Chinese Journal of
POLYMER SCIENCE

RESEARCH ARTICLE

https://doi.org/10.1007/s10118-023-2994-3
Chinese J. Polym. Sci. **2023**, *41*, 1836–1845

Synthesis of Sulfur/Selenium-containing Polyester with Recyclability and Controllable Hydrophilicity and Glass Transition Temperature

Wen-Jing Li, Xiang-Qiang Pan*, Jian Zhu*, and Zheng-Biao Zhang

Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Department of Polymer Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

Electronic Supplementary Information

Abstract We present a ring-opening polymerization of bridged cyclic lactone utilizing alcohol as the initiator and organic base as the catalyst. Bridged γ-butyrolactone monomers (PhSGBL and PhSeGBL) were synthesized efficiently from commercially available 3-cyclohexene-1-carboxylic acid. Due to the ring strain of the bridged structure, ring-opening polymerization of this type of γ-butyrolactone derivative was successfully carried out under mild conditions, *e.g.*, using ethylene glycol as the initiator and a commercial catalyst [1,5,7-triazabicyclo [4.4.0 dec-5-ene (TBD)] as the catalyst at 30 °C. The obtained polymer could be degraded to its monomer for recycling in the presence of $ZnCl_2$ as a catalyst. PhSGBL and PhSeGBL could also be copolymerized with ε-caprolactone to tune the glass transition temperature. Additionally, the hydrophilicity of the obtained sulfur-containing polymers could be adjusted by selectively oxidizing the thioether side group to sulfone/sulfoxide, which offered a way to tune the hydrophilicity of polyester. On the other hand, the obtained selenium-containing compound could be degraded in the presence of *m*-CPBA (3-chloroperbenzoic acid), which offered potential application in sustained drug release.

Keywords Ring-opening polymerization; Polyester; Closed-loop recycling; Selective oxidation

Citation: Li, W. J.; Pan, X. Q.; Zhu, J.; Zhang, Z. B. Synthesis of sulfur/selenium-containing polyester with recyclability and controllable hydrophilicity and glass transition temperature. *Chinese J. Polym. Sci.* **2023**, *41*, 1836–1845.

INTRODUCTION

Aliphatic polyester obtained by ring-opening polymerization (ROP) of cyclic lactone shows good degradability in the natural environment, which endows it with good biodegradability and biocompatibility.[1–3] Among various cyclic lactones, the five-membered γ-butyrolactone (GBL) is unique due to its naturally renewable and inexpensive sources. Its upstream chemical of succinic acid was recently ranked first in the US Department of Energy's top 12 biomass-derived compounds and was the best suited to replace petroleum-derived chemicals.[4] Poly(γ-butyrolactone) (PGBL) obtained by ROP of GBL has the same structure as poly(4-hydroxybutyrate) (P4HB) obtained by microbial fermentation with a suitable degradation rate and excellent biocompatibility.[5] As an alternative selection, ROP of GBL provides a simple and inexpensive chemical method for the preparation of P4HB. However, GBL is commonly referred to as a 'nonpolymerizable' monomer in textbooks and literature[6] due to its low strain energy.

In 2016, Hong and Chen[7] remeasured the thermodynamic parameters of the ROP of GBL. They found that the enthalpy change (ΔH_p^0) is actually a small negative value of −5.4 kJ·mol^{-1} rather than the positive value reported in the literature.[6] To achieve high-efficiency ROP of GBL under mild conditions, they proposed three crucial strategies: (1) controlling thermodynamic conditions to ensure that the polymerization temperature is lower than the ceiling temperature (T_c) and the initial concentration of monomer is higher than the equilibrium concentration; (2) controlling the kinetic conditions, that is, developing a highly efficient polymerization catalyst to achieve a high monomer conversion rate in a practical period of time; (3) adjusting the reaction conditions such that the polymer is continuously crystallized or precipitated from the solution during polymerization to break the equilibrium of polymerization and depolymerization to move in the chain growth direction. Based on these strategies, Hong and Chen achieved the ROP of GBL for the first time under normal pressure at −40 °C and efficiently synthesized relatively high molecular weight PGBL with a number average molecular weight (M_n) of 30 kg·mol^{-1} and with controlled linear and/or cyclic topologies. Subsequently, various organocatalysts, such as phosphazene bases (^{t}BuP$_4$, CTPB)[8,9] and thiourea/phosphazene base (TU/^{t}BuP$_4$)[10,11] or urea/alkoxides (U1/NaOMe)[12] have been developed for this polymerization. For example, Li and Liu *et al*. used a novel cyclic phosphazene superbase CTPB[13] to achieve controllable polymerization of GBL at −60 °C.[9] Zhang *et al*. selectively synthesized high mo-

* Corresponding authors, E-mail: panxq@suda.edu.cn (X.Q.P.)
E-mail: chemzhujian@suda.edu.cn (J.Z.)

Received March 18, 2023; Accepted April 28, 2023; Published online June 12, 2023

lecular weight linear PGBL with a M_n of 64.3 kg·mol^{-1} by a bifunctional organic catalytic system consisting of thiourea (urea)/^{t}Bu-P4 at −40 °C.[10] Zhu and Chen[14] synthesized a new monomer based on GBL named hexahydro-(3,4)-*trans* benzofuranone (3,4-T6GBL). The introduction of a bicyclic structure in the 3,4-position of GBL could fuse the cyclohexyl ring in the trans state. This structural design enhanced the ring strain of monomer 3,4-T6GBL, which reduced the enthalpy of the monomer to −20 J·mol^{-1}·K^{-1} for ROP.[15] This resulted in ROP of 3,4-T6GBL being achieved at room temperature under suitable conditions and catalysts. The obtained polymer also showed good recyclability with such a structural design. Guided by these studies,[16–20] we came to the conclusion that introducing a cyclohexyl ring at the 3,5-position of GBL could further enhance the ring strain of GBL, which would be helpful for both ROP and recycling.

For such consideration, herein, substituted γ-butyrolactones with cyclohexyl containing phenyl sulfide or phenyl selenide groups in the 3,5-position (labelled PhSGBL and PhSeGBL for sulfide and selenide, respectively) were synthesized according to the route shown in Scheme 1, Figs. S1 and S3 (in the electronic supplementary information, ESI). The fused ring structure of the monomer tunes the ring strain and the thermodynamic polymerizability. The sulfide or selenide groups were introduced for the following considerations: (a) the monomer could be prepared on relatively large scales with a one-pot reaction and high yield according to the literature;[21,22] (b) sulfide/selenide can be selectively modified to sulfoxide/selenoxide or sulfone/selenone in the presence of oxidants, such as H_2O_2, which offered the possibility for realizing the functional integration of polyester; (c) in the presence of $ZnCl_2$, depolymerization of PPhSeGBL occurs rapidly even at room temperature, which showed good recyclability.

EXPERIMENTAL

Materials

3-Cyclohexene-1-carboxylic acid (98%) and ε-caprolactone (99%) were purchased from Aladdin Industrials Corporation (Shanghai). Triethylamine (99.5%) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (97%) were purchased from Energy Chemical (Shanghai). Diphenyl disulfide (98%) was purchased from TCI (Shanghai). Ethylene glycol (EG) was obtained by distillation from anhydrous Mg_2SO_4 under reduced pressure. Sulfuryl chloride (98.5%) was purchased from Aldrich (Shanghai). Diphenyl diselenide was synthesized according to the literature, and phenylselenyl bromide was obtained from the reaction between diphenyl diselenide and Br_2. The other chemicals were purchased from Shanghai Chemical Reagent Co., Ltd., China, and used as received.

