Preparation of Degradable Polymenthide and Its Elastomers from Biobased Menthide via Organocatalyzed Ring-opening Polymerization and UV Curing

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INTRODUCTION

In recent years, degradable polymeric materials from renewable biomass have gained considerable attention in materials science.1−4 They could reduce our dependence on fossil fuels and mitigate the adverse environmental effects of white pollution. Various renewable biomass, including terpenes, fatty acids, plant oils, etc., has been widely explored in designing elastomers.5−7 Among the bio-based elastomers that may be considered, biodegradable polyester elastomers have undergone fast growth in recent years for their good biocompatibility and mechanical properties in tissue engineering and other biomedical applications.8−10 Polyesters are inherently biologically degradable due to the ester bonds subject to hydrolysis and/or enzymatic catalyzed degradation in vivo, which is crucial for their applications in tissue engineering.8,11

Polyester elastomers are polyesters that have an elastic region over a large strain or have the ability to recover its initial shape after a deformation.10 Thermoplastic elastomers based on ABA block copolymers with polylactide (PLA) hard end block and rubbery midblock have been well studied and exhibit good mechanical properties.11−13 Noncrystalline polymenthides (PMs), obtained via ring-opening polymerization (ROP) of menthide monomers derived from natural product menthol, are excellent soft segments for polyester elastomers.14−16 Fully renewable and degradable PLA-PM-PLA and poly(α-methylene-γ-butyrolactone)-b-poly(menthide)-b-poly(α-methylene-δ-butyrolactone) (PMBL-PM-PMBL) triblock thermoplastic elastomers have been reported as good substitutes for styrenic-based systems in varied applications.15,16 In addition to thermoplastic elastomers, chemically cross-linked polyesters have been proven to be degradable and mechanically competitive with petroleum-derived chemically cross-linked polymers.17−20 Hillmyer et al. have prepared the renewable cross-linked elastomers based on β- methyl-δ-valerolactone (MVL).18 High tensile strengths and elongations were obtained and the materials were capable of degradation in acidic and basic conditions at 60 °C. Recently, they reported the synthesis of cross-linked γ-methyl-ε-caprolactone (MCL) based polyester elastomers with tunable and competitive mechanical properties, and the materials could readily hydrolyze under mild enzymatic conditions.19

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Abstract Development of degradable polyester elastomers plays an important role in the applications of soft materials. Noncrystalline polymenthides (PMs) from menthol derived lactone monomers are excellent soft segments for preparing degradable polyester elastomers. By using cyclic trimeric phosphazene base (CTPB) as an organocatalyst, we successfully synthesized PMs with different molecular weights (8.2 kDa to 100.7 kDa) in high yields via ring-opening polymerization (ROP) of menthide. When a CTPB/urea binary catalytic system was adopted, the polymerizations proceeded in a more controlled manner. Using glycerol as initiator, star shaped PMs with well-defined structure were synthesized and subsequently end-capped by acrylate. UV irradiation of the terminal acrylate groups in the star-shaped PMs resulted in formation of chemically cross-linked polyester elastomers without heat or other stimuli. The obtained polyester elastomers exhibit matched modulus (3.8−5.5 MPa), tensile strength (0.56−0.68 MPa), and strain at break (280%−320%) with soft body tissues, displaying great potential in biomedical applications.

Keywords Polyester elastomer; Cyclic trimeric phosphazene base; Ring-opening polymerization; Menthide, Biobased polyester

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ARTICLE
Inspired by these studies, we intended to synthesize chemically cross-linked polyester elastomers using star-shaped PMs as the polymer precursors via UV-irradiation.

Menthide, a seven-membered lactone with two alkyl groups, has been synthesized from menthol through Baeyer-Villiger oxidation over a century ago (Scheme 1).[24] Metallic catalysts such as zinc-alkoxide, diethyl zinc, tin octanoate, and Mg(BHT)2(THF)2 have been successfully used to catalyze the ROP of menthide with high efficiency.[11,21–23] Compared with metal-based catalysts, organocatalysts exhibit great advantages, including higher availability, lower sensitivity, and better environmental friendliness.[24–30] In particular, cyclic trimeric phosphazene base (CTPB), a metal-free organocatalyst developed by our group, has been proved to be highly efficient for the ROP of different cyclic esters,[31–33] even for the strain free monomers γ-butyrolactone (γ-BL) and ω-pentadecalactone (PDL).[34–38] It is therefore possible to apply CTPB as the organocatalyst for the ROP of seven-membered menthide.

