

Preparation of Chemically Recyclable Poly(ether-*alt*-ester) by the Ring Opening Polymerization of Cyclic Monomers Synthesized by Coupling Glycolide and Epoxides

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 Electronic Supplementary Information

Abstract Polyester and polyether are two key oxygenated polymers, and completely alternative sequence of poly(ester-*alt*-ether) could efficiently combine the advantages (including flexibility, degradability, etc.) of both segments. Currently, despite their copolymers could be synthesized from one-pot mixture of cyclic esters and epoxides, perfectly alternative microstructure is very challenging to realize and typically restricted to certain monomer pairs. Moving forward, synthesizing poly(ester-*alt*-ether) from commercially available and largescale monomers would be a significant advance. For example, successfully commercialized poly(glycolic acid) (PGA), which is not easily soluble in polymers due to its high crystallinity and is brittle and difficult to control the degradation cycle, would encounter a new paradigm if engineered into poly(ester-*alt*-ether). In this work, starting from the design of monomer with hybrid structures, we successfully synthesized a series of 1,4-dioxan-2-one containing different substituents based on glycolide (GA) and epoxides using commercially available Salen-Cr(III) and PPNCI catalytic systems. The new monomers underwent ring-opening polymerization (ROP) to form a series of poly(ester-*alt*-ether) with perfectly alternating glycolic acid and propylene glycol repeat units under catalytic system of thiourea/base. The poly(ester-*alt*-ether) have significantly lower glass-transition temperature than PGA. Additionally, the poly(ester-*alt*-ether) can be chemically recovered to monomer using Sn(Oct)₂ or 1,8-diazabicyclo[5.4.0]undecane-7-ene (DBU) as a catalyst in solution, thus establishing a closed-loop life cycle. From monomers derived from GA and epoxides, this work furnishes a novel strategy for the synthesis of poly(ester-*alt*-ether) with chemical recyclability.

Keywords Polyester; Polyether; Alternative copolymer; Ring-opening polymerization

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INTRODUCTION

Recently, biodegradable polymers have attracted considerable attention in addressing the environmental pollution brought by non-degradable petroleum-based plastics and promoting sustainable development. Among the biodegradable polymers developed in the past decades, bio-polyester is one of the most ideal materials with excellent physical and mechanical properties, biodegradability and biocompatibility, which is widely used in the fields of fabric, packaging, agriculture, medical and health care, etc.^[1–4] It is regarded as a good substitute to plastics made from petroleum and can reduce environmental pollution. Among them, PGA is a successfully commercialized example. However, due to its high crystallinity, PGA is brittle, not easily soluble and difficult to control the

degradation cycle, which preclude its applications to widely replace traditional plastics. Copolymerization of glycolide with other monomers can alter the properties of PGA based materials, the more common of which is the copolymerization of lactide (LA) and GA, yielding a random copolymer with little control over monomer sequence. However, due to the potential importance of the monomer sequence for elevating the properties of the copolymer of LA and GA,^[5] Coates and co-workers reported the sequence-controlled synthesis of the alternating copolymer of LA and GA *via* a highly regioselective ROP of (*S*)-methyl glycolide.^[6]

By contrast, polyether is usually soluble in water and most organic solvents, and has excellent plasticity. Integrating polyether and polyester is a promising way to take advantage of both polymer's merits, however, physically blending polyester and polyether is not desirable because the blends are often incompatible, resulting in phase separation. Incorporating polyether chain segments into PLA and PGA to establish poly(ester-*co*-ether) is an effective modification method. This approach could control the amphiphilic behavior and

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regulate the degradation performance to improve the performance at the same time improve the flexibility of polyester materials.^[7–12] Although a certain degree of control over the individual block sizes was achieved through variation of the reaction conditions, prior copolymers all exhibited two melting transitions, indicating that the length of the blocks was sufficient for crystallization-induced microphase separation. Compared to block copolymers, random copolymers are expected to have better compatibility and uniformity, but full control over polymer microstructure has not been realized, let alone precise engineering of the material properties.

Therefore, the precise incorporation of two different linkages, ester and ether, into a uniform main chain of polymer is very desirable. Meanwhile, poly(ester-*alt*-ether) perfectly combines the flexibility of ether with the degradability of ester, perhaps exhibiting distinct properties from random, gradient or block copolymers. Presently, there are two main methods to obtain poly(ester-*alt*-ether), one method is the ring-opening copolymerization (ROCOP) of a cyclic ester with one or more epoxides, for example, dihydrocoumarin and epoxides, lactones and epoxides, etc. under appropriate catalysts (Scheme 1a);^[7,13–18] another method is to design and synthesize cyclic monomers containing ester and ether bonds, which can be ring-opening polymerized to produce alternating polyesters with precisely controlled sequences, such as 1,4-dioxan-2-one (DO), 3-methyl-1,4-dioxan-2-one (MDO), 1,5-dioxepan-2-one (DXO), 3,4-dihydro-2H-benzo[b][1,4]dioxepin-2-one (BDXO), 4-methyloctahydro-2H-benzo[b][1,4]dioxepin-2-one (4-MOHB) and other cyclic monomers (Scheme 1b).^[19–29] There are other ways in which a slight amount of alternating ether and ester segments can be obtained by the reaction between polyesters and epoxides.^[30,31]

