Correlation between the Structural Variations in Thiol-Based Hardeners and Properties of Thiol–Epoxy Polymers

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structure–property relationship between the thiol hardeners and epoxy elastomers. In this study, we carefully examined the effect of the hardener structure on the properties of thiol–epoxy polymers. While maintaining the structure of a tetrafunctional thiol as a cross-linker, we varied the structure of a bifunctional thiol to analyze its influence on the physical properties of the resulting thiol– epoxy material. Factors such as the presence or absence of an oxygen atom, the existence of a ring structure, the presence or absence of aromatics, and the geometric shape of the hardener all influenced the mechanical properties, such as modulus, stress, and toughness. Notably, the structure of the bifunctional hardener allowed precise control over the glass transition temperature of the thiol–epoxy material near room temperature, resulting in distinct mechanical behaviors (elastic or plastic) at room temperature. Based on these findings, we successfully developed a thiol–epoxy material exhibiting elastomeric behavior at room temperature and shape memory characteristics at temperatures close to room temperature (e.g., 40 °C).

KEYWORDS: thiol-epoxy polymer, thiol hardener, thiol-epoxy click reaction, epoxy elastomers, shape memory polymers

INTRODUCTION

Epoxy resins, a class of polymers with a diverse range of applications in materials like adhesives, coatings, paints, and packaging, have garnered significant attention.^{1,2} The global market size for epoxy resins was valued at US\$ 14.7 billion in 2021, and their compound annual growth rate (CAGR) is expected to be 6.7% from 2022 to 2030 owing to their increasing demand in the construction sector, particularly in coatings and paints.^{3,4} The unique properties of epoxy resins, such as excellent adhesion, high mechanical stress, low mold shrinkage, good electrical insulation, high chemical resistance, and good heat resistance, have contributed significantly to their relevance in the current industries.^{1,5–9}

Substantial efforts have been devoted by researchers to developing novel materials that exploit the advantages of epoxies, such as their extraordinary strength and minimal curing shrinkage.¹⁰ Consequently, the mixing of epoxies with other materials has emerged as an attractive way to impart additional properties and has been widely adopted. Using this strategy, epoxy-based elastomers with remarkable flexibility

have been successfully developed, with applications in sensors,¹¹ smart fabrics,¹² nanocomposites,^{13,14} thermally conductive composite materials,¹⁵ and so on.^{16,17}

In the early stages of research, epoxy-based elastomers were prepared by blending elastomers^{14,18,19} or polydimethylsiloxane (PDMS)²⁰ with epoxy resins, in order to enhance and control material properties such as strength, stiffness, and polarity. The inclusion of elastic materials like butadiene– acrylonitrile copolymer or styrene–butadiene–styrene block copolymer effectively reduced the modulus of the epoxy while increasing its elongation at break, imparting elastomeric characteristics.¹⁹ Moreover, the formation of hydroxyl functional groups following the opening of the epoxy ring,

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Figure 1. (a) Schematic illustration of the impact of incorporating bis-thiol hardeners into the conventional thiol-epoxy network: The quantity of bis-thiol hardener added affects the glass transition temperature of the epoxy-thiol network, consequently influencing its elastic and shape memory properties. (b) Structures of the synthesized hardeners and the influence of core modifications are given.

combined with well-designed backbones, endowed epoxy elastomers with valuable self-healing and vitrimeric properties, thereby expanding their range of potential applications.²¹ Despite these advantages, the mixing of rubber or PDMS with epoxy resins in the absence of additives such as silicone often results in phase separation, hindering the formation of a homogeneous mixture. Consequently, in the production of epoxy elastomers through physical blending, the incorporation of additives is necessary to prevent issues such as phase separation and high-temperature curing, which represent notable drawbacks.²⁰