Characterization

Nuclear magnetic resonance (NMR)

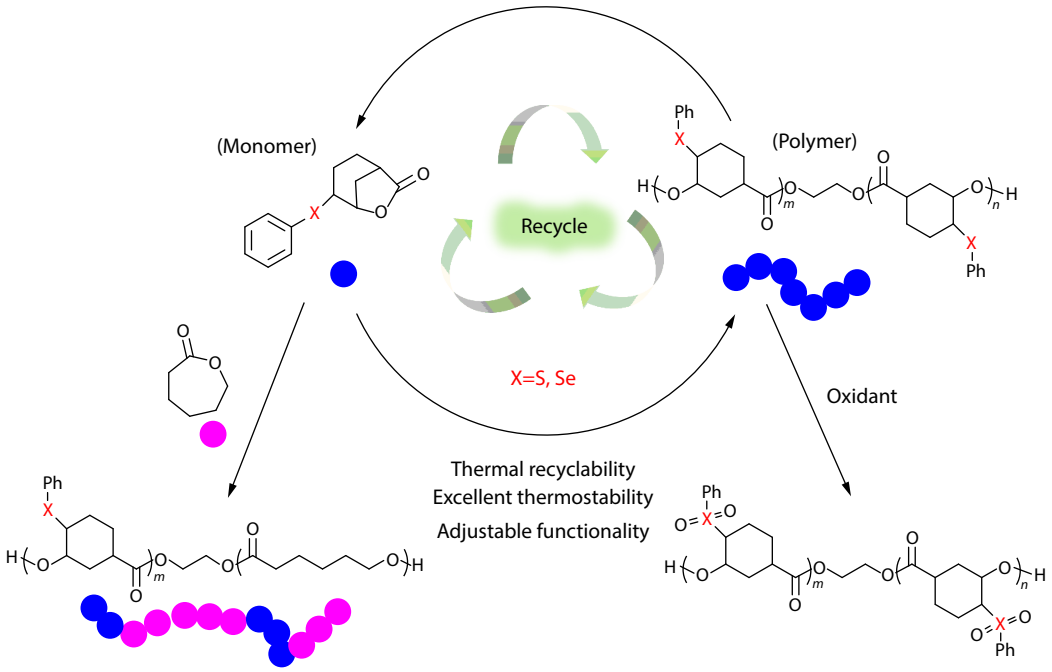
^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker Advance 300 spectrometer using $CDCl_3$ as a solvent.

Gel permeation chromatography (GPC)

The polydispersity indexes and molecular weights were determined on a TOSOH HLC-8320 gel permeation chromatograph equipped with a refractive-index detector using a TSK gel Multi pore HZ-N (3) 4.6 × 150 mm column and an RI detector. The flow rate was 0.35 mL·min^{-1} using THF as a carrier solvent. The test temperature was 40 °C. The molecular weight of the polymer was calibrated using PMMA as the standard.

Differential scanning calorimetry (DSC)

DSC measurements were carried out on a TA 2500 and taken within the temperature range of −80–200 °C. Each thermal scan was taken at a rate of 20 °C·min^{-1} upon the second heating.



Scheme 1 Ring-opening polymerization and copolymerization of PhXGBL and chemical closed-loop recycling and selective oxidation of PPhXGBL, X=S, Se.

https://doi.org/10.1007/s10118-023-2994-3

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was carried out on a Pyris1 thermogravimetric analyser with a heating rate of 10 °C·min^{-1} from room temperature to 800 °C under a nitrogen atmosphere. The sample weights ranged from 4 mg to 6 mg.

X-ray photoelectron spectroscopy (XPS)

The elemental composition of the surfaces was measured with X-ray photoelectron spectroscopy (XPS) (Thermo Fisher Scientific ESCALAB 250 XI, Al KR source).

Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) was recorded with a Bruker TENSOR 27 FT-IR Instrument using the conventional KBr pellet method.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS)

MALDI-TOF MS were carried out on a matrix-assisted laser desorption/ionization time-of-flight mass spectrometer. DCTB was used as the matrix, and sodium trifluoroacetate was used as the auxiliary salt. The test mode was reflection mode.

High performance liquid chromatography (HPLC)

High-performance liquid chromatography (HPLC) was performed on an Agilent 1260 Infinity, and acetonitrile was used as the solvent using a 254 nm ultraviolet wavelength as the detector.

Contact angle (CA)

The water contact angle of the polymers was measured by a JC2000D6 contact angle measuring instrument, and the stabilization time was 3 s. Images of the droplets were analysed to obtain the contact angles by fitting the contour of the water droplet. All measurements were made in triplicate for the polymer using separate samples, and the mean ± SEM of the values was reported.

Synthesis and Characterization of PhSeGBL

The monomer was synthesized following a literature procedure.[16] Triethylamine (4.04 g, 40 mmol) was added to a solution of 3-hexene-1-carboxylic acid (5.04 g, 40 mmol) in dry methylene chloride (80 mL) at 25 °C, and the mixture was stirred for 30 min. Then, the mixture was cooled to −78 °C and treated slowly with PhSeBr (10.384 g, 44 mmol). The reaction was traced by TLC and then warmed to room temperature followed by extraction with water/dichloromethane. Then, the solvent was evaporated, and the crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (5:1, *V*:*V*) as the eluent. Recrystallization from hexane gave analytically pure and colorless crystals (88.6%). ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 7.63–7.49 (m, 2H), 7.31 (dd, *J*=5.3, 1.9 Hz, 3H), 4.83 (s, 1H), 3.67 (t, *J*=5.2 Hz, 1H), 2.66 (q, *J*=3.8, 3.3 Hz, 1H), 2.43–2.23 (m, 3H), 2.04 (dt, *J*=15.1, 3.9 Hz, 1H), 1.89 (dq, *J*=10.9, 3.6, 3.0 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ, ppm): 178.22, 134.21, 129.44, 128.57, 128.16, 79.79, 41.11, 38.70, 33.73, 25.69, 23.70.

Synthesis and Characterization of PhSCl and PhSGBL

Phenylsulfenyl chloride was synthesized following a literature procedure.[17] Triethylamine (0.65 mL, 4.6 mmol, 0.1 equiv.) was added to a cooled solution (0 °C) of diphenyl disulfide (10.0 g, 45.8 mmol, 1.0 equiv.) in benzene (75 mL) under an atmosphere of nitrogen, and the resulting solution was stirred for 15 min at this temperature. This was followed by the dropwise addition of a 1 mol/L solution of sulfuryl chloride (109 mL, 110 mmol, 2.4 equiv.) in methylene chloride *via* an addition funnel. Following reaction completion, the crude reaction mixture was concentrated, followed by short-path distillation (0.75 torr, 40 °C) to give phenylsulfenyl chloride (11.8 g, 89%). ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 7.79–7.53 (m, 2H), 7.51–7.28 (m, 3H).

The monomer was synthesized following a literature procedure.[21] Triethylamine (40 mmol) was added to a solution of 3-hexene-1-carboxylic acid (40 mmol) in dry methylene chloride (80 mL) at 25 °C, and the mixture was stirred for 30 min. Then, the mixture was cooled to −78 °C and treated slowly with PhSCl (44 mmol). The reaction was traced by TLC and then warmed to room temperature followed by extraction with water/dichloromethane. Then, the solvent was evaporated, and the crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (10:1, *V*:*V*) as the eluent. Recrystallization from hexane gave analytically pure and colorless crystals (46%). ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 7.46–7.37 (m, 2H), 7.37–7.24 (m, 3H), 4.77–4.74 (m, 1H), 3.69–3.65 (dt, *J*=7.2, 2.8 Hz, 1H), 2.68–2.63 (td, *J*=4.9, 2.2 Hz, 1H), 2.46–2.42 (d, *J*=12.0 Hz, 1H), 2.30–2.13 (m, 2H), 1.94–1.93 (dddd, *J*=20.9, 11.8, 5.5, 3.1 Hz, 3H). ^{13}C-NMR (300 MHz, $CDCl_3$, δ, ppm): 178.26, 141.99–124.00 (m), 85.82–72.20 (m), 50.96–10.09 (m).