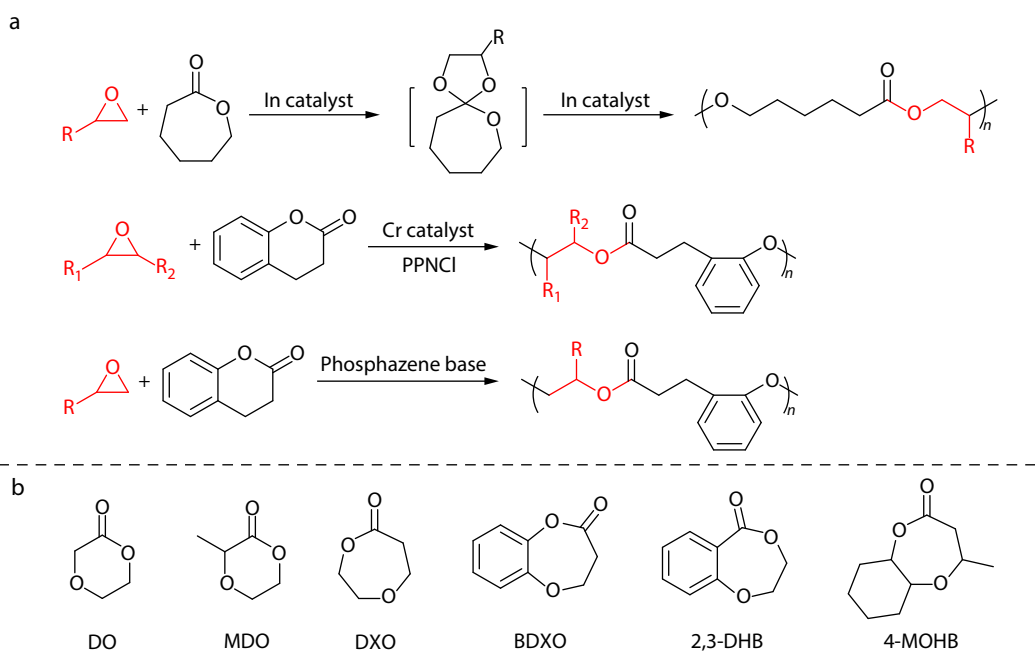
GA and epoxides are commercially available monomers with largescale global production. But up to now, the re-

search utilizing them to synthesize poly(ether-*alt*-ester) is still under-explored. Inspired by Chisholm *et al.* who succeeded in producing 3,6-dimethyl-1,4-dioxan-2-one by coupling propylene oxide (PO) and lactide (LA) *via* a backbiting mechanism utilizing a catalytic system of Porphyrin Cr(III) and bis(triphenylphosphine)iminium chloride (PPNCl),^[32] we chose commercially available Salen-Cr(III) and PPNCl as the catalyst system to successfully generate a variety of 1,4-dioxan-2-one with different substituents by reacting GA with multiple epoxides (Scheme 2a and Scheme S1 in the electronic supplementary information, ESI). Then, we conducted the ROP of these monomers with a traditional catalytic system consisting of thiourea and base, obtaining poly(ester-*alt*-ether) with perfectly alternating glycolic acid and propylene glycol repeat units. Of note, the resultant polymers can be depolymerized back to pristine monomers, establishing a monomer-polymer-monomer closed-loop life cycle.

