byproducts even after distillation because of the direct thioesterification from a carboxylic acid and thiol compound.¹⁷,²⁹ To characterize the byproducts, we used an LC−MS chromatographic method. Potential byproducts were identified by comparing their retention times, and LC−MS with ESI analysis was used to confirm them further (Supporting Information, Figure S1).

The high-performance liquid chromatography (HPLC) chromatogram of the di-functional sec-thiol, BDMB, and the expected chemical structures for each elution peak are shown in Figure 1. According to the LC−MS result, the desired product eluted at a retention time of 19.8 min on the HPLC chromatogram appearing at \(m/z\) 294 \([\text{M + Na}]^+\) (Calcld \(m/z\) 294.10) in the positive-ion mode, which was the sodium adduct of the desired BDMB. Based on the mass spectroscopic technique, the minor elution signal behind the major signal was

---

Scheme 1. Synthetic Route for 3-Mercaptobutanoic Acid (3-MBA) Synthesis

![Scheme 1](https://example.com/scheme1)

Scheme 2. Synthetic Route for the Synthesis of Multifunctional sec-Thiol Hardeners

![Scheme 2](https://example.com/scheme2)
To elucidate the effect of the number of reactive sites in the starting materials, the two reactants, trimethylolpropane and pentaerythritol, were chosen to react with 3-MBA. TMPMB and PETMB were obtained through the direct esterification reaction. The NMR result for TMPMB was similar to that of BDMS, which involved the clea signals of 13C NMR for the expected carbons in the distilled TMPMB product, but the 1H NMR signals of the methylene proton and the methine proton were multiplets. The HPLC chromatogram for TMPMB and the expected chemical structure for each elution peak are depicted in Figure 2. Three distinct peaks were detected. From the result of LC−MS data (Supporting Information, Figure S1), the elution peak of the desired product appeared at a retention time of 21.1 min on the HPLC chromatogram showing m/z 463 [M + Na]+ (Calcd m/z 460.14) in the positive-ion mode, which was the sodium adduct of the desired TMPMB. Further, two extra peaks were analyzed, which corresponded to uncompleted byproducts containing unreacted hydroxyl groups and byproducts including thioester linkage. The first elution peak was characterized as an uncompleted byproduct with m/z 361 [M + Na]+ (Calcd m/z 338.12) in the positive-ion mode, which was the sodium adduct of 2-ethyl-2-(hydroxymethyl)propane-1,3-diy1 bis(3-mercaptopbutanoate). The other byproduct peak was ascribed to the sec-thiol containing thioester linkage, detected at m/z 565 [M + Na]+ (Calcd m/z 542.15) in the positive-ion mode. The purity of the desired TMPMB was obtained up to 87.5%, and those of the uncompleted byproduct and the byproduct having a thioester linkage were 6.5 and 6.0%, respectively. There was no detected uncompleted byproduct in the synthesis of BDMS, but the uncompleted byproduct occurred in the synthesis of TMPMB because of the steric hindrance of the core section that leads to disturbance during the esterification reaction.

The tetra-functional sec-thiol (PETMB) was also synthesized through the direct esterification reaction and characterized by 1H and 13C NMR spectroscopy. Because the NMR analytic result for the distilled PETMB product was similar to that of TMPMB, the purity and byproduct types were analyzed using HPLC and LC−MS chromatography. Based on mass analysis, the HPLC chromatogram and the chemical structures for each elution peak are depicted in Figure 3. As expected, the desired PETMB appeared at a retention time of 20.5 min on the HPLC chromatogram, supported by the LC−MS results of m/z 567 [M + Na]+ (Calcd m/z 544.13) in the positive ion mode, which was the sodium adduct of PETMB. Indeed, the synthetic results of PETMB showed two types of byproducts as in the synthesis of TMPMB. The uncompleted byproduct and thioester byproduct were detected at m/z 465 [M + Na]+ (Calcd m/z 442.12) and 669 [M + Na]+ (Calcd m/z 646.14), respectively, as the sodium adduct of each byproduct. However, the purity of the desired PETMB was relatively low at 69.3%. Indeed, the byproduct containing thioester linkage (6.1%) was produced similar to that in the synthesis of TMPMB, whereas the uncompleted byproduct content drastically increased up to 24.6% because of the increased steric hindrance of the core section compared with that of the tri-functional core, which causes a disturbance during the direct esterification reaction.

