

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

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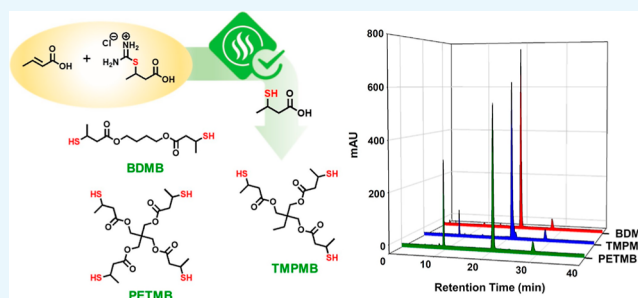


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ABSTRACT: 3-Mercaptobutanoic acid (3-MBA) was synthesized by the less odorous Michael addition pathway using an isothiuronium salt intermediate. Using the synthesized 3-MBA, multifunctional secondary thiol (*sec*-thiol) compounds were obtained and 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 epoxy mixtures with multifunctional *sec*-thiol hardeners were evaluated based 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 rate, excellent regioselectivity, versatility, and high conversion, making it suitable for the preparation of cross-linked polymeric thermosets.^{1–7} This addition reaction involves the nucleophilic ring-opening reaction of strained epoxide electrophiles yielding β -hydroxythioether, and the formation of the hydroxyl group provides enhanced adhesion to metallic surfaces and broad applicability to the synthesis and modification of polymers.^{8,9} 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.^{10,11}

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.^{12,13} 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.^{14,15} 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.^{16–18}

In this study, we report an alternative synthetic pathway using a building block, 3-mercaptoputanoic 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-mercaptoputanoic acid. In previous reports,^{19–23} *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 hard-

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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 Daejung Chemical (Goryeong-gun, Korea). Epoxy resin based on diglycidylether bisphenol-A (DGEBA; YD-128) with an epoxy equivalent weight of 184–190 g/eq was donated from Kukdo Chemical Co., Ltd. (Seoul, Korea).

Synthesis of 3-Mercaptobutanoic Acid. 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 filtered, and the solvent was evaporated under reduced pressure. The purification of the residue by short-path distillation gave colorless oil (68.1%). ¹H NMR (CDCl₃, 400 MHz): δ 1.41 (*d*, 3H, CH₃), 1.89 (*d*, 1H, CHSH), 2.68 (*m*, 2H, CH₂C=O), 3.38 (*m*, 1H, CHSH); ¹³C NMR (CDCl₃, 100 MHz): δ 24.4, 30.8, 45.9, 177.8; IR (KBr window): ν = 2540, 1720 cm⁻¹; ESI-MS: *m/z* 143 [M + Na]⁺ (Calcd *m/z* 120.02).

Synthesis of 1,4-Butanediol bis(3-Mercaptobutylate). A mixture of 1,4-butanediol (73.90 g, 0.82 mol), 3-mercaptoputanoic acid (216.79 g, 1.80 mol), and *p*-TSA (4.68 g, 25 mmol) in toluene (150 mL) was charged in a three-necked flask equipped with a mechanical stir, a cooling condenser, and a Dean–Stark trap. The mixture was refluxed for 3 h and then cooled to 25 °C. The reaction mixture was neutralized with NaOH (5% aqueous solution) until obtaining pH 7–8 and extracted with toluene. The combined organic phase was washed with brine, dried (MgSO₄), and filtered, and the toluene was evaporated under reduced pressure. The purification of the residue by short-path distillation gave 229.61 g BDMA as colorless oil (95.2%): SH value = 142 g/eq; ¹H NMR (CDCl₃, 400 MHz): δ 1.38 (*d*, 3H, CH₃), 1.73 (*m*, 2H, CH₂CH₂O), 1.82 (*d*, 1H, CHSH), 2.59 (*m*, 2H, CH₂C=O), 3.37 (*m*, 1H, CHSH), 4.14 (*s*, 2H, CH₂CH₂O); ¹³C NMR (CDCl₃, 100 MHz): δ 25.2, 31.5, 45.9, 64.1, 170.8.

Synthesis of Trimethylolpropane-*tris*(3-mercaptoputylate). A mixture of trimethylolpropane (110.00 g, 0.82 mol), 3-mercaptoputanoic acid (325.18 g, 2.71 mol), and *p*-TSA (4.68 g, 25 mmol) in toluene (200 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/eq; ¹H NMR (CDCl₃, 400 MHz): δ 0.86 (*t*, 3H, CH₂CH₃), 1.32 (*d*, 3H, CHCH₃), 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, 25.6, 31.8, 45.9, 64.1, 170.8.