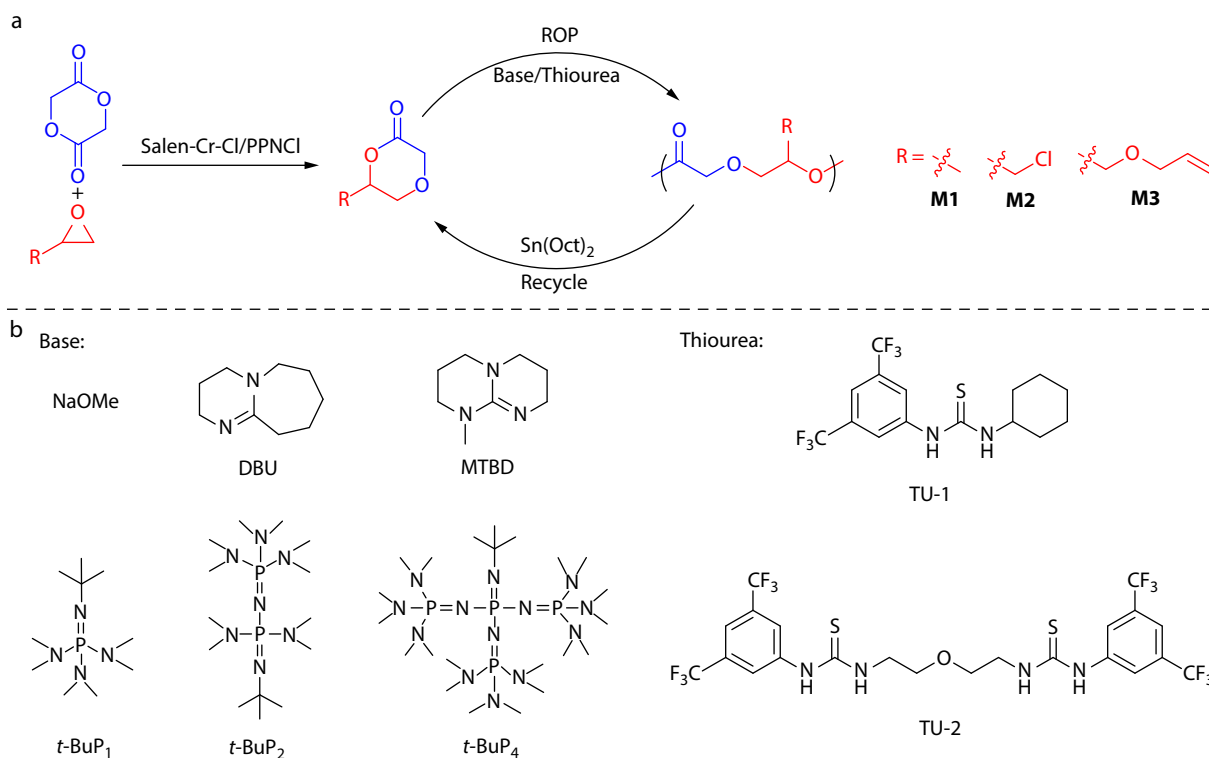
EXPERIMENTAL

General Considerations

All manipulations were carried out using standard Schlenk techniques under a dry argon atmosphere or an argon-filled glove box. PO were distilled from CaH₂ under an argon atmosphere. GA (Purac) was purified by recrystallization three times from ethyl acetate and dried under vacuum at room temperature before using. NMR spectra were recorded on a Bruker AV 300M or Bruker AV 600M in CDCl₃ or DMSO-d₆ or TOL-d₈ at 25 °C. Chemical shifts were given in parts permillion from tetramethylsilane. Gel permeation chromatography (GPC) measurements were conducted with a Waters 515 GPC with THF as the solvent (flow rate: 0.1 mL/min, at 30 °C). The molecular weights were calibrated against polystyrene (PS) standards. Differential scanning calorimetry (DSC) was carried out with a TA Q100 thermal analyzer. First heating: from 25 °C to 100 °C at a heating rate of 5 °C/min. First cooling: from 100 °C to



Scheme 1 (a) The ROCOP of cyclic esters with epoxides; (b) Previously reported cyclic monomers containing ester and ether bonds.



Scheme 2 (a) Synthesis and ring-opening polymerization of cyclic monomers; (b) Scope of base and thiourea catalysts.

–50 °C at a cooling rate of 5 °C/min. Second heating: from –50 °C to 100 °C at a heating rate of 5 °C/min.

Synthesis of Monomers

Mononuclear Salen-Cr(III)Cl (1 equiv.), PPNCI (1 equiv.), GA (200 equiv.) and epoxide (400 equiv.) except for epichlorohydrin (at 100 °C) were stirred at 80 °C for 3 days. The reaction mixture was purified by column chromatography on silica gel (*n*-hexane:CH₂Cl₂=1:1) to obtain the monomer, and then the monomer was dried with CaH₂.

M1 (64% yield)

¹H-NMR (CDCl₃, δ, ppm): 4.65 (m, 1H), 4.22 (q, 2H), 3.85 (dd, 1H), 3.39 (dd, 1H), 1.29 (d, 3H). ¹³C-NMR (CDCl₃, δ, ppm): 167.24, 75.58, 67.67, 65.34, 17.17.

M2 (21% yield)

¹H-NMR (CDCl₃, δ, ppm): 4.69 (m, 1H), 4.25(q, 2H), 3.96 (dd, 1H), 3.78 (dd, 1H), 3.67(m, 2H). ¹³C-NMR (CDCl₃, δ, ppm): 165.98, 77.16, 65.85, 63.87, 41.69.

M3 (25% yield)

¹H-NMR (CDCl₃, δ, ppm): 5.85 (m, 1H), 5.23 (m, 2H), 4.66 (m, 1H), 4.28(q, 2H), 4.00 (d, 1H), 3.94 (dd, 1H), 3.77 (dd, 1H), 3.62 (d, 2H). ¹³C-NMR (CDCl₃, δ, ppm): 166.75, 133.96, 117.71, 77.31, 72.57, 68.31, 65.90, 64.18.

Synthesis of Thiourea

Synthesis of TU-1

Cyclohexylamine (10.4 mmol, 1.04 g) and 3,5-bis(trifluoromethyl)phenyl isothiocyanate (10.4 mmol, 2.84 g) were dissolved in anhydrous THF (30 mL), and stirred at RT for 17 h, the reaction mixture was concentrated in vacuum and washed with cold CH₂Cl₂. The solid product was purified via recrystallization from CH₂Cl₂ (2.3 g, 61%). ¹H-NMR (DMSO-d₆, δ,

ppm): 9.86 (s, 2H), 8.23 (s, 4H), 8.16 (s, 2H), 7.71 (s, 2H), 4.11 (b, 4H), 1.91 (m, 2H), 1.70 (m, 2H), 1.56 (m, 1H), 1.27 (m, 5H). ¹³C-NMR (DMSO-d₆, δ, ppm): 179.09, 141.94, 130.55(q), 125.02, 121.67, 121.4, 115.78, 52.25, 31.53, 25.02, 24.38.