Using the multifunctional sec-thiol hardener, the curing behavior with a DGEBA-type epoxy resin was evaluated using differential scanning calorimetry (DSC). The DSC thermograms for these systems are depicted in Figure 4. The parameters of curing behavior including the curing onset temperature (T_onset), the exothermic maximum peak temperature (T_max), and the total curing reaction enthalpy are listed in Table 1. In addition, the gel time (T_gel) for the thiol−epoxy curing systems was monitored by a house-designed digital temper-
A temperature sensor, and the times to reach the maximum temperature are summarized in Table 1. The gel time ($T_{\text{gel}}$) is defined as the time estimated from the maximum temperature (Supporting Information, Figure S3). As shown in Figure 4, the exothermic peaks on the DSC thermograms indicated that the thiol–epoxy curing reaction between the epoxy group and the thiol group of the multifunctional sec-thiol hardener proceeded in all samples. The reactivity of the multifunctional sec-thiol hardeners toward the epoxy group could be analyzed from the onset temperature of the exothermic peak. The curing onset temperature of the epoxy–hardener curing system slightly increased with the decreased functionality of the multifunctional sec-thiol hardeners. Also, the single exothermic peak pattern during the cross-linking reaction indicates that the curing reaction shows autocatalytic behavior and involves the single thiol–epoxy click reaction and typical epoxy curing reaction including a homopolymerization reaction and etherification reaction. The relative reactivity of the synthesized multifunctional sec-thiol hardener to the epoxy group was further confirmed by comparing it with the curing behavior of trimethylolpropane-tris(3-mercaptopropionate) as the primary thiol hardener, which was reported previously. The exothermic maximum peak of the epoxy system with a trimethylolpropane-tris(3-mercaptopropionate) hardener appeared at 135.5 °C. Based on these DSC thermogram data, the sec-thiol group showed less reactivity to the epoxy group compared to that of the alkyl primary thiol group.

Figure 3 shows the curing behavior of the epoxy curing system with the multifunctional sec-thiol hardener under the presence of a base catalyst. Gelation, which increased the viscosity and temperature of the system simultaneously, occurred until the mixture was converted fully to the solid stage. The maximum exothermic temperature for each sec-thiol hardener was almost the same, but the gel time was delayed by the decreased functionality of the sec-thiol hardener. In comparison with the tri-functional sec-thiol hardener, the gel time of trimethylolpropane-tris(3-mercaptopropionate) as the primary thiol hardener was the shortest (32.5 min) in previous results. This result also supported that the reactivity of the sec-thiol is less than that of the primary thiol hardener in the presence of a catalyst.

After confirming the complete cure of the epoxy samples (Supporting Information, Figure S4), DSC thermograms for the cured epoxy samples are obtained and presented in Figure 5. As shown in Figure 5, the detected single $T_g$ for all cured epoxy samples indicated that the phase morphology of the cured epoxy samples was homogeneous. Upon introducing the PETMB hardener, the $T_g$ value for the cured epoxy sample was the highest at 44.4 °C because of the increased cross-linking density of the cured epoxy samples.

TGA was performed to examine thermal resistance based on the functionality of the sec-thiol hardener (Figure 6). Although the thermal stability of the cured epoxy samples with multifunctional sec-thiol hardeners was similar, the degradation temperature (5 wt % weight loss) slightly decreased in the case of BDMB (333.9 °C), suggesting that the functionality of the sec-thiol group showed less reactivity to the epoxy group.