Recent studies have explored the fabrication of epoxy elastomers using only epoxy resins and hardeners, avoiding the incorporation of elastic rubber or other substances that could lead to phase separation. This approach aims to enhance the convenience of the fabrication process by eliminating the need for additives. Conventional methods for preparing epoxy-based elastomers using epoxy resins and hardeners typically rely on amine-based hardeners with linear, long alkyl chains such as Jeffamine^{22,23} or involve adjusting the number of functionalities in thiol-based hardeners to modify the glass transition temperature $(T_g)^{24,25}$ Epoxy hardeners based on a primary amine structure facilitate the formation of a highly cross-linked polymeric structure by generating additional secondary and tertiary C-N covalent bonds during the curing process. Consequently, the formation of epoxy elastomers typically involves the use of amine hardeners that utilize long aliphatic chains to lower $T_{g'}$ and such elastomers exhibit elastomeric properties at room temperature. In contrast, thiol functional groups can generate only a single C-S covalent bond. Hence, the desired thiol-epoxy network with elastomeric properties at

room temperature can be achieved by simply mixing a bifunctional thiol hardener with a multifunctional hardener, without the need for introducing lengthy alkyl chains. Moreover, thiol-based hardeners offer distinct advantages due to their ability to cure rapidly at low temperatures and resistance to yellowing, presenting multiple benefits in comparison to amine-based hardeners.^{26,27} The demanding conditions of high temperature and/or extended curing time can elevate process expenses and might not align with specific applications sensitive to high-temperature processes, for example, electronics and semiconductor packings^{28,29} and flat panel displays.³⁰

Thus far, only a limited number of thiol-based hardeners has been developed (a comprehensive overview of these hardeners is provided in Figure S1). $^{31-34}$ The majority of thiol-based curing agents developed incorporate three or more functional groups, resulting in the formation of the thiol–epoxy network characterized by a relatively high cross-linking density and modulus. Consequently, these agents are employed to augment or even replace the performance of structural adhesives, which conventionally depend on amine-epoxy networks. On the other hand, in the pursuit of creating an epoxy with elastomeric properties as discussed above, the incorporation of a carefully blended bifunctional thiol hardener along with a multifunctional thiol hardener is indispensable. Importantly, it would offer significant advantages if the elastomeric properties of the thiol-epoxy network could be systematically governed through structural adjustments of the bifunctional hardener. Unfortunately, the investigation of such correlation studies between the structure and properties remains underexplored.



Figure 2. (a) Synthetic scheme of the bis-thiol hardener. (b) Proposed mechanistic pathways of thiol-epoxy ring-opening click reaction assisted by DBU as an amine catalyst.

In this study, we prepared various bifunctional thiol-based hardeners with tailored structures by using a simple modular chemical approach. We systematically designed and synthesized seven different thiol-based curing agents and compared their behavior in the presence of additional oxygen atoms (as a hydrogen bond acceptor), ring structures, and aromatic units and for different substituent positions (positional effect). The structure-property relationship studies revealed that even slight structural changes in the bifunctional hardener structure could result in significant differences in the thermal and mechanical properties of a thiol-epoxy network based on a tetrafunctional hardener as a cross-linker (i.e., pentaerythritol tetrakis(3-mercaptopropionate) (PETMP)). Interestingly, a loosely cross-linked epoxy network was found to exhibit a low T_{σ} and elastic mechanical behavior, which is not observed for conventional epoxy polymers (Figure 1a).^{22,33} Consequently, the synthesized epoxy network showed excellent shape memory properties, allowing the polymer to remember and switch its shape from a permanent form to a temporary form upon exposure to external stimuli.³⁵ The reversible thermal phase transitions facilitate the fixation of the temporary shape and recovery of the original shape, with adjustable recovery temperature and time based on T_{g} .^{22,36}

RESULTS AND DISCUSSION

Design of Thiol-Based Hardeners. We employed bisphenol A diglycidyl ether (DGEBA) as the epoxy resin, and the selection of hardeners was guided by considerations of structure-property relationships and synthetic convenience (Figure 1b). The hardener's structure can be divided into two parts, core and periphery, which are linked through efficient coupling reactions (Figure 2a). While various coupling chemistries such as azide-alkyne click reactions, imine formation, and enamine formation can be employed in principle, we chose to employ the traditional acid-catalyzed ester coupling reactions for synthetic convenience. To facilitate a systematic investigation of the structure-property relationship, we kept the peripheral groups fixed with mercaptopropionic acid at both ends. We then introduced systematically modified structural analogues for the core part. This approach was based on previous studies focused on the understanding of the structure-property relationship of amine-based epoxy hardeners.³⁷⁻³⁹ We synthesized thiol-based hardeners with mercaptopropionic acid on both sides, varying the core structure for each. These thiol hardeners were named as follows: pentane-1,5-diyl bis(3-mercaptopropanoate) (PBMP), oxybis(ethane-2,1-diyl) bis(3-mercaptopropanoate) (OBMP), (tetrahydrofuran-2,5-diyl)bis(methylene) bis(3-mercaptopropanoate) (TBMP), cyclohexane-1,4-diylbis(methylene) bis(3mercaptopropanoate) (CBMP), 1,4-phenylenebis(methylene)