Ring-opening Polymerization of PhSGBL/PhSeGBL

PhSeGBL (1.42 mmol), ethylene glycol (0.057 mmol) and TBD (0.0285 mmol) were dissolved in 1 mL of dichloromethane and added to a 5 mL ampoule in a glove box. After stirring for 12 h at 30 °C, the reaction mixture was diluted with THF (2 mL) and precipitated in diethyl ether (100 mL). The product was obtained after centrifugation and drying in a vacuum oven at 40 °C for 12 h. Monomer conversion was calculated by gravity. Specifically, the mass of the polymer after precipitation and drying is denoted as M_1, the mass of ethylene glycol is denoted as M_2 and the mass of the monomer is denoted as M_3. So the monomer conversion = $M_1/(M_2 + M_3) \times 100\%$. The molecular weight and molecular weight distribution were obtained by GPC. The polymer was obtained using PhSGBL as a monomer under the same conditions.

Copolymerization of PhSGBL/PhSeGBL with CL

Copolymers were prepared in dichloromethane with different ratios using ethylene glycol as the initiator and TBD as the catalyst. In a glove box, CL, PhSGBL/PhSeGBL, EG, TBD, and dichloromethane were mixed in a 5 mL ampoule in proper proportions. Then, copolymerization was performed at 30 °C. After the reaction, the mixture was diluted with THF (5 mL) and then precipitated in diethyl ether (100 mL). The product was obtained after centrifugation and drying in a vacuum oven at 40 °C for 12 h. The copolymers were analysed by GPC and ^{1}H-NMR.

Acid Degradation Procedures

In a typical acid degradation procedure, 20 mg of polymer was dissolved in 5 mL of THF. After the polymer was completely dissolved, 3 mL of acetic acid and 50 μL of sulfuric acid were added into the ampoule, and the mixture was stirred at 40 °C. The ampoule was removed at different time, and the solvent was removed by evaporation. The residual polymer was redissolved in THF, filtered with a filter, and then tested by GPC.

https://doi.org/10.1007/s10118-023-2994-3

RESULTS AND DISCUSSION

Homopolymerization

PhSeGBL and PhSGBL were prepared for our study according to the literature procedures. The NMR spectra of the two compounds showed that the fused ring structure of the monomers has only one configuration (Figs. S1–S4 in ESI). The tendency of a ring compound to polymerize depends upon the extent of ring strain.[15] In this study, the endocyclic structures of PhSeGBL and PhSGBL cause higher ring strain than γ-butyrolactone. The ROP of PhSeGBL was selected as a model monomer for optimizing polymerization conditions, *e.g.*, catalyst, temperature, and solvent. The results summarized in Table S1 (in ESI) show that polymerization could be successfully carried out under the catalysis of TBD, which is commonly used as a catalyst for anionic ROP. Homopolymer (PPhSeGBL) was obtained with a molecular weight ($M_{n,GPC}$) of 9.2 kg·mol^{-1} and a molecular weight distribution ($Đ$) of 1.52 after 12 h of polymerization with a monomer conversion of 95% and a feed molar ratio of $[PhSeGBL]_0$:$[EG]_0$:$[TBD]_0$=50:1:2 at 30 °C in methylene chloride (entry 1 in Table S1, in ESI). However, some other catalysts, such as DBU, DMAP, Et_3N, DPP, and TPP, could not catalyze the ROP of PhSeGBL. Benzyl alcohol and butane-1,4-diol could also initiate this type of ROP (entries 1 and 2 in Table 1). By comparing different amounts of catalyst, it was found that lowering the catalyst concentration led to a much lower conversion (entries 3 and 4 in Table 1). The ROP of PhSeGBL was carried out using a range of initial monomer-to-initiator ratios ($[PhSeGBL]_0$:$[EG]_0$=100:1 and 200:1) to control the product molecular weight (entries 5 and 6 in Table 1). The obtained PPhSeGBL shows narrow $Đ$ values of 1.36 and 1.29. As the monomer concentration decreases, the polymerization rate become slower. (entries 7 and 8 in Table 1). The ROP of PhSGBL under different conditions is summarized in Table 1. The result was similar to that of PhSeGBL.

The structure of PPhSeGBL was confirmed by ^{1}H-NMR and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) (Figs. 1a and 1b). For the ^{1}H-NMR spectrum in Fig. 1, the chemical shifts in the range of 1.2–2.4 ppm with corresponding protons labelled "5", "6", "7", and "8" demonstrated the remaining cyclohexyl ring in the main chain, which implied the ROP of the five-membered ring in the monomer. The phenyl selenide group remained in the side chain. The MALDI-TOF mass spectrum (Fig. 1b) consists

Table 1 Organocatalytic ring-opening polymerization of PhXGBL under different conditions. [a] (X = S, Se)

Entry	PhXGBL	ROH	$[PhXGBL]_0$:$[ROH]_0$:$[TBD]_0$	Time (h)	Conv. [b] (%)	$M_{n,GPC}$ [c] (kg·mol^{-1})	$M_{n,th}$ (kg·mol^{-1})	$Đ$
1	PhSGBL	BnOH	50:1:1	11	14.0	2.4	1.6	1.27
2		BDO	50:1:2	10.5	71.4	5.2	8.3	1.32
3		EG	50:1:1	11	44.9	4.7	5.3	1.24
4		EG	50:1:2	3.5	68.9	4.8	8.1	1.47
5		EG	50:1:4	10.5	79.1	7.2	9.3	1.31
6		EG	100:1:2	23	32.8	3.6	7.7	1.47
7		EG	200:1:2	48	51.2	5.9	24.0	1.18
8	PhSeGBL	BnOH	50:1:1	8	28.9	3.4	4.1	1.20
9		BDO	50:1:2	8	54.4	5.4	7.7	1.30
10		EG	50:1:1	8	38.4	3.7	5.4	1.41
11		EG	50:1:2	2.75	74.9	6.2	10.6	1.40
12		EG	50:1:4	7	58.1	5.0	8.2	1.43
13		EG	100:1:2	11.5	32.3	5.0	9.2	1.36
14		EG	200:1:2	24	62.1	6.3	17.7	1.29

[a] Polymerization conditions: in solution, PhXGBL: 0.5 mmol, V_{DCM}=0.3 mL at 30 °C; [b] Monomer conversion was calculated by gravity; [c] The flow rate was 0.35 mL·min^{-1} using THF as a carrier solvent. The test temperature was 40 °C. The molecular weight of the polymer was calibrated using PMMA as the standard.

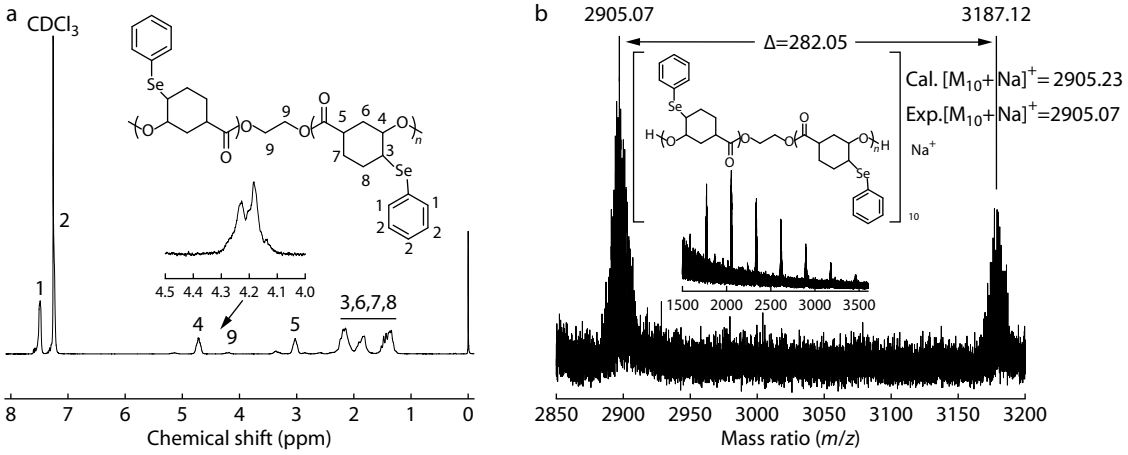


Fig. 1 (a) ^{1}H-NMR spectrum of PPhSeGBL in $CDCl_3$; (b) MALDI-TOF mass spectrum of PPhSeGBL produced by reaction of $[PhSeGBL]_0$:$[TBD]_0$:$[EG]_0$=50:1:1 for 60 min.

