

Shape memory polybenzoxazines based on polyetheramine



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ABSTRACT

Five difunctional benzoxazines were synthesized from polyetheramine, phenol, *o*-allylphenol, *o*-cresol, *p*-cresol, *m*-cresol, and formaldehyde. The substituent groups decrease the ring-opening polymerization to present the ascending order of *meta*-, *para*-, and *ortho*-positions in comparison to the unsubstituted phenol-based benzoxazines. The dynamic mechanical properties of the resultant polybenzoxazines depend on the structure of the starting phenols. The polybenzoxazines exhibit one-way dual-shape memory behavior in response to changes in temperature, and the shape memory effects are evaluated by tensile stress-strain and bending tests with a temperature programme based on glass transition temperature.

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1. Introduction

Shape memory polymers (SMPs) are a class of stimuli-responsive materials, which are capable of being fixed in a temporary shape and then recovered to their original shapes under an appropriate stimulus [1–5]. SMPs have a wide range of applications in self-deployable space structures, heat shrink tubes, intelligent medical devices, actuators, sensors, textiles, and packaging. In recent decades, substantial progress has been achieved in SMP research, and various SMPs, which recover their permanent shape in response to heat, light, electrical field, pH, and moisture, have been developed. Among various stimulus-sensitive SMPs, thermally induced SMPs are the most widely studied and applied in industry. Under an external applied stress, thermally induced SMPs can be deformed and temporarily fixed in a temporary shape via vitrification or crystallization of switching domains, and the thermally induced shape memory effect (SME) occurs upon exceeding a certain switching temperature under a stress-free condition [6].

In general, polymers that are designed to exhibit an SME require a suitable molecular architecture. An SMP network architecture consisted of two components on the molecular level: netpoints to determine the permanent shape and switching segments to fix the temporary shape [1–5]. The former can be achieved by the introduction of chemical cross-links, crystalline structures, or interpenetrating networks into polymers [3], whereas the latter ones are the flexible segments related to reversible thermal phase transitions, such as glass transition, melting–crystallization transition, and liquid crystal clearing transition [1–3].

Benzoxazines are a class of thermosetting resins, which can be used as shape memory materials, because the corresponding polybenzoxazines can provide a chemical cross-linking structure to determine a permanent shape for SMPs. Recently, bisphenol-A/aniline-type benzoxazine (BA-a) was used to copolymerize with the prepolymer of polyurethane or epoxy to form SMPs [7–10], in which the polybenzoxazine (PBA-a) is thought to serve as a second set of netpoints supporting a permanent shape. Jana et al. reported that the shape memory properties of the BA-a/urethane copolymers are higher than those of the neat polyurethane [7], and the PBA-a phase in the BA-a/urethane copolymers can induce shape memory behavior in non-shape memory polyurethane with amorphous soft segment and significantly improve the values of shape fixity, recovery ratio, and recovery stress in shape memory polyurethane [8]. Rimdusit et al. prepared a series of BA-a/epoxy copolymers and found that BA-a/epoxy copolymers exhibited a high value of shape fixity close to 100% and the thermomechanical performance of epoxy SMPs was enhanced, whereas the BA-a/epoxy SMPs with a higher BA-a content provided a longer shape recovery time [9,10]. However, to date, there has been only one study that reported on the shape memory properties of neat polybenzoxazines based on a siloxane-containing diphenol [11].

Benzoxazines possess the advantages of flexible molecular design, low manufacturing cost, good chemical resistance, excellent electrical insulation, high processability, and near-zero shrinkage on polymerization [12–15]. During the polymerization reaction, no reaction by-products are released and no catalyst is required [16–19]. In addition, on the basis of the molecular design flexibility of benzoxazines, different switch segments can be introduced into benzoxazine molecules to tune the glass transition temperature (T_g) and the mechanical property of the resultant polybenzoxazines in a wide range. Correspondingly, the

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polybenzoxazines may appear in different SMEs. Therefore, we decided to fabricate SMPs from benzoxazines.

In order to design polybenzoxazines with a thermally induced SME, suitable flexible chain segments should be introduced into polybenzoxazine networks to allow a certain orientation by conformational changes upon application of external stress to obtain a desired deformability, and the resultant polybenzoxazines can provide stimuli-sensitive molecular switches, providing additional temporary cross-links that stabilize the temporary shape.

The objective of this study is to develop benzoxazines with polyetheramine (PEA) and evaluate the SMEs of the resultant polybenzoxazines. Considering the structural effect on SME, five difunctional benzoxazines were synthesized from PEA, phenol, *o*-allylphenol, *o*-cresol, *p*-cresol, *m*-cresol, and formaldehyde, followed by thermally activated polymerization yielding the corresponding polybenzoxazines. The polymerization behavior of the benzoxazines and the structure change from benzoxazines to the resultant polybenzoxazines were studied, and the dynamical mechanical properties and shape memory properties for the polybenzoxazines were evaluated.

2. Experimental

2.1. Materials

Phenol, *o*-cresol, *p*-cresol, *m*-cresol, formaldehyde (37% aqueous), 1,4-dioxane, and chloroform were obtained from Tianjin Chemical Reagent Co., Ltd., China. *o*-Allylphenol was purchased from Shandong Laizhou Hualu Storage Battery Co., Ltd., China. PEA (Jeffamine D230, average molecular weight $M_n = 230 \text{ g mol}^{-1}$, polydispersity index (PDI) = 1.26) was offered by Shanghai Jingchun Chemical Reagent Co., Ltd., China. All chemicals were used as received.