bis(3-mercaptopropanoate) (p-PhBMP), 1,2-phenylenebis-(methylene) bis(3-mercaptopropanoate) (*o*-PhBMP), and 1,3-phenylenebis(methylene) bis(3-mercaptopropanoate) (*m*-PhBMP). These designed hardeners aimed to investigate the structure–property relationship with regard to the role of oxygen atoms as hydrogen bond acceptors, the influence of the ring structure (with and without aromaticity), and the impact of the shape of the hardener (bent versus linear, i.e., the positional effect). The synthesis of the hardeners was successfully accomplished under optimized conditions, as confirmed by ¹H NMR, ¹³C NMR, and mass spectrometry analyses.

Curing Behavior of the Thiol-Epoxy System. First, we investigated the curing behavior of the prepared hardeners. For the curing of the thiol-epoxy polymers, we used 0.5 mol % DBU as a catalyst at 60 °C for 3 h. In a study performed by Bowman et al.,⁴⁰ mechanistic pathways were proposed for the thiol-epoxy reaction in the presence of nonlatent tertiary amines. As illustrated in Figure 2b, this pathway centers on a base-catalyzed addition reaction. The process involves the generation of a thiol anion from the acid-base reactions between the thiol and tertiary amine. This thiol anion then attacks an epoxide moiety through an anionic addition reaction. Following the opening reaction of the epoxide, the resulting alkoxide intermediate can engage in a variety of reactions, leading to the formation of a thiol-epoxy system. These reactions include an acid-base reaction with a thiol group to generate thiol anions (i.e., autocatalysis) or with an ammonium ion to regenerate a tertiary amine (i.e., catalyst regeneration). Additionally, nucleophilic displacement can occur with another epoxide moiety. Recent studies have suggested that the mechanistic pathway is contingent on the nature of the amine catalyst.²⁹ Tertiary amines possessing high basicity, such as DBU and N-dimethylaniline (termed nonlatent catalysts), are expected to follow the aforementioned pathway. In contrast, amines with high nucleophilicity but low basicity (e.g., imidazole, and DMAP) are believed to follow different pathways, including those involving a nucleophilic substitution reaction of an amine with epoxy as the first step.

To compare the curing behaviors of the thiol and amine hardeners, we employed differential scanning calorimetry (DSC) to monitor the curing process (Figure 3a). Xylylenediamine (XDA) was used as a reference to assess the curing behaviors of the thiol-based hardeners. We first evaluated the epoxy curing behavior using XDA without a catalyst, resulting in a high T_{peak} value of approximately 120 °C. Subsequently, to evaluate the impact of the catalyst on the curing rate, we performed cocuring experiment involving XDA and DBU. DBU was chosen as the catalyst due to its ability to enable curing at a relatively lower temperature, and its reactivity can be regulated by adjusting the quantity. The DBU expedited the curing of the XDA without exerting significant influence on the overall curing behavior. In contrast to the XDA, when we attempted the curing of epoxy using a thiol-based hardener (in this case, PBMP) without a catalyst, no curing occurred.⁴¹ However, upon the introduction of a catalyst, the curing process initiated and proceeded at a markedly lower T_{peak} .

We then proceeded to monitor the curing behavior of the thiol-epoxy system, using PBMP as the thiol-based hardener, with varying DBU catalyst stoichiometries (0.5, 1, and 2 mol % DBU) (Figure 3b). Since curing at room temperature can result in significant issues in terms of the pot life and storage stability, it is recommended to carry out curing at temperatures



Figure 3. (a) Curing behavior using both amine and thiol hardeners, with or without DBU, was monitored by DSC. (b) The curing behavior using thiol hardeners with varying DBU contents was monitored by DSC.

higher than room temperature. Table 1 shows that lower enthalpy change (ΔH_{a}) was observed in all samples when 1 and 2 mol % catalyst were used, while 0.5 mol % catalyst exhibits the highest value. ΔH_a is calculated by integrating the heat flow within the exothermal peak area from an unreacted sample (Figure S2). All measured samples consist of the same amount of resins and hardeners except the catalyst. Consequently, the total measured enthalpy should remain constant. However, unwanted precuring may decrease the measured enthalpy value. Indeed, lower enthalpy values were measured when 1 and 2 mol % catalyst were added, implying that the reaction took place at room temperature. As a result, a catalyst quantity of 0.5 mol % was selected. The same curing conditions were maintained in the subsequent stages of the investigation to facilitate the study of the structure-property relationship.