In this work, the prepolymer PMs were conveniently prepared via metal-free CTPB catalyzed ROP of renewable lactone menthide followed by end-capping of acrylics, which are subject to UV irradiation to form crosslinkings. We employed several alcohols including biobased glycerol and xylitol as initiators to prepare polyester polyols with well-defined polymer structure. After end group functionalization and UV irradiation, the resultant elastomers showed good thermal stability and mechanical properties. To the best of our knowledge, this is the first report of metal-free organocatalyzed ROP of menthide, and the polymerization rate is competitive among the metal-based catalytic systems.

**EXPERIMENTAL**

**Materials**

Tetrahydrofuran (THF), dichloromethane (DCM), and toluene were purified by purging with dry nitrogen, followed by passing through columns of activated alumina. Benzyl alcohol (BnOH) was purchased from Aladdin Co., and stirred with CaH2 for 24 h, then distilled under reduced pressure and stored over activated 4Å molecular sieves in a glove box. CTPB was synthesized according to the procedure reported before.[34] 1-Cyclohexyl-3-(4-trifluoromethyl)phenylurea (U1) was prepared from commercially available isocyanates and amines. U1 was dried under vacuum at 50 °C for at least 8 h and then stored in a glove box. All other chemicals were purchased from commercial suppliers and used without further purification unless otherwise noted.

**Instruments**

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE NEO 400 MHz NMR spectrometer (400 MHz for 1H-NMR and 100 MHz for 13C-NMR). Chemical shifts were reported in δ (ppm) and the residual deuterated solvent signal was used as reference. Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) analyses were conducted on a Bruker Microflex MALDI-TOF MS spectrometer equipped with a 337 nm nitrogen laser. The sample solutions (10 mg/mL in THF), trans-2-[2-(3-4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCBT) solution (10 mg/mL in THF), and sodium trifluoracetate solution (5 mg/mL) were mixed in a volume ratio of 4:6:1, 1 μL of which was then deposited on the target plate and dried before measurement. The gel permeation chromatography (GPC) measurements were performed on an Agilent HPLC system equipped with a model 1260 Hip degasser, a model 1260 Iso pump, and a model 1260 refractometer detector. Three Mz-Gel SDSplus (10 Å, 10 Å, and 10 Å) columns were connected in series. THF was used as the eluent at a flow rate of 1.0 mL/min at 40 °C. The molecular weight and polydispersity were calculated using polystyrene standards with narrow molecular weight distribution as references. The sample concentration used for GPC analysis was about 10 mg/mL. Differential scanning calorimetry (DSC) was performed using a TA differential scanning calorimeter DSC 25 that was calibrated using high purity indium at a heating rate of 10 °C/min. DSC data were determined from the second scan at a heating rate of 10 °C/min following a slow cooling rate of 10 °C/min to remove the influence of thermal history. Thermogravimetric analysis (TGA) measurements were performed on a TA Q50 thermogravimetric analyzer. The samples were heated from 40 °C to 500 °C at a heating rate of 10 °C/min under N2 atmosphere with a flow rate of 50 mL/min. Instron 5900 instruments was used to conduct mechanical tests of polymer at ambient temperature. The rectangular shaped samples had dimensions of 20 mm × 4 mm × 0.5 mm (length × width × thickness). The initial span length was 10 mm. The tensile measurements were performed with a uniaxial extension rate of 10 mm/min. Three different specimens at least from the same sample were tested for each PM elastomer.