Table 1. Curing Behaviors of Epoxy Curing Systems with Multifunctional sec-Thiol Hardeners and the Thermal Characteristics of the Epoxy Samples Cured Using a Base Catalyst

| hardener | onset temp. (°C) | peak temp. (°C) | enthalpy (J/g) | $T_{\text{gel}}$ (min) | $T_g$ (°C) | $T_d$ (°C) |
|----------|------------------|-----------------|---------------|------------------------|------------|------------|
| BDMB     | 119.3            | 154.7           | 274.5         | 160.6                  | 5.5        | 333.9      |
| TMPMB    | 110.1            | 142.0           | 296.7         | 76.4                   | 35.9       | 340.4      |
| PETMB    | 98.2             | 122.7           | 308.9         | 46.6                   | 44.4       | 340.6      |

*Measured at 5 wt % loss.

Figure 4. DSC thermograms corresponding to the dynamic curing of epoxy curing systems with multifunctional sec-thiol hardeners.

Figure 5. DSC thermograms for base-catalyzed epoxy curing systems with multifunctional sec-thiol hardeners.

Figure 6. TGA thermograms for base-catalyzed epoxy curing systems with multifunctional sec-thiol hardeners.
epoxy curing system. Industrial-grade epoxy-based materials require not only a short curing time but also long-term stability. To evaluate the storage stability of the epoxy mixture with multifunctional sec-thiol hardeners when equivalently formulated with an epoxy resin without a base catalyst, a storage test was performed at three different temperatures (25, 40, and 60 °C) by monitoring the viscosity change (Table 2). At 25 °C, the viscosities of the epoxy mixtures were maintained for 7 days. Even at 40 °C, their viscosities did not substantially increase (maximum ~110%). In contrast, when stored at 60 °C, although the viscosity change was greater than that at 25 °C, their viscosities slightly increased to a maximum of ~121%. Thus, the sec-thiol hardener offers long-term storage stability for use in a thiol–epoxy curing system.

## CONCLUSIONS

3-MBA was synthesized from crotonic acid and thiourea through the less odorous Michael addition pathway using an isothiouronium salt intermediate. Multifunctional sec-thiols were obtained by the direct esterification between 3-MBA and multifunctional alcoholic compounds, 1,4-butanediol, trimethylolpropane, and pentaerythritol. With the increase in the functionality of the multifunctional alcoholic compounds, 1,4-butanediol, trimethylolpropane, and pentaerythritol, the purities of the products obtained after distillation increased. The reduced reactivity of the sec-thiol hardener provided long-term stability compared to that of the primary thiol hardener. In addition, the glass transition temperature increased with the increased functionality of the sec-thiol hardeners, but their thermal stability did not noticeably change. The reduced reactivity of the sec-thiol hardener provided long-term stability compared to that of the primary thiol hardener. The adopted synthetic pathway for the synthesis of 3-MBA may facilitate mass production, and sec-thiol hardeners can prolong pot life for thiol–epoxy mixtures in industrial applications.

## ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02511.

H and C NMR spectra, as well as LC–MS for the synthesized sec-thiol hardeners and FT-IR spectra and thermograms of curing behavior for a sec-thiol-epoxy mixture with base catalysts (PDF)

### AUTHOR INFORMATION

**Corresponding Author**
Seok-Ho Hwang – Materials Chemistry & Engineering Laboratory, Department of Polymer Science & Engineering, Dankook University, Yongin, Gyeonggi-do 16890, Republic of Korea; orcid.org/0000-0002-0130-1556; Email: bach@dankook.ac.kr

**Author**
Seung-Mo Hong – Materials Chemistry & Engineering Laboratory, Department of Polymer Science & Engineering, Dankook University, Yongin, Gyeonggi-do 16890, Republic of Korea

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c02511

**Author Contributions**
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**
The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

This work was supported by the Korea Institute for Advancement of Technology (KIAT) grant funded by the Korea Government (MOTIE) (P0002007, The Competency Development Program for Industry Specialist) and the Technology Innovation Program (20012770, High Permeability Thermoplastic Elastomer for Solar Module) funded by the Koran Government (MOTIE).