Synthesis of TU-2

To bis(2-aminoethyl) ether (5 mmol, 0.52 g) was added the solution of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (10 mmol, 2.71 g, in 60 mL of anhydrous CH₂Cl₂), and stirred at RT for 21 h, the reaction mixture was filtered and washed with cold CH₂Cl₂. The obtained solid was then dried under high vacuum to yield the product as a white solid (2.5 g, 80%). ¹H-NMR (DMSO-d₆, δ, ppm): 10.16 (s, 2H), 8.24 (s, 6H), 7.73 (s, 2H), 3.68 (m, 8H). ¹³C-NMR (DMSO-d₆, δ, ppm): 181.09, 142.29, 130.79(q), 122.24, 121.88, 116.53, 68.45, 44.07.

Ring-opening Polymerization of Monomers

Table 1, entry 1: A flame-dried Schlenk tube was charged with NaOMe (0.18 mmol, 10 mg), TU-1 (0.55 mmol, 205 mg) in a glove box, **M1** (9 mmol, 1.075 g) was then added into the Schlenk tube. The Schlenk tube was sealed and immersed into a cooling bath at 0 °C for 12 h. The reaction was quenched by addition of 0.5 mL of benzoic acid in CHCl₃ (10 mg/mL). The polymer was isolated and purified by precipitation from ether three times and then dried under vacuum at 50 °C.

Table 1, entry 14: A flame-dried Schlenk tube was charged with **M1** (11 mmol, 1.288 g), benzyl alcohol (BnOH) (0.11 mmol, 12 mg), DBU (0.11 mmol, 17 mg), TU-2 (0.16 mmol, 106 mg) in a glove box. The Schlenk tube was sealed and immersed into a cooling bath at 0 °C for 12 h. The reaction was quenched by addition of 0.5 mL of benzoic acid in CHCl₃ (10 mg/mL). The polymer was isolated and purified by precipitation from ether three times and then dried under vacuum at

50 °C.

Catalytic Degradation with Sn(Oct)₂

A flame-dried 5 mm thick wall NMR sample tube was charged with **P(M1)** (20 mg), Sn(Oct)₂ (10 mol% relative to repeating units) and TOL-d₈ (0.5 mL). The NMR tube was sealed by a Teflon stopcock and then immersed into an oil bath at 140 °C for 6 h before subject to ¹H-NMR measurements. We integrate the methine (a) of the monomer ($\delta=4.58\text{--}4.70$ ppm) and the methine (a) of the polymer ($\delta=5.10\text{--}5.23$ ppm) to obtain the integral area, so as to calculate the degree of degradation.

RESULTS AND DISCUSSION

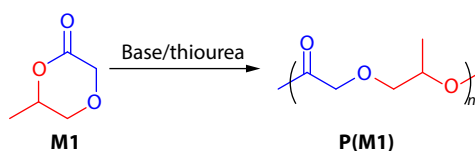
During our initial study in copolymerization of PO/CO₂ with LA under dinuclear Salen-Cr(III) complex/PPNCl, only cyclic by-product was observed due to frequent chain transfer to PO and backbiting, mirroring the previously observed cyclization (Scheme S2 in ESI).^[33] We isolated and purified the cyclic by-product and identified it as 3,6-dimethyl-1,4-dioxan-2-one, which contains both ester and ether bonds. Unfortunately, attempts to the ROP of the monomer were unsuccessful. Based on this scheme, we use a commercially available mononuclear Salen-Cr(III) complex with a simpler structure to couple GA with PO under the corporation of PPNCl to obtain **M1** with a yield of 64%. The chemical structure of **M1** was clearly characterized by ¹H-NMR and ¹³C-NMR (Figs. 1a and 1b).

To better optimize the reaction conditions, new monomers were synthesized using a variety of epoxides coupled with GA and further applied as newly developed monomers for the preparation of poly(ether-*alt*-ester) by ROP. Initially, using **M1** as a model monomer, a type of H-bonding organocatalysts

consisting of thiourea and base cocatalysts was selected as catalysts for ROP of **M1**, which has been shown to be a type of superior catalysts for the ROP of LA, δ -valerolactone (VL), ϵ -caprolactone (CL), or other type of cyclic esters (Scheme 2b).^[20,34–40] Usually, H-bonding organocatalysts were acknowledged to achieve a “living” ROP of monomers and precisely control the molecular weight and dispersity of polymer *via* dual activation of monomer by thiourea and activation of chain end by base cocatalyst.