https://doi.org/10.1007/s10118-023-2994-3

of one series of molecular ion peaks, which presumably correspond to the linear PPhSeGBL with H/OCH_2CH_2O/H as the chain ends, denoted as H-[PhSeGBL]$_n$-OCH_2CH_2O-[PhSeGBL]$_n$-H. These results are consistent with the mechanism of anionic polymerization catalyzed by TBD.[23,24] Under the optimized conditions, ROP of PhSGBL was also successfully carried out using EG as the initiator and TBD as the catalyst at 30 °C. PolyPhSGBL (PPhSGBL) was obtained with a $M_{n,GPC}$ of 6.7 kg·mol^{-1} and $Đ$ of 1.32 after 570 min of polymerization with a feed molar ratio of [PhSGBL]$_0$:[EG]$_0$:[TBD]$_0$=50:1:2. The structure of the obtained PPhSGBL was confirmed by ^{1}H-NMR (Fig S5 in ESI).

Second, the polymerization kinetics of these two monomers were investigated. Monomer conversion was calculated by gravity. The molecular weights and molecular weight distributions of the obtained polymers were determined by GPC (Figs. 2a and 2b). The ROP showed a linear relationship between the semilog of the monomer concentration (ln([M]$_0$/[M]$_t$)) and polymerization time (Fig. 2c). The M_n increased with monomer conversion (Fig. 2d). The GPC profiles displayed unimodal distributions. All these data demonstrated controlled characteristics of the ROP. The molecular weight of polymers determined by GPC differs from the theoretical molecular weight. The reason was caused by inter- and intratransesterification reactions during the ROP.[25]

To further verify the controlled nature of the polymerization, a chain extension experiment was carried out by using the obtained P(PhSGBL/PhSeGBL) as a macroinitiator. As shown in Fig. S6 (in ESI), the GPC trace shifted in the direction of the high molecular weight.

Copolymerization of PhSeGBL/PhSGBL with ε-Caprolactone (CL)

The copolymerization of PhSeGBL and PhSGBL with CL was an efficient way to adjust the properties of the polyesters. On the other hand, the cost of synthesis of functionalized lactones is higher than that of common lactones. To broaden the application of functionalized lactones, copolymerization was carried out. GPC curves of the obtained polymers are shown in Figs. S7 and S8 (in ESI). The molar fractions of PhSGBL or PhSeGBL units in copolymers (F) were measured by ^{1}H-NMR spectroscopy and were consistent with the molar fraction in the comonomer feed (f) (Table 2). The MALDI-TOF mass spectra of poly(PhSGBL-*co*-CL) and poly(PhSeGBL-*co*-CL) further suggested that PhXGBL and CL were copolymerized (Figs. S9 and S10 in ESI). The thermostability of copolymers was examined by thermogravimetric analysis (TGA) in terms of onset decomposition temperature T_d (defined by the temperature of 5% weight loss). The curves are shown in Fig. 3. Comparing the TGA curves of poly(PhSGBL-*co*-CL) with poly(PhSeGBL-*co*-CL), it reveals that PPhSeGBL has a noticeably higher T_d (231 °C) than PPhSGBL (T_d=194 °C) (Fig. 3a and Fig. S3c in ESI). As the molar

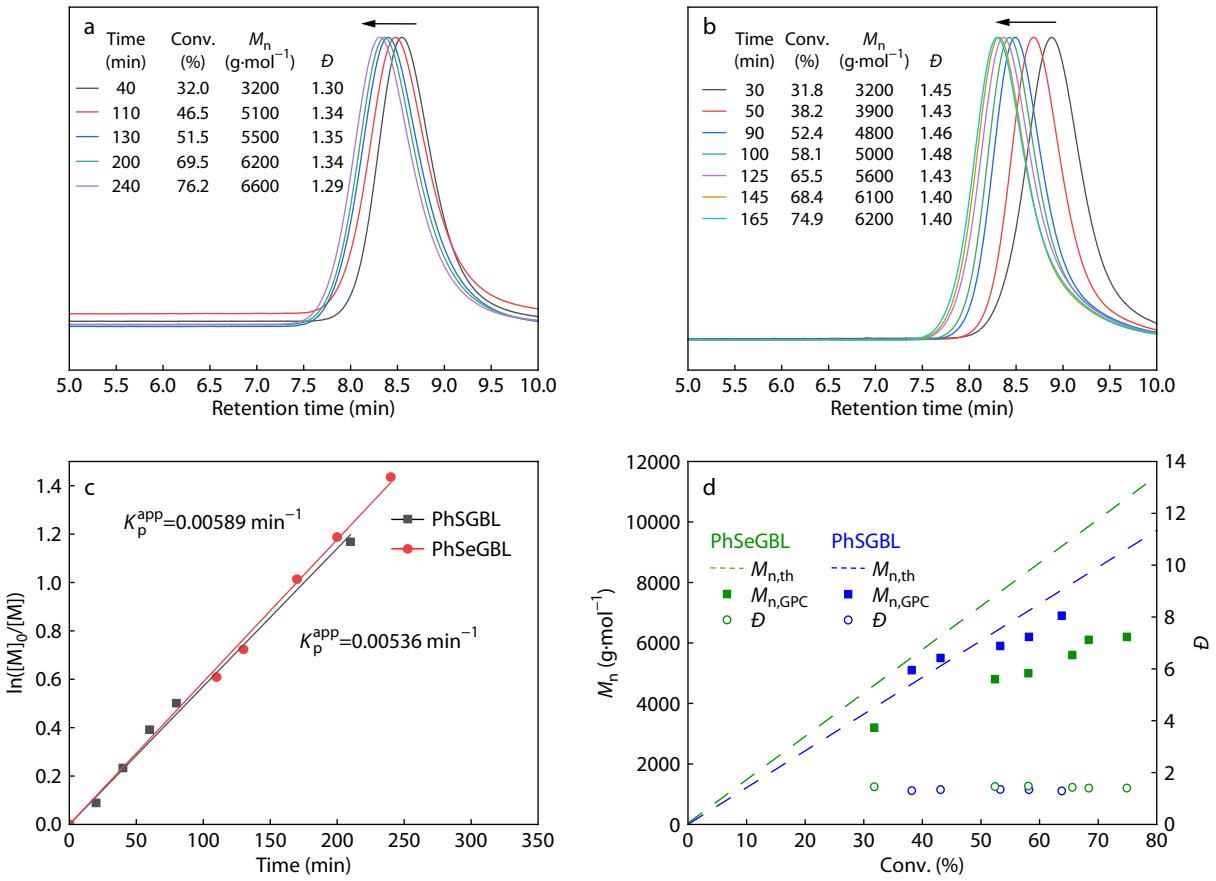


Fig. 2 GPC curves of kinetics study for the polymerization in CH_2Cl_2 at 30 °C. GPC curves of (a) PPhSGBL and (b) PPhSGBL, [lactone]$_0$:[EG]$_0$:[TBD]$_0$=50:1:2; (c) Plots of PhSeGBL and PhSGBL of ln[M]$_0$/[M]$_t$ versus reaction time; (d) Plots of PhSeGBL and PhSGBL of M_n and $Đ$ versus conversion.

https://doi.org/10.1007/s10118-023-2994-3

fraction of PhSeGBL and PhSGBL units in the copolymers increases, the T_d of copolymers gradually decreases toward the homopolymer of PhSeGBL and PhSGBL, respectively, ranging from 254 °C (F=0.12) to 235 °C (F=0.82) and from 244 °C (F=0.27) to 218 °C (F=0.89). Differential scanning calorimetry (DSC) curves for the second heating scans of poly(PhSGBL-*co*-CL) and poly(PhSeGBL-*co*-CL) show that PPhSeGBL has a higher T_g (112 °C) than PPhSGBL (T_g=94 °C) (Figs. 3b and 3d). As the molar fraction of PhSeGBL and PhSGBL units in the copolymers increases, the T_g of copolymers gradually decreases toward the homopolymer of PhSeGBL and PhSGBL, respectively, ranging from −43 °C (F=0.12) to 69 °C (F=0.82) and −24 °C (F=0.27) to 75

Table 2 T_g and T_d of random copolymers with different molar ratios. f and F are the molar fractions of PhSeGBL or PhSGBL in the feeding ratio and polymers, respectively.