**Synthesis of Menthide**[21]

Pyridinium chlorochromate (PCC, 16.2 g, 75.0 mmol) was ground with silica gel (16.2 g, 200–300 mesh). The resulting mixture was suspended in a 1000 mL round-bottom flask containing 200 mL of methylene chloride. To the resulting orange suspension was added a solution of (−)-menthol (7.8 g, 50.0 mmol) in 300 mL of methylene chloride while stirring at room temperature. After 2 h, the resulting dark brown suspension was diluted with 400 mL of diethyl ether and filtered through a Buchner funnel layered with celite and silica gel. The filtrate was concentrated under reduced pressure and low temperature to give crude (−)-menthone as a colorless oil (7.7 g, 100%). The crude (−)-menthone was used for the next step without further purification. 3-Chloroperoxycarboxylic acid (85%, 12.2 g, 60.0 mmol) was added in batches to a solution of (−)-menthone (7.7 g, 50.0 mmol) in anhydrous dichloromethane (500 mL) under a flow of nitrogen at 0 °C with stirring. The mixture was allowed to warm to room temperature and was stirred overnight. Some white precipitate formed and was removed by filtration. The filtrate was then washed with saturated aqueous solutions of Na2SO3, Na2CO3, distilled water, and brine. The organic layer was separated, dried over anhydrous MgSO4, and filtered. Evaporation of solvent from the filtrate afforded the crude product as yellow oil, which was
purified by passing through a silica column using a mixture of pentane and ethyl acetate (3:1, v/v) as eluent. Colorless oil was obtained and dissolved in minimal pentane. By allowing the pentane solution to stand at −20 °C overnight, the product was obtained as white needles (6.0 g, 70%). These were further purified by sublimation (45–50 °C, 53.3 Pa). 1H-NMR (400 MHz, CDCl3, δ, ppm): 4.01 (q, 1H), 2.54–2.40 (m, 2H), 1.93–1.76 (m, 4H), 1.60–1.50 (m, 1H), 1.30–1.20 (m, 1H), 1.00 (d, 3H, J = 6.8 Hz), 0.93 (q, 6H). The characterization data are consistent with those reported in the literature.

**General Procedures for CTPB Catalyzed ROP of Menthide**

Polymerizations were performed in 25-mL flame-dried Schlenk tubes interfaced to the dual-manifold Schlenk line. The reactor was charged with a predetermined amount of CTPB, initiator, and solvent, and kept stirring for 10 min in the glovebox. Then the menthide solution (3.0 mol/L in toluene) was added to the reaction mixture. The reactor was sealed, taken out of glovebox, and immersed in the oil bath under the predetermined temperature. After a desired period of time, the polymerization was quenched by addition of acetic acid. The quenched mixture was then precipitated with 50 mL of cold pentane twice to remove unreacted monomer, and dried in a vacuum oven at 30 °C to a constant weight.

**Synthesis of Acrylate Terminated Star-shaped PMs**

This step was performed according to the literature report.[39] Hydroxyl terminated PMs and powdered K2CO3 (20 equiv.) were dissolved in DCM in an oven-dried double-neck round-bottom flask and stirred at 0 °C under N2. A solution of acryloyl chloride (20 equiv.) in DCM was added dropwise over 30 min after which the reaction was heated to reflux overnight. K2CO3 in cooled reaction mixture was filtered off and the organic phase was washed with water. The volume of organic phase reduced before precipitation into a 20-fold volume excess of cold methanol.

**Preparation of UV-cured Elastomers**

Star-shaped PM30/PM90 (1.5 g) and 2,2-dimethoxy-2-phenylethylmethacrylate (45 mg, photo initiator) were dissolved in DCM (2 mL) and poured into Teflon rectangular mold (3 cm × 4 cm). A small amount of DCM (1 mL) was used to finish the transfer, and the solvent cast mixtures were put under a stream of air in dark for 24 h to evaporate the solvent. After drying, the mold was exposed to ultraviolet light at the wavelength of 365 nm, cured several minutes. The notation of the cross-linked elastomer is CEₙ, where n represents the polymerization degree of the PM used to prepare the elastomer. Each elastomer was characterized using swelling, DSC, TGA, and tensile testing.

**RESULTS AND DISCUSSION**

**ROP of Menthide**

We attempted to realize controlled ROP of menthide by using CTPB as the organocatalyst (Scheme 2). So, the ROP experiment was firstly carried out in bulk at 135 °C using BnOH as initiator (Table 1, run 1). After 72 h, 90% of monomer was converted to polyester with a molecular weight of 8.8 kDa and a polydispersity of 1.73. The bulk polymerization rate was competitive with stannous octoate but slower than previously reported ROP of menthide using metal based zinc catalyst.[11,12,22] Then the ROP reactions of menthide with 1% CTPB loading were performed in toluene at 80 or 110 °C using BnOH as initiator (Table 1, runs 2 and 3). The results showed that both polymerizations proceeded in a controlled manner and the monomer conversions after 5 h were 72% at 80 °C and 84% at 110 °C. There was no clear difference on the polymerization activities between the two reaction temperatures, so the following ROPs were conducted at 80 °C.