Synthesis of Pentaerythritol tetra(3-Mercaptobutylate). A mixture of pentaerythritol (111.62 g, 0.82 mol), 3-mercaptoputanoic acid (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/eq; ¹H NMR (CDCl₃, 400 MHz): δ 1.38 (*d*, 3H, CHCH₃), 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 VNMR400 400 MHz NMR spectrometer (Agilent Technologies Inc., Santa Clara, CA, USA), using chloroform-*d*₁ (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 (Shimadzu, Japan) under acetonitrile and H₂O as the eluent, and the gradient ranged from 40% acetonitrile at 0 min to 70% acetonitrile at 20 min. The purity characterization was performed on an Agilent 1220 Infinity HPLC system equipped with a Hecator C18 column (Agilent, USA) under acetonitrile and H₂O as the eluent, and the gradient ranged from 40% acetonitrile at 0 min to 70% acetonitrile 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 Multifunctional *sec*-Thiol Hardeners. After adding 0.1 g of multi-functional *sec*-thiol hardener sample in a beaker, 40 mL

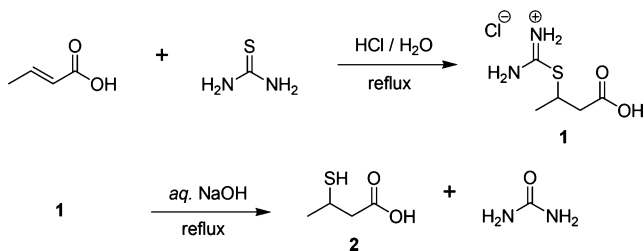
of CH_3Cl was added with stirring for 10 min, and then added 20 mL of isopropyl alcohol. The solution was titrated using a 0.1 N iodine standard solution with determining that the end point is the color of the titrated solution changing from white to dark red. The SH value (g/equiv) was calculated by the following equation

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

RESULTS AND DISCUSSION

A thiol compound is commonly synthesized using an indirect but versatile process involving an alkyl halide with thiourea to give an isothiuronium 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 α,β -unsaturated carboxylic acid, crotonic acid, *via* a two-step reaction process (Scheme 1). The first step involved the

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

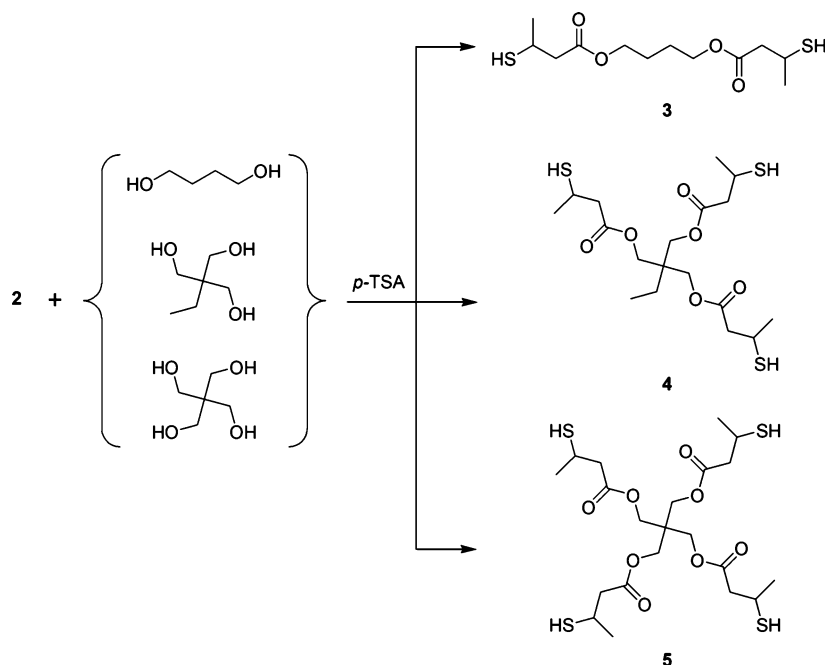


Michael addition of the isothiuronium salt (**1**) as the Michael donor to crotonic acid as the Michael acceptor. Thiourea was protonated to maximize its reactivity in the Michael addition reaction.^{26,27} To ensure the formation of the isothiuronium