2.2. Synthesis of PEA-based main-chain benzoxazines

In this study, the phenol, *o*-allylphenol, *o*-cresol, *p*-cresol, and *m*-cresol-PEA-based benzoxazines are hereafter referred to as **m**₁, **m**₂, **m**₃, **m**₄, and **m**₅ (Scheme 1), respectively.

The **m**₁ is synthesized by the following procedure. In a 250-mL, three-necked round-bottom flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser, 50 mL of 1,4-dioxane and 12.7 mL of formaldehyde were added. The mixture was stirred in an ice bath, and 10 mL of Jeffamine D230 was added dropwise with a pressure-equalizing dropping funnel. After 30 min, 7.2 mL of phenol was added. Then, the temperature was gradually increased up to 85 °C and stirring was maintained for approximately 12 h. Thereafter, the solvent was removed by distillation under reduced pressure, and the residue was dissolved in approximately 20 mL of chloroform, followed by washing several times with a 1 mol L⁻¹ NaOH aqueous solution and deionized water. Subsequently, the solution was dried over anhydrous Na₂SO₄ and the chloroform was evaporated under reduced pressure. Finally, the product was dried at 70 °C in a vacuum oven for 24 h, and a yellow-brown, transparent, high-viscous liquid was obtained. The yield of **m**₁ was approximately 78%.

The **m**₂, **m**₃, **m**₄, and **m**₅ were synthesized by a procedure similar to **m**₁, except the phenol (7.2 mL) was substituted by *o*-allylphenol (10.7 mL), *o*-cresol (8.5 mL), *p*-cresol (8.5 mL), and *m*-cresol (8.5 mL), respectively, and the reaction temperature was maintained at 90 °C rather than 85 °C. The yields of benzoxazines ranged from 74% to 86%.

2.3. Preparation of polybenzoxazines

First, benzoxazine was poured into a steel mold, and the mold was put into a vacuum oven. Then, for **m**₁, the vacuum oven was step-heated to 100, 120, 140, and 160 °C, and held at each temperature for 1 h, and then held at 180 °C for 6 h; for **m**₂ and **m**₃, the vacuum oven was step-heated to 100, 120, 140, 160, and 180 °C, and held at each temperature for 1 h, and then held at 200 °C for 6 h; and for **m**₄ and **m**₅, the vacuum oven was step-heated to 100, 120, 140, and 160 °C and held at each temperature for 1 h, and then held at 190 °C for 6 h. The resultant polybenzoxazines from **m**₁, **m**₂, **m**₃, **m**₄, and **m**₅ are designated as **p**₁, **p**₂, **p**₃, **p**₄, and **p**₅, respectively.

2.4. Measurements

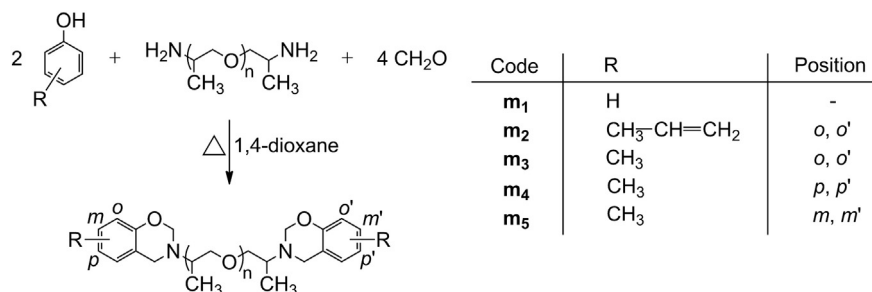
¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III 600 NMR spectrometer. Deuterated chloroform (CDCl₃) was used as the solvent and tetramethylsilane (TMS) as the internal standard. Solid-state NMR experiments were performed at room temperature (25 °C) on a Bruker Avance III 400 NMR spectrometer operating at a ¹³C resonance frequency of 100.568 MHz. The samples were analyzed under cross-polarization/magic-angle spinning (CP/MAS) conditions using 4-mm zirconium rotors at a spinning frequency of 5 kHz. A 90° pulse width of 4 ms was used, and the CP Hartmann–Hahn contact time was set at 3.0 ms. The chemical shifts of ¹³C spectra were externally referenced to the carbon signal of solid adamantane (38.48 ppm relative to TMS).

The Fourier transform infrared (FTIR) spectra were obtained with a Nicolet 380 FTIR spectrometer at a resolution of 4 cm⁻¹. A benzoxazine sample was dissolved in chloroform, and the solution was coated on a KBr disk to form a thin uniform film. When the solvent was completely evaporated at 50 °C in a vacuum oven, the disk was scanned by the FTIR spectrometer. Thereafter, the disk was heated isothermally in a static air oven. During the polymerization reaction, the disk to be scanned was removed periodically.

The dynamic polymerization reactions for benzoxazines based on PEA were monitored by a PerkinElmer Diamond differential scanning calorimeter operating in nitrogen, and the samples were scanned at a heating rate of 10 °C min⁻¹.

A PerkinElmer DMA-8000 dynamic mechanical analyzer was used to determine the dynamic storage modulus (E') and loss factor ($\tan \delta$) for polybenzoxazines based on PEA using single cantilever bending mode. Measurements were performed on rectangular specimens with dimensions of approximately 10.0 × 6.0 × 2.0 mm by heating from -50 to 200 °C, at a heating rate of 2 °C min⁻¹ and frequency of 1 Hz.

The shape memory properties of **p**₃ were qualitatively examined by a series of photos recorded in the shape recovery process for specimens



Scheme 1. Synthesis of benzoxazines based on PEA.

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