Then we tried to prepare polymenthides with different molecular weights using glycerol as initiator (Table 1, runs 4–8) under the same polymerization conditions. With fixed CTPB/initiator ratio of 1/1, the monomer/initiator ratio was varied from 100/1 to 500/1 (Table 1, runs 4–7). As shown in Fig. 1, the number-average molecular weight (Mn) of the resulting polymenthides increased from 17.3 kDa to 77.9 kDa, which matched well with the theoretical molecular weights. When the monomer/initiator ratio was further raised to 1000/1, the lower catalyst loading (0.1% molar ratio) reduced the polymerization efficiency dramatically. So the amount of CTPB was increased to 1/500 (Table 1, run 8) and a 93% monomer conversion was achieved after polymerizing at 80 °C for 24 h. The molecular weight of the resulting polymer was 100.7 kDa. To synthesize different polyester polyols, pentaerythritol and xylitol were also used as initiators in the ROP of menthides (Table 1, runs 9 and 10). Due to the poor solubility of these two alcohols in toluene, the reaction temperature was elevated to 110 °C and the initial concentration of the monomer was lowered to 2 mol/L. High conversions of 91% were achieved for both two polymerizations, leading to polymenthides with controlled molecular weights (8.2 kDa for run 9 and 9.1 kDa for run 10).

The molecular structures of the resulting polymenthides were further examined using matrix-assisted laser desorp-
Table 1 ROP of menthide in the presence of CTPB. a

| Run | Initiator | [M]/[C]/[I] | (M)5 (mol/L) | Solvent | T (°C) | t (h) | Conv. b (%) | Mₙtheor (kDa) | MₙGPC d (kDa) | D d |
|-----|-----------|-------------|--------------|---------|--------|-------|-------------|---------------|---------------|-----|
| 1   | BnOH      | 50/1/1      | Bulk None    | Toluene | 135    | 72    | 90          | 7.8           | 8.8           | 1.74 |
| 2   | BnOH      | 100/1/1     | Toluene     | 80      | 5      | 72    | 12.4        | 15.6          | 1.61          |     |
| 3   | BnOH      | 100/1/1     | Toluene     | 110     | 5      | 84    | 14.4        | 18.4          | 1.69          |     |
| 4   | Glycerol  | 100/1/1     | Toluene     | 80      | 12     | 91    | 15.6        | 17.3          | 1.66          |     |
| 5   | Glycerol  | 200/1/1     | Toluene     | 80      | 12     | 95    | 32.4        | 29.5          | 1.86          |     |
| 6   | Glycerol  | 300/1/1     | Toluene     | 80      | 12     | 91    | 41.5        | 44.2          | 1.84          |     |
| 7   | Glycerol  | 500/1/1     | Toluene     | 80      | 24     | 96    | 81.8        | 77.9          | 1.68          |     |
| 8   | Glycerol  | 1000/2/1    | Toluene     | 80      | 24     | 93    | 158.4       | 100.7         | 1.62          |     |
| 9   | Pentaerythritol | 50/1/1 | Toluene | 110     | 12     | 91    | 7.9         | 8.2           | 1.67          |     |
| 10  | Xylitol   | 50/1/1      | Toluene     | 110     | 12     | 91    | 7.9         | 9.1           | 1.94          |     |

a Conditions: CTPB 0.05 mmol; CTPB and initiator were firstly mixed in toluene, followed by addition of menthide. b Monomer conversion was determined by ¹H-NMR analysis in CDCl₃ before polymer purification. c Mₙtheor = Mmenthide (170.13 Da) × [menthide]₀ × [initiator]₀ × conversion + Minitiator. d Number-average molecular weight (Mₙ) and dispersity (D) values were determined by GPC at 40 °C in THF relative to polystyrene standards.

Fig. 1 The molecular weights of different polymenthide samples in Table 1, runs 4–7: (a) GPC traces and (b) theoretical molecular weights (square) versus GPC measurement (circle).