Structure–Property Relationship Studies of the Thiol–Epoxy System. To analyze the influence of the core structure of the synthesized thiol-based hardener on the properties of the epoxy system and establish a structure– property relationship, mechanical and thermal properties were assessed. To achieve this, DGEBA and thiol-based hardeners were blended with a catalyst at a molar ratio of 1:1, and the mechanical and thermal properties were explored. Notably, a glass transition temperature below room temperature, decent thermal stability, and distinctive mechanical properties attributed to the thiol hardener structures were observed (Figures S3–S6). Furthermore, upon heating to 200 °C using DSC, no melting peak was detected and the synthesized thiol– epoxy film exhibited transparency, indicating its amorphous

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Table 1. Result of the Curing Behavior of the Thiol-Epoxy Network with Different Molar Ratios of the DBU Catalyst

entry	epoxy resin	thiol hardener	DBU equivalent (compared to DGEBA) (mol %)	T_{onset} (°C)	$T_{\text{peak}} (^{\circ}\text{C})$	T_{endset} (°C)	$\Delta H_{\rm a} \left({\rm J}/{\rm g} \right)$
1	DGEBA	PBMP	0.5	34.2	67.4	105.4	307.9
			1.0	23.8	53.9	83.8	185.3
			2.0	17.0	48.1	73.4	114.9
2		OBMP	0.5	78.1	103.5	121.8	349.5
			1.0	25.1	52.9	78.6	210.9
			2.0	14.1	42.3	66.6	106.0
3		TBMP	0.5	17.7	46.0	73.0	358.0
			1.0	34.9	64.8	94.7	228.4
			2.0	51.1	89.1	113.5	129.0
4		CBMP	0.5	35.5	80.4	147.0	246.3
			1.0	34.9	61.8	92.0	238.0
			2.0	23.3	47.5	74.1	160.1
5		p-PhBMP	0.5	40.3	95.5	135.1	221.2
			1.0	28.0	58.0	91.0	171.7
			2.0	17.2	43.7	69.8	148.7
6		o-PhBMP	0.5	37.8	77.3	106.7	241.2
			1.0	29.8	57.9	82.0	236.5
			2.0	14.5	44.9	71.0	100.6
7		m-PhBMP	0.5	39.6	77.9	124.0	230.6
			1.0	32.9	68.2	101.8	164.0
			2.0	20.2	47.0	71.8	134.5



HS



OBMP bis-thiol hardener (Spacer)



0.5 mol% DBU (Non-latent base catalyst)



Epoxy-Thiol network



Figure 4. (a) Synthetic scheme of the bis-thiol hardener and epoxy-thiol network. (b) Mechanical properties of the thiol-epoxy network were evaluated with varying molar ratios of the cross-linker. (c) Gel fraction measurements were conducted, accompanied by descriptions of the corresponding molar ratios for each entry.

nature (Figure S7). The synthesized curing agents possess two thiol functionalities that play a primary role in the epoxide

ring-opening reaction, contributing to the polymer backbone. However, the epoxide ring opening also occurs via the alkoxide



Ring effect 5 5 Positional effect Oxygen effect 0 0 0 200 400 600 0 200 400 600 Tensile strain (%) Tensile strain (%)

Figure 5. (a) Summary of thermal and mechanical properties of the prepared thiol-epoxy networks, utilizing various thiol hardeners with a 20 mol % of cross-linker content. (b) Stress-strain curves of epoxy network polymers were generated using synthesized thiol hardeners to investigate ring and oxygen effects in entries 1-4. (c) The stress-strain curves of epoxy network polymers in entries 4-7 were measured to observe aromatic and positional effects.

intermediate formed through the reaction of the epoxy ring and thiolate, acting as a side reaction.^{29,42} This reaction results in the formation of C–O bonds via the alkoxide ring-opening reaction, creating a mildly cross-linked network. Despite the small amount, a gel fraction of the synthesized thiol-epoxy polymer without a cross-linker remains (Scheme S1) However, due to the low cross-linking density, the mechanical properties are poor and the elastic behavior is unsatisfactory, rendering it unsuitable for various applications.