First, the ROP of **M1** catalyzed by sodium methoxide/TU-1 was investigated in bulk conditions. The polymerization of **M1** with a [NaOMe]:[TU-1]:[M] ratio of 1:3:50 was unsuccessful at room temperature (RT), as a comparison, when the polymerization was conducted at 0 °C, the monomer conversion reached 35% within 12 h. Then the effect of solvent on the ROP of **M1** was explored, the polymerization was carried out at 0 °C in different solvents, including dimethylformamide (DMF), tetrahydrofuran (THF), dichloromethane (DCM), toluene, however the polymerizations did not proceed. Therefore, it was determined that the subsequent ROP of **M1** would be carried out at 0 °C under bulk conditions. At an increased [NaOMe]:[TU-1]:[M] ratio of 1:3:100, the polymerizations still proceeded to 32% conversions of **M1** in 12 h. In an effort to improve the polymerization efficiency of the system, various organic bases and thioureas were studied. The results are summarized in Table 1. Generally, all types of base/thiourea can catalyze the ROP of **M1**, but there were differences in polymerization activity, NaOMe/thiourea, MTBD/thiourea, *t*-BuP₁/thiourea, *t*-BuP₂/thiourea, *t*-BuP₄/thiourea and DBU/TU-1 did not show good activity for the ROP of **M1**, but DBU/TU-2 exhibited the best activities and the highest molecular weight

Table 1 Results of ROP of **M1** with base/thiourea as catalysts.^a



Entry	Base	Thiourea	[I]:[B]:[TU]:[M]	Sol. ^b	Temp. (°C)	Time (h)	Conv. ^c (%)	$M_n(\text{GPC})^d$ (kDa)	\mathcal{D}^d
1	NaOMe	TU-1	0:1:3:50	Bulk	RT	12	–	–	–
2	NaOMe	TU-1	0:1:3:50	Bulk	0	12	35	5.0	1.10
3	NaOMe	TU-1	0:1:3:50	DMF	0	12	–	–	–
4	NaOMe	TU-1	0:1:3:50	THF	0	12	–	–	–
5	NaOMe	TU-1	0:1:3:50	DCM	0	12	–	–	–
6	NaOMe	TU-1	0:1:3:50	TOL	0	12	–	–	–
7	NaOMe	TU-1	0:1:3:100	Bulk	0	12	32	4.7	1.15
8	DBU	TU-1	1:1:3:100	Bulk	0	12	33	5.6	1.08
9	MTBD	TU-1	1:1:3:100	Bulk	0	12	37	5.4	1.09
10	<i>t</i> -BuP ₁	TU-1	1:1:3:100	Bulk	0	12	32	5.6	1.09
11	<i>t</i> -BuP ₂	TU-1	1:1:3:100	Bulk	0	12	27	3.1	1.10
12	<i>t</i> -BuP ₄	TU-1	1:1:3:100	Bulk	0	12	18	2.1	1.09
13	NaOMe	TU-2	1:1:1.5:100	Bulk	0	12	33	6.4	1.10
14	DBU	TU-2	1:1:1.5:100	Bulk	0	12	44	7.3	1.12
15	MTBD	TU-2	1:1:1.5:100	Bulk	0	12	35	6.5	1.09
16	<i>t</i> -BuP ₁	TU-2	1:1:1.5:100	Bulk	0	12	43	7.0	1.11
17	<i>t</i> -BuP ₂	TU-2	1:1:1.5:100	Bulk	0	12	38	5.9	1.08
18	<i>t</i> -BuP ₄	TU-2	1:1:1.5:100	Bulk	0	12	18	4.4	1.11

^a Initiator [I] = benzyl alcohol; ^b The **M1** concentration was 4 mol/L; ^c Determined by ¹H-NMR; ^d Determined by gel permeation chromatography (GPC) in THF, calibrated with polystyrene standards.

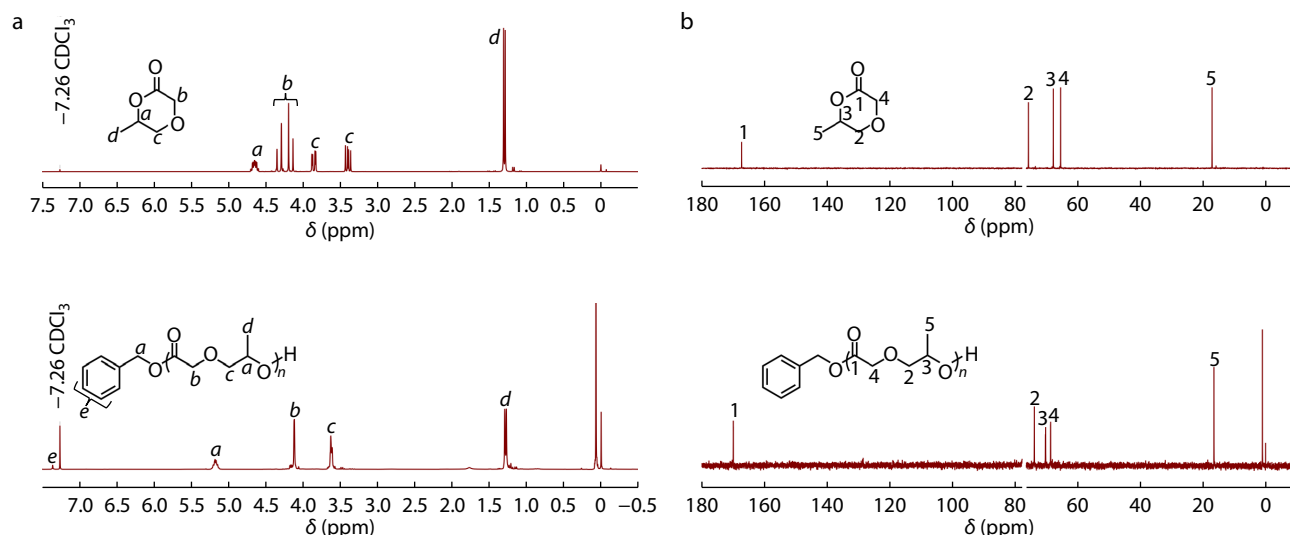


Fig. 1 Structural characterization of **M1** and **P(M1)**: (a) ^1H -NMR spectra of **M1** and **P(M1)**; (b) ^{13}C -NMR spectra of **M1** and **P(M1)**.

with narrow molecular weight distribution. Further study on the ROP of **M1** was conducted using the highly reactive DBU/TU-2.