Results and Discussion

In our previous work, we found that CTPB/urea binary catalyst showed better selectivity for ring opening relative to intramolecular transesterification toward the ROP of γ-butyrolactone. So we tried the CTPB/U1 catalytic system for the ROP of menthides (Scheme 3) to reduce cyclic by-products and the formation/ionization time-of-flight mass spectroscopy (MALDI-TOF MS). As shown in Fig. S2 (in the electronic supplementary information, ESI), the main product obtained from 50/1/1 menthide/CTPB/glycerol ratio was the three arm polyesters. However, the molecular ion peaks corresponding to cyclic polyesters also existed in the low molecular region. In our previous work, we found that CTPB/urea binary catalyst showed better selectivity for ring opening relative to intramolecular transesterification toward the ROP of menthides than CTPB organocatalyst alone. Therefore, we chose CTPB/U1 as the catalyst to prepare the polymenthide precursors for the cross-linked elastomers. In addition, glycerol with three hydroxyl groups was good candidate for the initiator in star-shaped polymenthide precursors owing to its high solubility and reactivity. Gram-scale polymerizations under same conditions with runs 2 and 3 in Table 2 were conducted to synthesize enough polymenthide precursors with different molecular weights.

Preparation of Polyester Elastomers

With well-defined star-shaped polymenthide polyls ready, we then tried to transform terminal hydroxyls into double bonds for the following UV crosslinking as shown in Scheme 4. Three-armed polymenthides obtained from runs 2 and 3 in Table 2 were used as precursors, i.e., PM₃₀-OH and PM₃₀-OH. Acrylation was performed using acryloyl chloride and the acrylate groups were incorporated successfully, affording corresponding acrylate terminated three-armed PM₃₀ and PM₃₀ precursors, respectively. As shown in Fig. 3, the signals representing terminal acryl groups at 6.39, 6.12, and 5.81 ppm appeared in the ¹H-NMR spectrum of acrylated polymenthide PM₃₀ (Fig. 3b). The amount of acrylate groups could be calculated by comparing the integration of the peak area corresponding to acryl groups and glycerol protons (Figs. S3 and S4 in ESI). After end group functionalization, all of the terminal hydroxyls in glycerol initiated polyesters were converted to acrylate groups completely.

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The crosslinked elastomer films CE30 and CE90 were prepared by UV irradiation of the solvent casted mixtures of acrylated polymenthides PM30 and PM90 with prescribed photo initiators. The degree of cross-linking was evaluated by swelling the films in DCM and extracting the soluble fraction. The results showed that the gel fraction of the cured polyester elastomers CE30 and CE90 was 0.84 and 0.78, respectively, which indicated highly effective crosslinkings of terminal acrylate groups.

Properties of UV-cured Polymenthide-based Elastomers
The thermal properties of polymenthides and corresponding cured elastomers were investigated with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). As shown in Fig. 4, the glass transition temperatures (Tg) of the three-armed PM-OH samples with different molecular weights (Table 1, runs 4–7) were all approximately −24 °C. Tg of the UV-cured polymenthide-based elastomers CE30 and CE90 decreased slightly to −27 °C after cross-linking. TGA curves of cross-linked elastomers CE30 and CE90 and their corresponding PM30-OH and PM90-OH precursors are demonstrated in Fig. 5. The 5% weight loss temperatures for UV-cured elastomers were greater than 280 °C, which was comparable to those of the polymenthide precursors, suggesting a general good thermal stability. The detailed thermal properties of different PMs and resultant cross-linked elastomers are listed in Table S1 (in ESI).

The mechanical properties of resultant polyester elastomers CE30 and CE90 were finally investigated using tensile tests at a tensile speed of 10 mm/min. At least three specimens were measured and the average values with standard deviations were reported. Table S2 (in ESI) shows the Young’s modulus, tensile strength, and strain at break of two cross-linked elastomers CE30 and CE90. The Young’s modulus was calculated from the slope of the stress-strain curve between 0%–10% strain. The Young’s moduli of CE30 and CE90 were 3.8 and 5.5 MPa, respectively, suggesting the similar elasticity. Compared with CE30 (0.56 ± 0.05 MPa, 320% ± 30%), the tensile strength of CE30 slightly increased to 0.68 ± 0.07 MPa but the strain at break decreased to 280% ± 40%. These two cross-linked elastomers both exhibited matched mechanical properties with soft body tissues.[9] However, the tensile strengths were lower than the previously reported PLA-PM-PLA triblock copolymers that contained semicrystalline PLA end blocks.[14,16] It is probably due to the noncrystalline nature of PMs resulting from the nonpolar methyl and isopropanol groups on the polymer chain.