Entry	Monomer	f [a]	F [b]	$M_{n,GPC}$ [c] (kg·mol^{-1})	$Đ$	T_g (°C)	T_{d5} [d] (°C)
1	PPhSeGBL and CL	0.00	0.00	15.8	1.58	−60	315
2		0.20	0.12	15.3	1.57	−24	254
3		0.30	0.25	13.2	1.96	−1	279
4		0.50	0.44	17.7	1.62	26	247
5		0.60	0.54	18.9	1.57	30	270
6		0.80	0.82	10.1	1.54	75	235
7		1.00	1.00	17.1	1.57	94	231
8	PPhSGBL and CL	0.00	0.00	15.8	1.58	−60	315
9		0.20	0.27	20.6	1.36	−43	244
10		0.40	0.42	26.6	1.46	−29	240
11		0.50	0.61	21.3	1.51	17	213
12		0.60	0.67	16.4	1.41	28	213
13		0.80	0.89	17.4	1.50	69	218
14		1.00	1.00	26.6	1.28	112	194

[a] f: the molar fractions of PhSGBL or PhSeGBL in the comonomer feed; [b] F: the molar fractions of PhSGBL or PhSeGBL units in copolymers; [c] The flow rate was 0.35 mL·min^{-1} using THF as a carrier solvent. The test temperature was 40 °C. The molecular weight of the polymer was calibrated using PMMA as the standard; [d] Onset decomposition temperature T_{d5} was defined by the temperature of 5% weight loss.

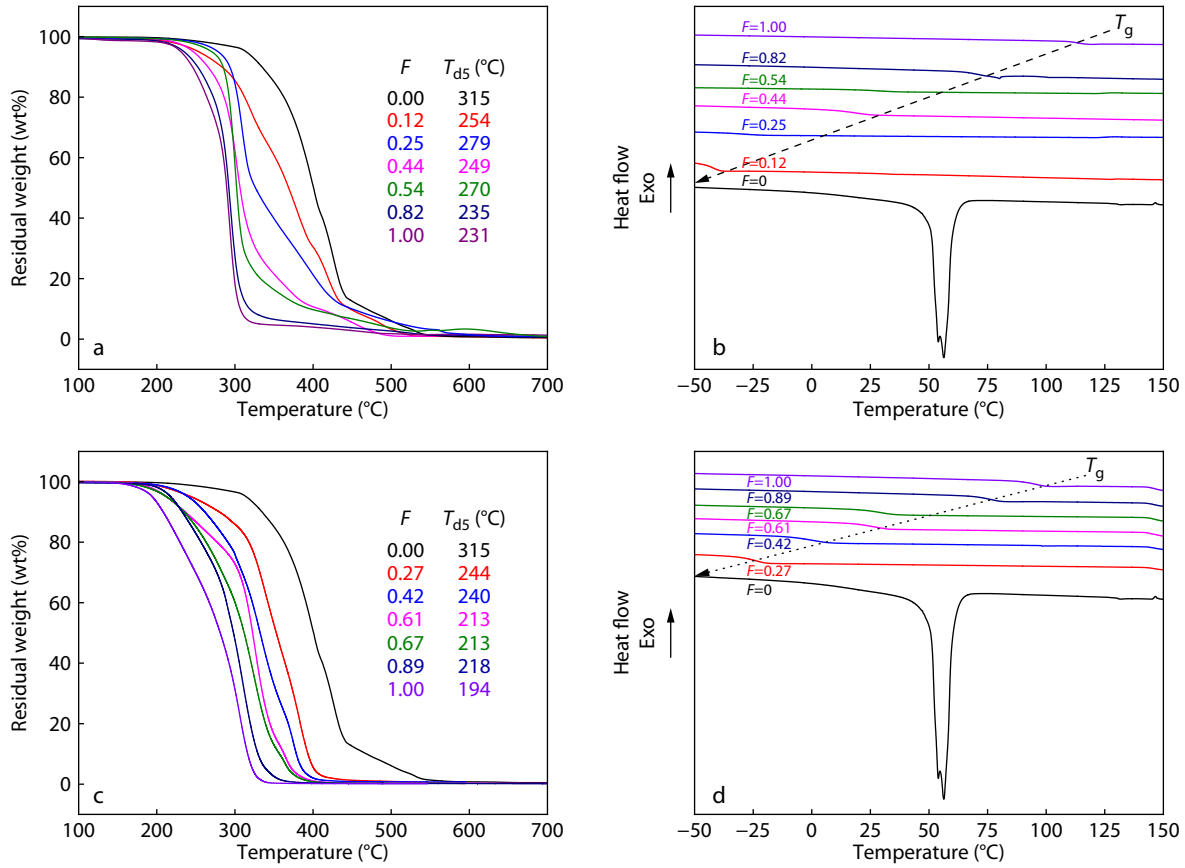


Fig. 3 (a) TGA and (b) DSC curves of poly(PhSeGBL-*co*-CL) with different molar ratios of PPhSeGBL and PCL; (c) TGA and (d) DSC curves of poly(PhSGBL-*co*-CL) with different molar ratios of PPhSGBL and PCL. F is the molar fractions of PhSGBL or PhSeGBL units in copolymers.

https://doi.org/10.1007/s10118-023-2994-3

°C (F=0.89). Significantly, all copolymers do not show melting or crystallization peaks, indicating that random copolymers were obtained. Compared with 3,4-T6GBL reported by Zhu and Chen,[14] the excellent thermal performance of PhSeGBL and PhSGBL is attributed to the introduction of sulfide or selenide functional groups in the side chain and the rigid cyclohexane ring in the main chain. The results revealed that the thermal properties of polyester can be adjusted by copolymerization of CL with functionalized lactones.

Degradation of PPhSeGBL and PPhSGBL

The degradability of aliphatic polyesters allows them to be used in a vast range of applications.[26–28] For example, PCL shows long-term degradation. A resurgence in interest has propelled PCL back into tissue engineering.[29,30] The degradation behavior of PPhSGBL, PPhSeGBL, poly(PhSGBL-*co*-CL) and poly(PhSeGBL-*co*-CL) was assessed. Because of the rapid degradation of polyesters under alkaline conditions within a few hours or tens of minutes,[31] an acid degradation procedure was used instead of degradation under alkaline conditions. The GPC curves of polymers before and after treatment are shown in Figs. S11 and S12 (in ESI). The degradability of the polyester was evaluated by the reduction in molecular weight of the polyester. As shown in Figs. S12 and S14 (in ESI), copolymers with different molar fractions of PhSeGBL and PhSGBL units show almost the same magnitude of molecular weight reduction with the extension of degradation time. These results indicated that the degradation rates of random copolymers are similar.