### REFERENCES

1. Hwang, J.; Lee, D. G.; Yeo, H.; Rao, J.; Zhu, Z.; Shin, J.; Jeong, K.; Kim, S.; Jung, H. W.; Khan, A. Proton Transfer Hydrogels: Versatility and Applications. *J. Am. Chem. Soc.* 2018, 140, 6700−6709.
2. Zivic, N.; Kuroishi, P. K.; Dumur, F.; Gigmes, D.; Dove, A. P.; Sardon, H. Recent Advances and Challenges in the Design of Organic Photocatalyst and Photoactive Generators for Polymerizations. *Angew. Chem., Int. Ed.* 2019, 58, 10410–10422.
3. Gadwal, I.; Rao, J.; Baettig, J.; Khan, A. Ternary Graft Copolymers and Their Use in Nanocapsule Preparation. *Macromolecules* 2014, 47, 35−40.
4. Huynh, C. T.; Liu, F.; Cheng, Y.; Coughlin, K. A.; Alsb erg, E. Thiol-Epoxy “Click” Chemistry to Engineer Cytocompatible PEG-Based Hydrogel for siRNA-Mediated Osteogenesis of hMSCs. *ACS Appl. Mater. Interfaces* 2018, 10, 25936−25942.
5. Gadwal, I.; Stuparu, M. C.; Khan, A. Homopolymer Bifunctionalization through Sequential Thiol–Epoxy and Esterification Reactions: An Optimization, Quantification, and Structural Elucidation Study. *Polym. Chem.* 2015, 6, 1393−1404.
6. De, S.; Khan, A. Efficient Synthesis of Multifunctional Polymers via Thiol–Epoxy “Click” Chemistry. *Chem. Commun.* 2012, 48, 3130−3132.
7. Cengiz, N.; Rao, J.; Sanyal, A.; Khan, A. Designing Functionalizable Hydrogels through Thiol–Epoxy Coupling Chemistry. *Chem. Commun.* 2013, 49, 11191−11193.
8. Stuparu, M. C.; Khan, A. Thiol-Epoxy “Click” Chemistry: Application in Preparation and Postpolymerization Modification of Polymers. *J. Polym. Sci., Part A:* Polym. Chem. 2016, 54, 3057−3070.
(9) Carioscia, J. A.; Stansbury, J. W.; Bowman, C. N. Evaluation and Control of Thiol–Ene/Thiol–Epoxy Hybrid Networks. *Polymer* 2007, 48, 1526–1532.

(10) Brändle, A.; Khan, A. Thiol–Epoxy ‘Click’ Polymerization: Efficient Construction of Reactive and Functional Polymers. *Polym. Chem.* 2012, 3, 3224–3227.

(11) Nowak, A. P.; Rodríguez, A. R. A.; Boundy, T. I.; Pajel, C. A.; Adjorlolo, A. A. Rapid Curing Thiol Epoxy Resin with Improved Compression Strength Performance. U.S. Patent 10,035,873 B2, 2018.

(12) Node, M.; Kumar, K.; Nishide, K.; Ohsugi, S.-I.; Miyamoto, T. Odorless Substitutes for Foul-Smelling Thiol: Syntheses and Applications. *Tetrahedron Lett.* 2001, 42, 9207–9210.

(13) Nishide, K.; Ohsugi, S.-I.; Miyamoto, T.; Kumar, K.; Node, M. Development of Odorless Thiols and Sulfides and Their Applications to Organic Synthesis. *Monatsh. Chem.* 2004, 135, 189–200.

(14) Guzmán, D.; Ramis, X.; Fernández-Francos, X.; Serra, A. New Catalysts for Diglycidyl Ether of Bisphenol A Curing Based on Thiol–Epoxy Click Reaction. *Eur. Polym. J.* 2014, 59, 377–386.