Besides, previous investigations on the enzymatic hydrolysis of PMs precursors, suggesting a general good thermal stability. The detailed thermal properties of different PMs and resultant cross-linked elastomers are listed in Table S1 (in ESI).

### Table 2: ROP of menthide in the presence of CTPB and urea.

| Run | Initiator | Cat. | [M] (mol/L) | [I]/[C]/[I] | T (°C) | t (h) | Conv. (%) | \( M_n^{\text{theor}} \) (kDa) | \( M_n^{\text{GPC}} \) (kDa) | \( M_n^{\text{NMR}} \) (kDa) | D^a |
|-----|-----------|------|-------------|-------------|--------|-------|-----------|----------------|----------------|----------------|------|
| 1   | Pentaerythritol | CTPB + U1 | 3          | 60/1/1     | 60     | 24    | 91        | 9.3            | 7.1            | 8.8            | 1.57 |
| 2   | Glycerol | CTPB + U1 | 3          | 30/1/1     | 60     | 24    | 92        | 4.7            | 4.5            | 4.9            | 1.80 |
| 3   | Glycerol | CTPB + U1 | 3          | 90/1/1     | 60     | 24    | 85        | 13.1           | 10.5           | 13.2           | 1.32 |

^a Conditions: [CTPB]/[U1] = 1/3; CTPB, U1 and initiator were firstly mixed in toluene, followed by addition of menthide. ^b Monomer conversion was determined by ^1H-NMR analysis in CDCl₃, before polymer purification. ^c 170.13 Da × ([menthide]:[initiator]:[glycerol] = 5.3 kDa) prepared with [menthide]:[CTPB]:[U1]:[glycerol] = 30/1/3/1. Run 2, Mₙ = 5.3 kDa) prepared with [menthide]:[CTPB]:[U1]:[glycerol] = 30/1/3/1. The Young’s modulus, tensile strength, and strain at break of two cross-linked elastomers CE30 and CE90. The Young’s modulus was calculated from the slope of the stress-strain curve between 0%–10% strain. The Young’s moduli of CE30 and CE90 were 3.8 and 5.5 MPa, respectively, suggesting the similar elasticity. Compared with CE30 (0.56 ± 0.05 MPa, 320% ± 30%), the tensile strength of CE30 slightly increased to 0.68 ± 0.07 MPa but the strain at break decreased to 280% ± 40%. These two cross-linked elastomers both exhibited matched mechanical properties with soft body tissues.[9] However, the tensile strengths were lower than the previously reported PLA-PM-PLA triblock copolymers that contained semicrystalline PLA end blocks.[14,16] It is probably due to the noncrystalline nature of PMs resulting from the nonpolar methyl and isopropanol groups on the polymer chain.

**Scheme 4** Synthesis of UV-curable polymenthide based cross-linked elastomer.
rolysis of polyesters have shown that the amorphous nature of the polyesters could typically accelerate hydrolysis,[18,40] indicating the biodegradability of the noncrystallizable PM based elastomers. Also, the hydrolytic degradation behavior of CE30 was studied in basic condition. As shown in Fig. S5 (in ESI), CE30 proved to be degradable in 5% NaOH solution at 37 °C. In general, these flexible and elastic chemically cross-linked polyester elastomers will display potential applications in soft tissue engineering.

CONCLUSIONS

We demonstrated that degradable polymenthides could be efficiently prepared via CTP8 catalyzed ROP of biobased menthide with high yields and controlled molecular weights. The introduction of urea cocatalyst made the polymerizations proceed in a more controlled manner to obtain star-shaped polymenthides. The terminal hydroxyl group of prepolymer PM30-OH and PM90-OH can be efficiently acrylated to afford PM30 and PM90 with UV crosslinkable groups. The polyester elastomers CE30 and CE90 were prepared via UV irradiation of the solvent casted mixtures of acrylated polymenthides PM30 and PM90 and photo initiators. DSC and TGA studies indicated that cured elastomers have good thermal stability similar to menthide precursors. These menthide based polyester elastomers are promising sustainable alternatives to petroleum-derived elastomers and have a promising prospect in biomedical applications.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-020-2415-9.

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