The structures of the monomer and resultant polymer were also fully demonstrated. **P(M1)** was characterized by ^1H - and ^{13}C -NMR spectroscopy, and matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS). From the ^1H -NMR spectra (Fig. 1a), because the monomer is a six-membered ring, the long-range coupling effect of methylene protons in "c" position on the protons in "b" at $\delta=4.22$ causes the protons in "b" position to split into quartet peaks; there is a geminal coupling effect between the two protons in "c" position, and the vicinal coupling effect of the proton in "a" position on the protons in "c" position cause the two protons in "c" position split into double doublet peaks respectively. After the ROP of **M1**, the long-range coupling and the geminal coupling in the ring disappeared, it can be found that the protons in "b" position become a singlet peak and the protons in "c" position become a doublet peak. All characteristic resonance peaks of monomers and polymers were well explained and consistent with the reported results. Fig. 1(b) shows the ^{13}C -NMR spectrum of **M1** and **P(M1)**, which are also consistent with the chemical structures of **M1** and **P(M1)**, respectively.

The molecular structure and terminal groups of **P(M1)** separately initiated by BnOH and NaOMe were characterized in detail by MALDI-TOF MS. The MALDI-TOF MS spectra of **P(M1)** both display only one series of molecular ion peaks, the spacing between the two neighboring molecular ion peaks is 116 Da, which exactly corresponds to the molecular weight of the **M1** repeat units. Careful analysis of each molecular ion peak of the two MALDI-TOF MS spectra demonstrates that the linear **P(M1)** structure bearing with BnO/H chain-end groups and MeO/H chain-end groups, respectively (Figs. 2a and 2b).

Then, an attempt was made to change the molecular weight of **P(M1)** by changing the feeding molar ratio of BnOH/**M1**, when BnOH/**M1** ratio increased from 1:50 to 1:100 to 1:200, the molecular weight of **P(M1)** increased from 6.5 kDa to 7.3 kDa to 10.1 kDa, respectively (Fig. 3a). The at-

tempts to conduct ROP of **M1** at lower temperatures (-10 and -20 °C) with DBU:TU-2=1:1.5 did not work out, the monomer conversion at -10 and -20 °C decreased to 15% and 18%, respectively. Moreover, when the polymerization temperature was decreased to -20 °C, **M1** solidified, based on this phenomenon, it was speculated that the melting point of **M1** was between -10 and -20 °C, so it was not necessary to conduct ROP at lower temperatures.

To elucidate the equilibrium polymerization behavior of **M1**, the kinetics of its bulk ROP at 0 °C catalyzed by DBU/TU-2 was investigated. The monomer conversions at different time were measured by ^1H -NMR spectra. Fig. 3(b) shows the curve of monomer conversion versus polymerization time. In the early stage of the bulk ROP, the monomer conversion of **M1** increased slowly with the extension of reaction time, but finally reached the equilibrium monomer conversions of 40% after 10 h. The incomplete conversion of monomers is attributed to the thermodynamic characteristics of the six-membered monomer structure.

Under optimized polymerization conditions, **M2**, **M3** were exploited for this process with an attempt toward the formation of poly(ether-*alt*-ester), as shown in Table 2. Because of the electronegativity of chlorine, **M2** can be polymerized at RT, the resultant **P(M2)** has the molecular weight of 7.4 kDa and a relatively narrow distribution of molecular weight ($\mathcal{D}=1.10$). Interestingly, (2-propenyloxy)methyl substituent was well tolerated to afford the corresponding poly(ether-*alt*-ester) with $M_n=11.1$ kDa ($\mathcal{D}=1.07$).

Furthermore, differential scanning calorimetry (DSC) analysis was conducted to evaluate the thermal properties of a series of **P(M1)** samples with varied molecular weights, as well as **P(M2)** and **P(M3)** with different substituents. All of the poly(ether-*alt*-ester) samples were found to be amorphous polymers without melting temperatures. The glass transition temperatures (T_g) of these polymers were in the range of -34 °C to -9 °C at a heating rate of 5 °C/min (Figs. 3c and 3d).