(15) Romano, A.; Roppolo, I.; Giebler, M.; Dietlker, K.; Možina, Š.; Šket, P.; Mühlbacher, L.; Schlögl, S.; Sangermano, M. Stimuli-Responsive Thiol-Epoxy Networks with Photo-Switchable Bulk and Surface Properties. *RSC Adv.* 2018, 8, 41904–41914.

(16) Fernández-Francos, X.; Konuray, A.-O.; Belmonte, A.; de la Flor, S.; Serra, Á.; Ramis, X. Sequential Curing of Off-Stoichiometric Thiol–Epoxy Thermosets with a Custom-Tailored Structure. *Polym. Chem.* 2016, 7, 2280–2290.

(17) Loureiro, R. M.; Amarelo, T. C.; Abuin, S. P.; Souké, E. R.; Williams, R. J. J. Kinetics of the Epoxy–Thiol Click Reaction Initiated by a Tertiary Amine: Calorimetric Study using Monofunctional Components. *Thermochim. Acta* 2015, 616, 79–86.

(18) Konuray, A. O.; Fernández-Francos, X.; Ramis, X. Latent Curing of Epoxy-Thiol Thermosets. *Polymer* 2017, 116, 191–203.

(19) Li, Q.; Zhou, H.; Hoyle, C. E. The Effect of Thiol and Ene Structures on Thiol–Ene Networks: Photopolymerization, Physical, Mechanical and Optical Properties. *Polymer* 2009, 50, 2237–2245.

(20) Long, K. F.; Bongiordana, N. J.; Mayerdomo, P.; Olin, M. J.; Ortega, A. D.; Bowman, C. N. Effects of 1°, 2°, and 3° Thiols on Thiol–Ene Reactions: Polymerization Kinetics and Mechanical Behavior. *Macromolecules* 2020, 53, 5805–5815.

(21) Long, K. F.; Wang, H.; Dimos, T. T.; Bowman, C. N. Effects of Thiol Substitution on the Kinetics of Epoxy–Thiol-Michael Reactions and Polimerizations. *Macromolecules* 2021, 54, 3093–3100.

(22) Chen, L.; Wu, Q.; Wei, G.; Liu, R.; Li, Z. Highly Stable Thiol–Ene Systems: from Their Structure–Property Relationship to DLP 3D Printing. *J. Mater. Chem. C* 2018, 6, 11561–11568.

(23) Bongiordana, N. J.; Long, K. F.; Podgorski, M.; Bowman, C. N. Substituted Thiols in Dynamic Thiol–Thioester Reactions. *Macromolecules* 2021, 54, 8341–8351.

(24) Garamszegi, L.; Donzel, C.; Carrot, G.; Nguyen, T. Q.; Hilborn, J. Synthesis of Thiol End-Functional Polystyrene via Atom Transfer Radical Polymerization. *React. Funct. Polym.* 2003, 55, 179–183.

(25) Magenau, A. J. D.; Hartlage, T. R.; Storey, R. F. Thiol-Terminated Polyisobutylene: Synthesis, Characterization, and Derivation. *J. Polym. Sci., Part A: Polym. Chem.* 2010, 48, 5505–5513.

(26) Mehrotra, M.; Mehrotra, R. N. The Kinetics of the Oxidation of Thiourea by 12-Tungstocobaltate(III) Ion: Evidence of Anionic, Neutral and Protonated Thiourea Species in Acetic Acid-Acetate Butter and Perchloric Acid Solution. *Dalton Trans.* 2003, 37, 3606–3611.

(27) Schiessl, W. C.; Sumna, N. K.; Weber, C. F.; Gubo, S.; Dümker-Benfer, C.; Puchta, R.; van Eikema Hommes, N. J. R.; van Eldik, R. Experimental and Theoretical Approaches to the Protonation of Thiourea: a Convenient Nucleophile in Coordination Chemistry Revisited. *Z. Anorg. Allg. Chem.* 2005, 631, 2812–2819.

(28) Qiu, T.; Li, H.; Gao, Y. Pre-Staining Thin Layer Chromatography Method for Amino Acid Detection. *Afr. J. Biotechnol.* 2010, 9, 8679–8681.