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 isothiuronium salt with excellent yield. The isothiuronium salt was then deprotected under basic conditions to give the desired 3-MBA (68.1%). The structure of this building block was confirmed (¹³C NMR) by the resonance at 30.8 ppm for tertiary carbon (CHSH) as well as a mass peak (ESI-MS) at m/z 143 [$M + \text{Na}$]⁺ (Calcd 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 ¹H and ¹³C NMR (Supporting Information, Figure S2). On the ¹³C NMR spectrum, all resonances for the corresponding nuclei in the expected product were observed without any other peaks. However, the ¹H 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 [$M + \text{Na}$]⁺ (Calcd 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 2. Synthetic Route for the Synthesis of Multifunctional *sec*-Thiol Hardeners



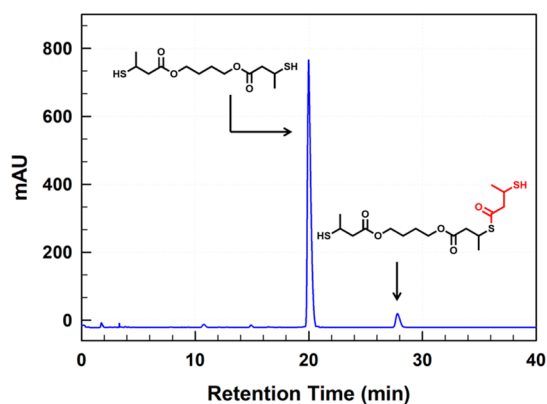


Figure 1. HPLC chromatogram of 1,4-butanediol bis(3-mercaptopbutylate) (BDMB) and the expected chemical structure for each elution peak analyzed using the mass technique.

analyzed as the byproduct including a thioester linkage. In addition, the purity of BDMB was analyzed to be 93.7%.

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 BDMB, which involved the clean signals of ^{13}C 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

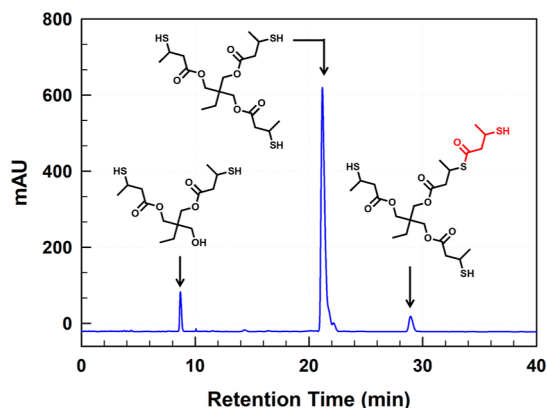


Figure 2. HPLC chromatogram of trimethylolpropane tris(3-mercaptopbutylate) (TMPMB) and the expected chemical structures of each eluted peak analyzed through a mass technique.

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 $[\text{M} + \text{Na}]^+$ (Calcd m/z 440.14) 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 $[\text{M} + \text{Na}]^+$ (Calcd m/z 338.12) in the positive-ion mode, which was the sodium adduct of 2-ethyl-2-(hydroxymethyl)propane-1,3-diyl bis(3-mercaptopbutanoate). The other byproduct peak was ascribed

to the *sec*-thiol containing thioester linkage, detected at m/z 565 $[\text{M} + \text{Na}]^+$ (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 BDMB, 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 ^{13}C 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

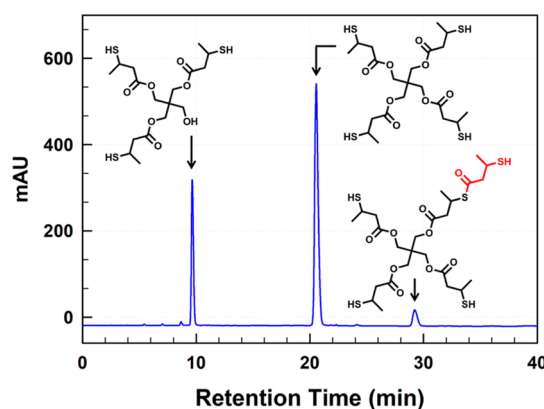


Figure 3. HPLC chromatogram of pentaerythritol tetra(3-mercaptopbutylate) (PETMB) and the expected chemical structures of each eluted peak analyzed through a mass technique.