The development of chemical recyclable polymers is a grand challenge in polymer chemistry, and the chemical recovery of polymers to monomers creates an ideal, circular

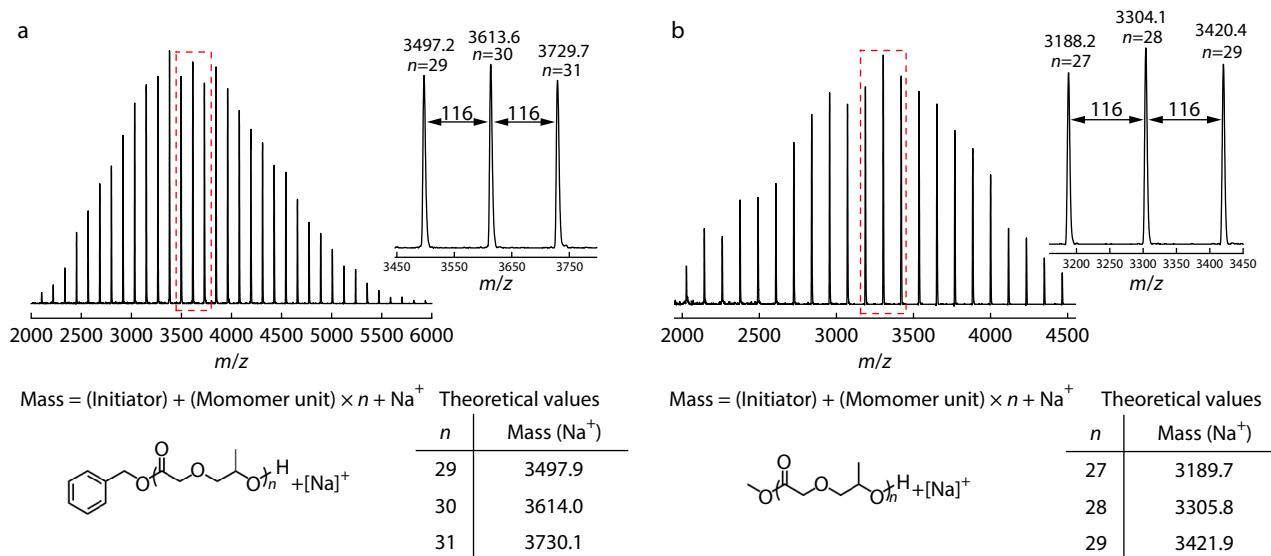


Fig. 2 (a) MALDI-TOF MS spectrum of **P(M1)** initiated by BnOH; (b) MALDI-TOF MS spectrum of **P(M1)** initiated by NaOMe.

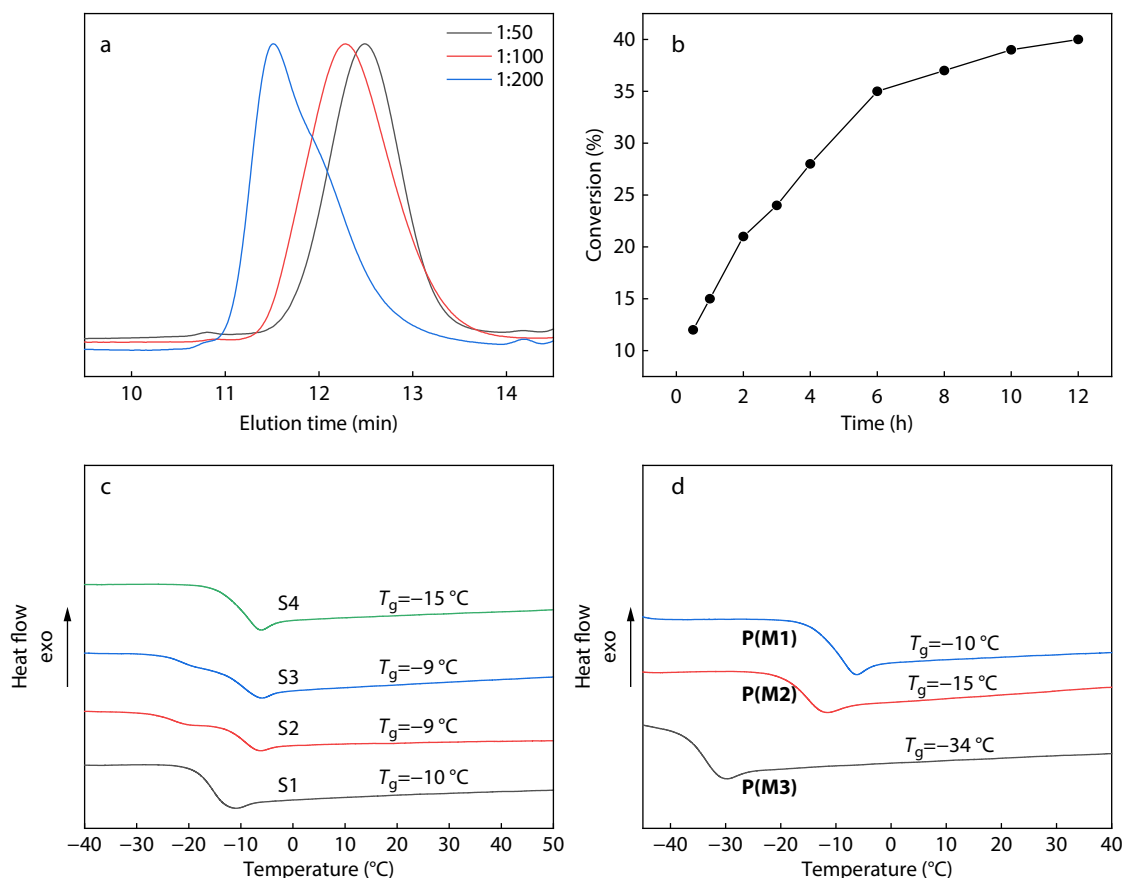
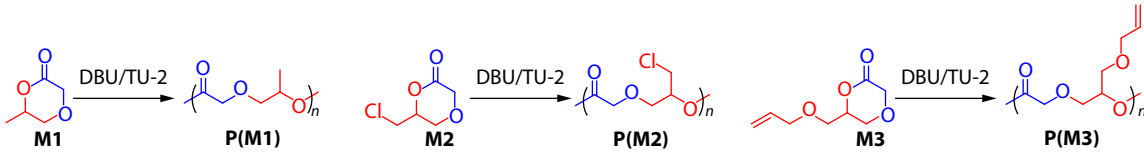