Thermal Recyclability of PPhSeGBL and PPhSGBL

Direct thermal degradation of poly(L-LA) produced many kinds of degradation products, including LA diastereomers, cyclic oligomers and several small molecules.[32] In contrast, in the presence of $ZnCl_2$, depolymerization of PGBL occurred rapidly even at room temperature without side products, which showed good recyclability.[7,33] Herein, the main chains of PPhSeGBL and PPhSGBL are similar to that of PGBL, which offers the possibility of recyclability. The recyclability of PPhSeGBL and PPhSGBL was investigated under different conditions. First, the catalyst was investigated using PPhSGBL as the model compound. Different Lewis acids, including $Al(OH)_3$, $FeCl_3$, $ZnSO_3CF_3$ and $ZnCl_2$, were applied with the same molar loading ratio of 42.0%. The results showed that only $ZnCl_2$ effectively catalyzed the degradation of the polymer. Second, the degradation was investigated by using different molar ratios of $ZnCl_2$, *e.g.*, 21.0%, 34.5%, 42.0%, 52.5% and 63.0%. The results showed that as high as 52.5% of PhSGBL could be obtained using a 42.0% molar ratio $ZnCl_2$ obtained by high-performance liquid chromatography (HPLC).

Thus, the reactions of PPhSeGBL and PPhSGBL were investigated in detail at 100 °C using $ZnCl_2$ as the catalyst with a molar ratio of 42.0% in toluene (Fig. 4a). The final product was obtained with a yield of 60% after column separation. The structure of the obtained product was characterized by ^{1}H-NMR, as shown in Fig. 4(b) and Fig. S15 (in ESI). The results confirmed that the degradation products were PhSeGBL and PhSGBL for PPhSeGBL and PPhSGBL, respectively. It was found that in addition to the recycled monomer, diphenyl diselenide and diphenyl disulfide were the main byproducts. The relatively high reactivity of functional groups may cause side reactions, which decrease the formation of monomers. By tracking the reactions, it can be found that the side reaction of thermal degradation of PPhSeGBL hardly happens in the first 10 min, and the side reaction of thermal degradation of PPhSGBL inevitably always exists. Thus, PPhSeGBL can be recycled in high yield by recycling multiple times. Here, we perform one loop as a model (Fig. 4a). One gram of PPhSeGBL was added into a 100 mL three-necked flask and dissolved in 60 mL of toluene. Then, 200 mg (50%) of $ZnCl_2$ was added to the solution. Stirring for 10 min at 100 °C. $ZnCl_2$ was filtered, and toluene was removed after the reaction. Then, the mixture was precipitated. The supernatant was removed, and PPhSeGBL (740 mg) was obtained. The solvent in the supernatant was removed, and the monomer was obtained (240 mg, with a recycle yield of 92.3%). On the other hand, both diphenyl diselenide and diphenyl disulfide are easy to separate and can be reused to prepare monomers.

Our previous work[34] reported that the phenyl selenide group of ε-(α-phenylseleno) caprolactone eliminates the formation of double bonds through oxidation, which has built a broader platform for the functionalization of polyesters. Herein, the oxidation process of PPhSeGBL was investigated. PPhSeGBL (100 mg, $M_{n,GPC}$=28.9 kg·mol^{-1}, $Đ$=2.04) was dissolved in 20 mL of $CHCl_3$ in a 100 mL single neck bottle. Then, an equivalent amount of *m*-CPBA was added, and the mixture was stirred at room temperature for 30 min. After the reaction, the polyester was analysed by GPC. The results are shown in Fig. S16 (in ESI). The GPC curves of PPhSeGBL (Fig. S16a in ESI) before and after oxidation show that the molecular weight of the polyester after oxidation decreased from 28.9 kg·mol^{-1} to 5.5 kg·mol^{-1}, and the molecular weight distribution also changed from 2.04 to 4.18. This result indicates that PPhSeGBL has degraded in the process of oxidation. The XPS spectrum (Fig. S16b in ESI) of PPhSeGBL before and after oxidation shows that, in addition to the existence of the electron binding energy of the selenium ether structure after oxidation, there were structures with higher electron binding energy that correspond to selenone and selenoxide. Therefore, there was no process of elimination of the phenyl selenide group to form double bonds by oxidation. Instead, selenone and selenoxide are formed, and further degradation occurs.

Sulfide groups can be oxidized to form hydrophilic sulfoxide and sulfone groups. This means that the hydrophilicity of the polyester containing the thioether group can be changed by oxidizing the sulfide group to sulfone/sulfoxide. To demonstrate this hypothesis, 100 mg of PPhSGBL ($M_{n,GPC}$=16.5 kg·mol^{-1}, $Đ$=1.19) was dissolved in 20 mL of $CHCl_3$ in a 100 mL single neck bottle. Then, *m*-CPBA was added to the solution. Each time, a 27% molar amount of *m*-CPBA was added, the mixture was stirred for 5 min at room temperature. The progress of oxidation was tracked by infrared testing and is shown in Fig. S17 (in ESI). In the representative FTIR spectrum of oxidation, the characteristic absorption bands at 1304 cm^{-1} are assigned to the O=S=O bond asymmetric stretching. The absorption bands at 1042 cm^{-1} correspond to S=O stretching. As revealed in Fig. S17 (in ESI), the sulfoxide groups were almost completely formed when *m*-CPBA was added to approximately 1.08 equiv., and the sulfone group was almost completely formed when *m*-CPBA was added to approximately 2.70 equiv. These results