PETMB appeared at a retention time of 20.5 min on the HPLC chromatogram, supported by the LC–MS results of m/z 567 $[\text{M} + \text{Na}]^+$ (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 $[\text{M} + \text{Na}]^+$ (Calcd m/z 442.12) and 669 $[\text{M} + \text{Na}]^+$ (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_i), the exothermic maximum peak temperature (T_p), 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-

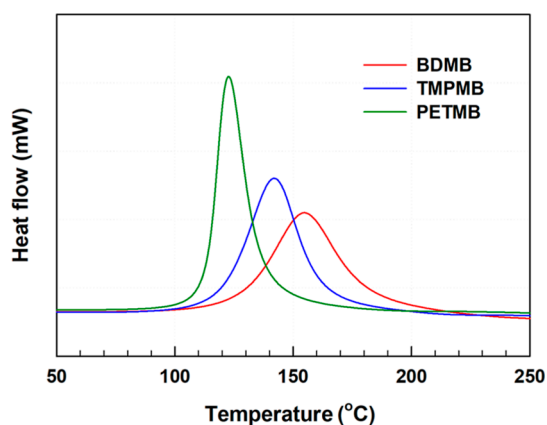


Figure 4. DSC thermograms corresponding to the dynamic curing of epoxy curing systems with multifunctional *sec*-thiol hardeners.

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	curing behavior			thermal characteristics		
	onset temp. (°C)	peak temp. (°C)	enthalpy (J/g)	T_{gel} (min)	T_g (°C)	T_d^a (°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

^aMeasured at 5 wt % loss.

ature recording device equipped with a temperature sensor, and the times to reach the maximum temperature are summarized in Table 1. The gel time (T_{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^{17,29} and involves the single thiol–epoxy click reaction and typical epoxy curing reaction including a homopolymerization reaction and etherification reaction.¹⁶ 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.³⁰ 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 S3 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.³⁰ 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

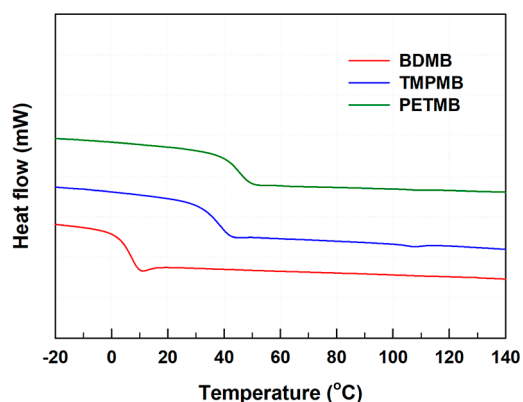


Figure 5. DSC thermograms for base-catalyzed epoxy curing systems with multifunctional *sec*-thiol hardeners.

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

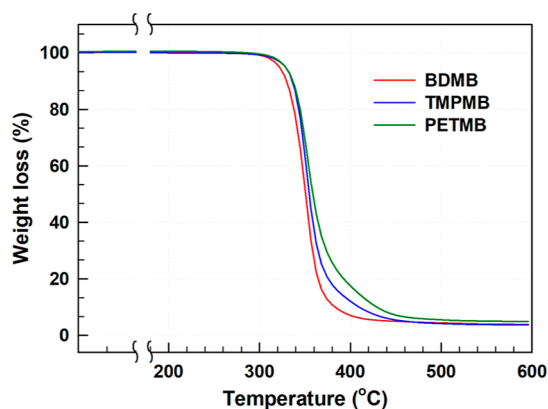


Figure 6. TGA thermograms for base-catalyzed epoxy curing systems with multifunctional *sec*-thiol hardeners.

sec-thiol hardener did not significantly affect the thermal resistance of the cured epoxy.

Industrial-grade epoxy-based materials require not only a short curing time but also long-term stability.^{31,32} 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

Table 2. Viscosities of Epoxy Mixtures with Multifunctional *sec*-Thiol Hardeners under Different Storage Temperatures and Times (Viscosity Unit = cP)

hardener	storage temp. (°C)	storage time (day)				
		0	1	3	4	7
BDMB	25	450	450	460	450	450
	40	450	460	470	470	470
	60	450	470	510	640	720
TMPMB	25	1300	1300	1300	1310	1300
	40	1300	1330	1380	1380	1430
	60	1300	1300	1360	1470	1550
PETMB	25	2760	2760	2750	2750	2760
	40	2760	2760	2810	2820	2810
	60	2760	3020	3150	3270	3340

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 isothiuronium 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 core compounds during the esterification reaction, the purities of the products obtained after distillation decreased, and the production of the uncompleted byproduct increased. The DSC results showed that the curing kinetics of the *sec*-thiol hardener with DGEBA was slower than 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>.

¹H and ¹³C 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)

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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.

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