Fig. 3 (a) Overlay of GPC curves at various $[\text{M}]_0:[\text{I}]_0$ ratios; (b) Plots of monomer conversion versus polymerization time; (c) DSC curves for second heating scans of **P(M1)** samples with various molecular weights at a heating rate of $5^\circ\text{C}/\text{min}$. (S1: $M_n=2.1$ kDa, $\bar{D}=1.09$; S2: $M_n=3.1$ kDa, $\bar{D}=1.10$; S3: $M_n=5.6$ kDa, $\bar{D}=1.08$; S4: $M_n=7.3$ kDa, $\bar{D}=1.12$); (d) DSC curves for second heating scans of **P(M1)**, **P(M2)** and **P(M3)** at a heating rate of $5^\circ\text{C}/\text{min}$. (**P(M1)**=7.3 kDa, $\bar{D}=1.12$; **P(M2)**=7.4 kDa, $\bar{D}=1.10$; **P(M3)**=11.1 kDa, $\bar{D}=1.07$).

polymer economy.^[41] Accordingly, we examined the chemical recycling performance of the purified poly(ether-*alt*-ester). The purified **P(M1)** with $M_n=7.3$ kDa was dissolved in Toluene- d_8 at a concentration of 40 mg/ml, 10 mol% DBU (relat-

ive to the repeating units of polymer) was added as catalyst, and 89 % of **P(M1)** was depolymerized back to pristine monomers at 130°C within 6 h (Fig. S1 in ESI). $\text{Sn}(\text{Oct})_2$ was also used as catalyst for the solution depolymerization of

Table 2 Results of ROP of monomers with DBU/TU-2 as catalysts.^a


Entry	M	[I]:[B]:[TU]:[M]	Time (h)	Conv. ^b (%)	M_n (GPC) ^c (kDa)	\bar{D} ^c
1 ^d	M1	1:1:1.5:100	12	43	7.7	1.13
2	M1	1:1:1.5:200	24	43	10.1	1.09
3	M1	1:1:1.5:50	12	44	6.5	1.07
4 ^e	M1	1:1:1.5:100	12	15	5.3	1.12
5 ^f	M1	1:1:1.5:100	12	18	5.5	1.10
6 ^g	M2	1:1:1.5:100	12	49	7.4	1.10
7	M2	1:1:1.5:100	1	41	3.3	1.13
8	M3	1:1:1.5:100	12	48	11.1	1.07

^a Condition: initiator [I] = benzyl alcohol, bulk polymerization, the polymerization was conducted at 0 °C; ^b Determined by ¹H-NMR; ^c Determined by gel permeation chromatography (GPC) in THF, calibrated with polystyrene standards; ^d Initiator [I] = 1,4-benzenedimethanol; ^e The polymerization was conducted at -10 °C; ^f The polymerization was conducted at -10 °C; ^g The polymerization was conducted at RT.

P(M1), and Sn(Oct)₂ showed a higher catalytic activity compared to DBU, achieving >99% conversion under the same conditions (Figs. S2 and S3 in ESI). The degradation experiments of **P(M2)** with $M_n=7.4$ kDa and **P(M3)** with $M_n=11.1$ kDa were carried out under the same conditions, both **P(M2)** and **P(M3)** were selectively recycled with high conversions of >99%, respectively (Figs. S7 and S11 in ESI). These results demonstrated the good chemical recycling performance of the purified poly(ether-*alt*-ester).

CONCLUSIONS

In conclusion, we have successfully synthesized a variety of 1,4-dioxan-2-one with different substituents in one step using mononuclear Salen-Cr(III)/PPNCl as catalyst from GA and epoxides, and further applied them as novel monomers with perfectly alternative ether and ester bonds for the construction of poly(ester-*alt*-ether). We prepared poly(ester-*alt*-ether) with well-defined chain ends and narrow dispersity by using thiourea/base binary catalysts. Thermal analysis revealed that the polymers exhibited an amorphous state with lower T_g than PGA. Importantly, the resultant polymers can be efficiently recycled back to pristine monomers through solution depolymerization catalyzed by Sn(Oct)₂ at 130 °C for 6 h, establishing a monomer-polymer-monomer closed-loop life cycle. The results reported herein provided an ingenious route for the synthesis of poly(ester-*alt*-ether) with chemical recyclability from monomers derived from GA and epoxides.

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/s10118-023-3040-1>.

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