https://doi.org/10.1007/s10118-023-2994-3

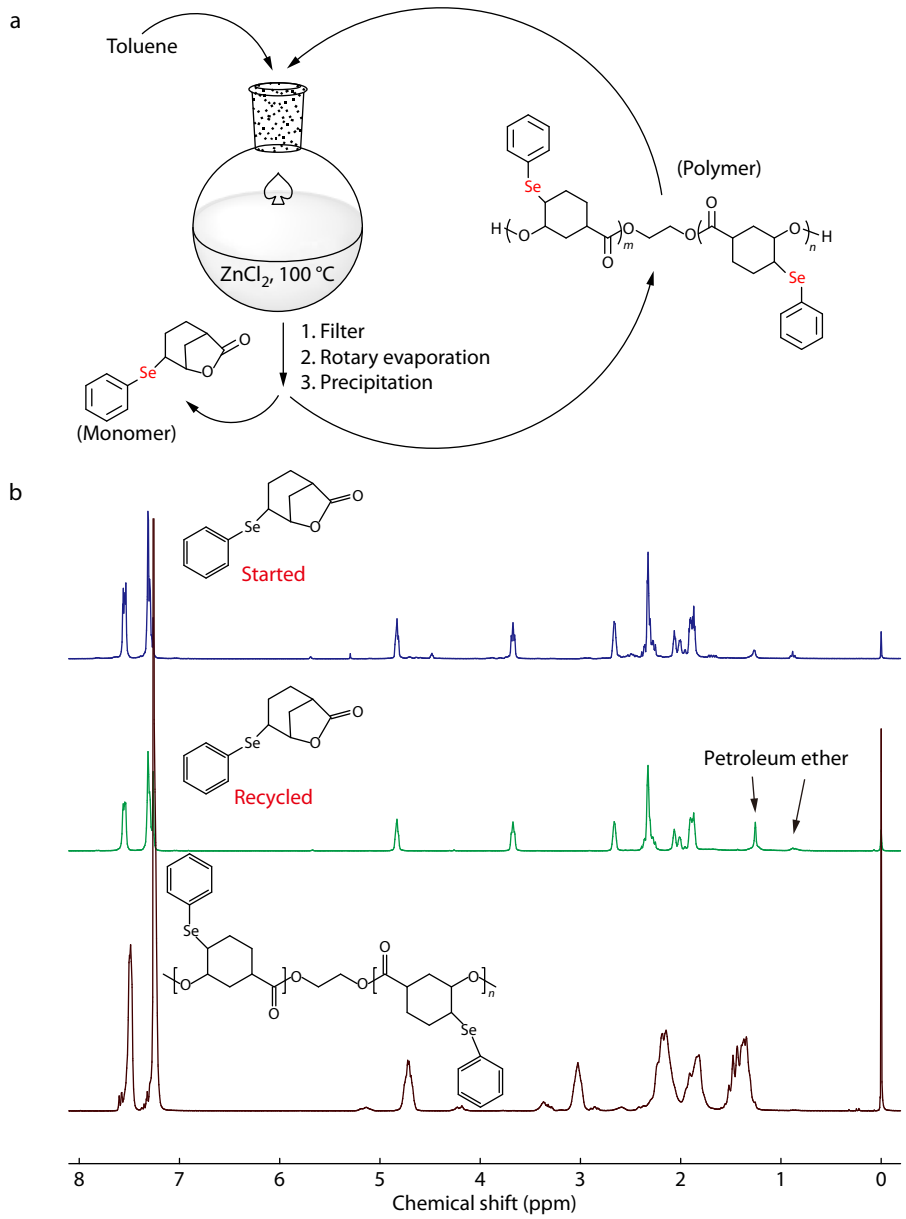


Fig. 4 (a) Chemical closed-loop recycling of PPhSeGBL; (b) ^{1}H-NMR spectra of the recyclability of PPhSeGBL back into its monomer.

indicated that phenyl sulfide in PPhSGBL could be selectively oxidized to sulfoxide or sulfone. The structures of the oxidized products were also characterized by XPS analysis (Fig. S18 in ESI). The binding energy revealed that sulfone and sulfoxide groups were selectively formed after oxidation (Fig. S19 in ESI).

The properties of polyester were investigated before and after the process of oxidation. The thermal properties of sulfoxide-containing ($M_{n,GPC}$=16.8 kg·mol^{-1}, $Đ$=1.22) and sulfone-containing ($M_{n,GPC}$=21.1 kg·mol^{-1}, $Đ$=1.19) polyesters produced by its sulfur-containing precursor PPhSGBL ($M_{n,GPC}$=16.5 kg·mol^{-1}, $Đ$=1.19) were investigated by TGA (Fig. S20 in ESI) and DSC (Fig. S21 in ESI). The TGA curves show that the sulfoxide-containing polyester exhibits a reduced one-step degradation profile with a T_{d5} of 183 °C. In contrast, the TGA curves show that sulfone-containing polyester exhibited an increased one-step degradation profile with a T_{d5} of 270 °C (Fig. S20 in ESI). The reason was that sulfoxide groups are unstable and easily decomposed, while sulfone groups are not.[35] The DSC curves show that sulfoxide-containing and sulfone-containing polyesters both exhibit increasing T_g values of 133 °C and 189 °C (Fig. S21 in ESI), respectively. At the same time, from water contact angle measurements, higher hydrophilicity of sulfoxide-containing and sulfone-containing polyesters was observed. The results are shown in Figs. S22–S24 and Table S2 (in ESI). These results offered PPhSGBL with adjustable hydrophilicity after selective oxidation.

The use of polyester fibre in textile materials is extensive. However, these fibres have some shortcomings, including poor moisture absorption and handling, similar to PET fibres.[36] To demonstrate the application of adjustable hydrophilicity of PPhSGBL, the following example was carried out.

https://doi.org/10.1007/s10118-023-2994-3

Mixtures of PET/sulfone-containing polyester were prepared by blending with different mass ratios of 100/0, 100/5, 100/10, 100/14, 100/20, and 100/30. The mixtures were treated at 200 °C for 0.5 h for the transesterification between PET and sulfone-containing polyester. The viscosity of the resulting products was measured by an Ubbelohde viscometer. The inherent viscosity ([η]) was calculated according to the literature.[37] The results are shown in the supporting information (Table S3 in ESI).

The results show that the molecular weight of the mixture decreased as the mass ratio of sulfone-containing polyester increased. This proves the occurrence of transesterification in the mixture. Fibres of these polyester mixtures were prepared. The fibres were dried in a hot oven at 150 °C for 12 h. After drying, the fibres were exposed to ambient conditions for 48 h. The hygroscopicity of the fibres was measured by the change in the mass of the fibres. The results are shown in Table S4 (in ESI). As shown in the table, the hygroscopicity of the fibres improved from 0.845% for PET to 1.56% for the mixture as the mass ratio of sulfone-containing polyester increased. This result shows that the fibres of PET can be modified to improve moisture absorption by blending the sulfone-containing polyester we synthesized, which could be used as a hydrophilic enhance additive.

CONCLUSIONS

In summary, phenyl sulfide groups and phenyl selenide groups were introduced into lactones, and γ-butyrolactone-based functionalized lactones with fused ring structures containing phenyl sulfide groups and phenyl selenide groups were synthesized. The fused ring structure of lactones tunes the ring strain and the thermodynamic polymerizability, and the ROP of PhSeGBL and PhSGBL was successfully carried out under mild conditions. At the same time, the introduction of phenyl sulfide groups and phenyl selenide groups gives the polyester material a high glass transition temperature and adjustable functionality.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://doi.org/10.1007/s10118-023-2994-3.

ACKNOWLEDGMENTS

This work was financially supported by National Key Research and Development Program of China (No. 2022YFB3704905), and the Priority Academic Program Development (PAPD) of Jiangsu Higher Education Institutions.