Consequently, to explore the structure-property relationship of an elastomer that maintains a high modulus while increasing stretchability, a tetrafunctional PETMP cross-linker was introduced (Figure 4a). As the quantity of incorporated PETMP increased, both tensile stress and gel fraction elevated, accompanied by a decrease in tensile strain (Figure 4b,c). This trend indicates improved stretchability alongside a maintained high modulus, leading to the selection of the 20 mol % PETMP inclusion for the subsequent experiments.

After introducing PETMP at a concentration of 20 mol % relative to DGEBA, we utilized both DSC and dynamic mechanical analysis (DMA) to investigate the thermal and viscoelastic properties of the thiol-based hardeners with distinct core structures (Figure 5a). In DSC measurements to determine $T_{g'}$ it was observed that the linear chain PBMP exhibited the lowest T_g , while o-PhBMP had the highest T_g . This difference is likely attributed to the shorter chain length between the thiol functionalities connected to the ortho position as well as the presence of aromaticity inducing $\pi - \pi$ interactions, which contributed to the elevated $T_{\rm g}$ in *o*-PhBMP. The $T_{\rm g}$ values of the other hardeners showed only slight variations, ranging from 20 to 22 °C. However, it is important to note that the T_g values obtained from the DMA differed from those obtained through DSC analysis. DSC measures T_{g} primarily based on the differences between the heats of exothermic and endothermic reactions at different temperatures, whereas DMA considers the material response to the oscillatory strain applied at varying frequencies alongside temperature. As a result, the $T_{\rm g}$ values measured by DSC and DMA may vary due to factors including polymer cross-linking density.³⁶

We then employed DMA to determine the $T_{\rm g}$ and storage modulus at 25 °C for elastic properties at room temperature. Specifically, PBMP and OBMP with linear chain core structures exhibited lower T_{g} and storage modulus values at room temperature than the other hardeners with ring-based structures. While investigating the impact of oxygen incorporation in the core structure (as seen in TBMP and CBMP), no significant variation was observed in the thermal properties. The T_g value of OBMP was slightly higher than that of PBMP, and the additional oxygen in TBMP yielded a higher storage modulus value at 25 °C than CBMP, which had a higher T_{σ} value. This yielded fewer apparent differences in the thermal



Figure 6. (a) Shape memory properties and polymer chain variations of the synthesized epoxy network polymer are illustrated. (b) Shape memory property across entries 1-7 under different recovery conditions of 40 and 25 °C.

properties compared to other hardeners. Further analysis of the thermal properties indicated that T_{g} values of the hardeners CBMP and PhBMPs, possessing cycloalkane or aromatic rings, exhibited only negligibly differences. Among them, m-PhBMP showed the highest G', which denotes the storage modulus with a value of 1304 MPa at 25 °C, corresponding to its highest maximum stress and toughness, consistent with a previous study.⁴⁵ This phenomenon can be explained by the fact that the phenylene rings substituted at the para- and orthopositions can rotate on their axis (known as π flips), whereas rotation is impossible for the meta-position, resulting in the highest yield stress due to the absence of energy dissipation pathways. The second highest G' at room temperature was observed for TBMP, which incorporated an additional oxygen atom into the ring structure, resulting in a high maximum stress and toughness. Consequently, the thermal and mechanical property measurements confirmed that introducing a ring into the core structure of the epoxy hardener led to increased stress, known as the ring effect.

To establish the structure-property relationship based on the core structure of the epoxy hardeners, mechanical properties were measured at room temperature (Figure Sb,5c). The first observed phenomenon can be attributed to the existence of the cycloalkane ring structure observed when comparing PBMP and TBMP. The ring structure provides a larger contact area compared to linear alkane structures, resulting in increased van der Waals forces and enhanced interaction between polymer chains. As a consequence, introducing a ring structure into the epoxy hardener led to an elevated initial modulus and ultimate strength, ultimately increasing the toughness of the epoxy network. The introduction of additional oxygen in the hardener core structure, forming extra hydrogen bond acceptors for the hydroxyl groups of the polymer chains, led to an increase in the stress and strain. This was evidenced by comparing the mechanical behaviors of PBMP and OBMP, as well as TBMP and CBMP with the ring core structures. These findings highlight that the oxygen atoms interact with the hydroxyl groups in the cured epoxy network, inducing additional physical cross-linking and effecting the spatial distance between polymer chains. This trend aligns with observations from other studies (Figure S10)^{43,44}