REFERENCES

1 Lecomte, P.; Jérôme, C. Recent developments in ring-opening polymerization of lactones. *Adv. Polym. Sci.* **2011**, *245*, 173–217.
2 Tardy, A.; Nicolas, J.; Gigmes, D.; Lefay, C.; Guillaneuf, Y. Radical ring-opening polymerization: scope, limitations, and application to (bio)degradable materials. *Chem. Rev.* **2017**, *117*, 1319–1406.
3 Hillmyer, M. A.; Tolman, W. B. Aliphatic polyester block polymers: renewable, degradable, and sustainable. *Acc. Chem. Res.* **2014**, *47*, 2390–6.
4 Bozell, J. J.; Petersen, G. R. Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy's "Top 10" revisited. *Green Chem.* **2010**, *12*, 539–554.
5 Zhang, L. J.; Deng, X. X.; Du, F. S.; Li, Z. C. Chemical synthesis of functional poly(4-hydroxybutyrate) with controlled degradation via intramolecular cyclization. *Macromolecules* **2013**, *46*, 9554–9562.
6 Houk, K. N.; Jabbarim,A.; Hall, H. K.; Alemán, C. Why δ-valerolactone polymerizes and γ-butyrolactone does not. *J. Org. Chem.* **2008**, *73*, 2674–2678.
7 Hong, M.; Chen, E. Y. Completely recyclable biopolymers with linear and cyclic topologies *via* ring-opening polymerization of gamma-butyrolactone. *Nat. Chem.* **2016**, *8*, 42–49.
8 Hong, M.; Chen, E. Y. X. Towards truly sustainable polymers: a metal-free recyclable polyester from biorenewable non-strained γ-butyrolactone. *Angew. Chem. Int. Ed.* **2016**, *55*, 4188–4193.
9 Zhao, N.; Ren, C.; Li, H.; Li, Y.; Liu, S.; Li, Z. Selective ring-opening polymerization of non-strained γ-butyrolactone catalyzed by a cyclic trimeric phosphazene base. *Angew. Chem. Int. Ed.* **2017**, *56*, 12987–12990.
10 Zhang, C. J.; Hu, L. F.; Wu, H. L.; Cao, X. H.; Zhang, X. H. Dual organocatalysts for highly active and selective synthesis of linear poly(γ-butyrolactone)s with high molecular weights. *Macromolecules* **2018**, *51*, 8705–8711.
11 Li, Y. Y.; Xing, D.; Pan, X. Q.; Zhu, J. Synthesis and antibacterial activity of selenium-functionalized poly(ε-caprolactone). *Chinese J. Polym. Sci.* **2022**, *40*, 67–74.
12 Lin, L.; Han, D.; Qin, J.; Wang, S.; Xiao, M.; Sun, L.; Meng, Y. Nonstrained γ-butyrolactone to high-molecular-weight poly(γ-butyrolactone): facile bulk polymerization using economical ureas/alkoxides. *Macromolecules* **2018**, *51*, 9317–9322.
13 Liu, S.; Ren, C.; Zhao, N.; Shen, Y.; Li, Z. Phosphazene bases as organocatalysts for ring-opening polymerization of cyclic esters. *Macromol. Rapid Commun.* **2018**, *39*, 1800485.
14 Zhu, J. B.; Watson, E. M.; Tang, J.; Chen, E. Y. X. A synthetic polymer system with repeatable chemical recyclability. *Science* **2018**, *360*, 398–403.
15 Shi, C.; Reilly, L. T.; Phani Kumar, V. S.; Coile, M. W.; Nicholson, S. R.; Broadbelt, L. J.; Beckham, G. T.; Chen, E. Y. X. Design principles for intrinsically circular polymers with tunable properties. *Chem* **2021**, *7*, 2896–2912.
16 Liu, Y.; Wu, J.; Hu, X.; Zhu, N.; Guo, K. Advances, challenges, and opportunities of poly(γ-butyrolactone)-based recyclable polymers. *ACS Macro Lett.* **2021**, *10*, 284–296.
17 Walther, P.; Frey, W.; Naumann, S. Polarized olefins as enabling (co)catalysts for the polymerization of γ-butyrolactone. *Polym. Chem.* **2018**, *9*, 3674–3683.
18 Puchelle, V.; Latreyte, Y.; Girardot, M.; Garnotel, L.; Levesque, L.; Coutelier, O.; Destarac, M.; Guégan, P.; Illy, N. Functional poly(ester-*alt*-sulfide)s synthesized by organo-catalyzed anionic ring-opening alternating copolymerization of oxiranes and γ-thiobutyrolactones. *Macromolecules* **2020**, *53*, 5188–5198.
19 Shi, C.; Clarke, R. W.; McGraw, M. L.; Chen, E. Y. X. Closing the "one monomer-two polymers-one monomer" loop *via* orthogonal (de)polymerization of a lactone/olefin hybrid. *J. Am. Chem. Soc.* **2022**, *144*, 2264–2275.
20 Shi, C.; Li, Z. C.; Caporaso, L.; Cavallo, L.; Falivene, L.; Chen, E. Y. X.

Hybrid monomer design for unifying conflicting polymerizability, recyclability, and performance properties. *Chem* **2021**, *7*, 670–685.
21 Nicolaou, K. C. Organoselenium-induced cyclizations in organic synthesis. *Tetrahedron* **1981**, *37*, 4097–4109.
22 McCune, C. D.; Beio, M. L.; Sturdivant, J. M.; de la Salud-Bea, R.; Darnell, B. M.; Berkowitz, D. B. Synthesis and deployment of an elusive fluorovinyl cation equivalent: access to quaternary *α*-(1′-fluoro)vinyl amino acids as potential PLP enzyme inactivators. *J. Am. Chem. Soc.* **2017**, *139*, 14077–14089.
23 Jaffredo, C. G.; Carpentier, J. F.; Guillaume, S. M. Organocatalyzed controlled ROP of *β*-lactones towards poly(hydroxyalkanoate)s: from *β*-butyrolactone to benzyl *β*-malolactone polymers. *Polym. Chem.* **2013**, *4*, 3837.
24 Jaffredo, C. G.; Carpentier, J. F.; Guillaume, S. M. Poly(hydroxyalkanoate) block or random copolymers of *β*-butyrolactone and benzyl *β*-malolactone: a matter of catalytic tuning. *Macromolecules* **2013**, *46*, 6765–6776.
25 Pascual, A.; Sardón, H.; Ruipérez, F.; Gracia, R.; Sudam, P.; Veloso, A.; Mecerreyes, D. Experimental and computational studies of ring-opening polymerization of ethylene brassylate macrolactone and copolymerization with *ε*-caprolactone and TBD-guanidine organic catalyst. *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *53*, 552–561.
26 Nsengiyumva, O.; Miller, S. A. Synthesis, characterization, and water-degradation of biorenewable polyesters derived from natural camphoric acid. *Green Chem.* **2019**, *21*, 973–978.
27 Häußler, M.; Eck, M.; Rothauer, D.; Mecking, S. Closed-loop recycling of polyethylene-like materials. *Nature* **2021**, *590*, 423–427.
28 De Hoe, G. X.; Zumstein, M. T.; Tiegs, B. J.; Brutman, J. P.; McNeill, K.; Sander, M.; Coates, G. W.; Hillmyer, M. A. Sustainable polyester elastomers from lactones: synthesis, properties, and enzymatic hydrolyzability. *J. Am. Chem. Soc.* **2018**, *140*, 963–973.
29 Peponi, L.; Sessini, V.; Arrieta, M. P.; Navarro-Baena, I.; Sonseca, A.; Dominici, F.; Gimenez, E.; Torre, L.; Tercjak, A.; Lopez, D.; Kenny, J. M. Thermally-activated shape memory effect on biodegradable nanocomposites based on PLA/PCL blend reinforced with hydroxyapatite. *Polym. Degrad. Stabil.* **2018**, *151*, 36–51.
30 Vollmer, I.; Jenks, M. J. F.; Roelands, M. C. P.; White, R. J.; van Harmelen, T.; de Wild, P.; van der Laan, G. P.; Meirer, F.; Keurentjes, J. T. F.; Weckhuysen, B. M. Beyond mechanical recycling: giving new life to plastic waste. *Angew. Chem. Int. Ed.* **2020**, *59*, 15402–15423.
31 Hedir, G. G.; Bell, C. A.; O'Reilly, R. K.; Dove, A. P. Functional degradable polymers by radical ring-opening copolymerization of MDO and vinyl bromobutanoate: synthesis, degradability and post-polymerization modification. *Biomacromolecules* **2015**, *16*, 2049–2058.
32 H.A. Leiper, I. C. M. Degradation studies of some polyesters and polycarbonates—2. Polylactide: degradation under isothermal conditions, thermal degradation mechanism and photolysis of the polymer. *Polym. Degrad. Stabil.* **1985**, *11*, 309–326.
33 Liu, Y. H.; Yuan, X.; Wu, J. Q.; Luo, M. X.; Hu, X.; Zhu, N.; Guo, K. Fully chemical recyclable poly(*γ*-butyrolactone)-based copolymers with tunable structures and properties. *Chinese J. Polym. Sci.* **2022**, *40*, 456–461.
34 Wu, J. a.; Ding, C.; Xing, D.; Zhang, Z.; Huang, X.; Zhu, X.; Pan, X.; Zhu, J. The functionalization of poly(*ε*-caprolactone) as a versatile platform using *ε*-(*α*-phenylseleno) caprolactone as a monomer. *Polym. Chem.* **2019**, *10*, 3851–3858.
35 Mir, A. A.; Wagner, S.; Krämer, R. H.; Deglmann, P.; Emrick, T. Deoxybenzoin-containing polysulfones and polysulfoxides: synthesis and thermal properties. *Polymer* **2016**, *84*, 59–64.
36 Chen, S.; Guo, J.; Zhang, B.; Zhang, S.; Gong, Y.; Gong, X. Hydrophilic modified polyester based on waste PET bottles. *AATCC J. Res.* **2018**, *5*, 15–20.
37 Mancini, S. D. M., Itley G.; Almeida, Rômulo F. Determinação da Variação da Viscosidade Intrínseca do Poli (Tereftalato de Etileno) de Embalagens. *Polymers* **2004**, *14*, 69–73.

https://doi.org/10.1007/s10118-023-2994-3