Furthermore, CBMP and *p*-PhBMP were employed to explore the effect of aromatic units present in the hardener on the characteristics of the epoxy system (Figure 5c). However, no notable differences were observed in their mechanical properties. This indicates minimal variation in the interaction energy between cyclohexane–cyclohexane and benzene–benzene, supported by energy calculations.⁴⁶ Additionally, PhBMPs with the mercapto moiety attached at distinct positions of the aromatic ring (*para-, ortho-,* and *meta-*positions) were analyzed to assess the positional effects of the epoxy hardener. However, no noteworthy differences in the mechanical properties were observed.

Shape Memory Polymer. Based on the results of the structure-property relationship study, we prepared various thiol-epoxy networks demonstrating excellent elastomeric properties near room temperature. For the epoxy network to function as an elastomer, a chemical cross-linker (a multifunctional thiol hardener) responsible for the elastic properties must be incorporated. An appropriate combination of bifunctional thiol hardeners is also vital for interactions between polymer chains and cross-linking points. Notably,

the structure of the bifunctional hardener influences the $T_{\rm g}$ value of thiol–epoxy polymers. The $T_{\rm g}$ values of the epoxy networks stemming from linear chain-based hardeners are below room temperature, resulting in elastic behavior at room temperature. In contrast, the epoxy materials possessing the hardeners with ring-based structures exhibit plastic behavior but can transition to elastic behavior with a slight increase in temperature. This distinction in deformation behavior at different temperatures holds promise for applications like shape memory, as exemplified by our investigation.

To explore the shape memory properties of the thiol–epoxy polymer system, we conducted an experiment (Figure 6a). The shape memory behavior observed in amorphous polymers is linked to domain transformation during glass transition. This phenomenon can be modulated by utilizing polymers with varying T_g values.^{47,48} When amorphous polymers exist below $T_{g'}$ they retain a temporary shape in the glassy state. Conversely, when they exist above $T_{g'}$ the polymer network returns to its original shape.

The specimens used in this study were prepared using the same procedure as that used for the earlier samples. These samples underwent a series of steps to create a temporary shape, involving heating in a 40 °C water bath for 5 s, deformation, and fixation in a cold bath (Figure 6b). Recovery of the original shape was assessed by immersing the samples in a 40 °C bath. Notably, all samples exhibited rapid recovery, regaining the original shape within 3 s, even at a low temperature of 40 °C. Consequently, these samples reverted to their original shapes within 2 min at ambient temperature. This finding underscores the crucial role of T_g in determining the trigger temperature for the shape memory behavior of amorphous polymers.

CONCLUSIONS

In this study, we synthesized and cured a range of thiol-based hardeners with diverse core structures and examined their mechanical and thermal properties to establish the structureproperty relationship for thiol-epoxy systems. By evaluating samples cross-linked with epoxy resin and PETMP, we compared the properties of various hardeners with different core structures, considering factors such as hydrogen bonding, ring structure, aromatic units, and positional effects. Specifically, the hardeners containing linear chains (PBMP and OBMP) exhibited higher elongation than those with ring chains (TBMP and CBMP). Additionally, hardeners with additional oxygen increased stress and strain in accordance with their linear and ring core structures, respectively. The increased stress was attributed to aromaticity, and the mechanical behaviors showed a minimal change as their position varied. Shape memory properties were evaluated through shape fixation and recovery experiments. Samples with $T_{\rm g}$ values lower than room temperature promptly restored their original shape at room temperature. Furthermore, all samples regained their shape within 3 s when immersed in a 40 °C water bath, confirming the shape memory properties across all samples. Through the investigation of the structure-property relationship, we expanded the understanding of thiol-based epoxy elastomers. The versatility of epoxy materials has been further enhanced by enabling a wide range of mechanical and viscoelastic properties through T_g control, achieved by varying synthesized bifunctional thiol hardeners.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.3c01502.

¹H and ¹³C NMR for synthesized thiol–epoxy hardeners, procedures of polymerization, mechanical behavior of thiol–epoxy polymers, curing behavior, thermomechanical properties of synthesized thiol–epoxy polymers, additional supporting figures and tables, and brief statement of the contents of the material (PDF)

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Notes

The authors declare no competing financial interest.

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