

Readily Degradable and Recyclable High Molecular Weight Thiosalicylic Acid-based Copolyesters

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Electronic Supplementary Information

Abstract Most commercial plastics cannot easily degrade, which raises a number of sustainability issues. To address the current problem of plastic pollution, the research and development of easily degradable and recyclable polymers has become an attractive subject. Herein, a new monomer of thiosalicylic methyl glycolide (TSMG) was synthesized using one-pot method and high molecular weight poly(thiosalicylic methyl glycolide) (PTSMG, M_n up to 300 kDa) can be obtained via the ring-opening polymerization (ROP) of TSMG. PTSMG exhibits good closed-loop recyclability and hydrolytic degradability, where PTSMG can generate pristine monomers through sublimation thermal depolymerization conditions due to the presence of thiophenol ester bond in the polymer chains, and can be degraded rapidly in aqueous solution, which provides a potential solution to the current plastic pollution problem.

Keywords Hydrogen-bonding catalysts; Closed-loop recycling; Hydrolytic degradation; Ring-opening polymerization; Poly(thiophenol ester)

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INTRODUCTION

The use of petroleum-based plastics has greatly facilitated and enriched the lives of people. Global plastic production has grown rapidly since 1964. By 2023, the total global plastic production exceeded 10 billion tons.^[1] However, the rapid growth of commercial plastics has led to problems with plastic waste disposal. Because of the stability of plastics, most plastic products piled in landfills or discarded in the natural environment can remain in the environment for decades or even hundreds of years, which not only results in serious environmental pollution but also causes a waste of resources.^[2,3] The need for closed-loop recyclable or readily degradable plastics from biologically sourced feedstock has received extensive attention from polymer scientists in parallel with the development of existing methods for the degradation of petroleum-based plastics.^[4–7] The introduction of salicylic acid into the polymer backbone is an ideal strategy to enhance the degradability of polymers as previously proposed by Hillmyer *et al.*^[8,9] On the other hand, Chen *et al.* achieved the first ROP of γ -butyrolactone in 2016, and the resulting polymer could be recycled to obtain γ -butyrolactone by

ring-closing.^[10] In recent years, closed-loop recyclable polyesters have been rapidly developed; for example, the corresponding recyclable polyesters can be obtained by the ROP of six- or seven-membered cyclic ester monomers with only moderate ring strain energies.^[4,11–18] In addition, the introduction of more dynamic bonds (e.g., thioester bonds) in thermodynamically close equilibrium systems may be a feasible approach to improve the closed-loop recyclability and degradability of polymers.^[11,19–23]

In recent years, polythioesters (PTEs) have been developed as degradable, closed-loop recyclable polymers.^[24] Representative closed-loop recyclable PTEs were synthesized by Chen, Lu, Tao, Li *et al.*^[16,20,21,24,25] The degradability of PTEs has not been adequately investigated. On the other hand, most of the current aliphatic PTEs generally have low glass transition temperatures and breaking strengths, while the introduction of thiosalicylic acid (with a benzene ring rigidity group) into the main chain of PTEs not only improves the thermal/mechanical properties but also greatly improves the degradability.^[16,26,27] Nonetheless, at present, the research on PTEs still required flourished. This is due to the fact that PTEs contain more reactive thiophenol ester bonds and their controlled synthesis remains a challenge.^[16,28,29]

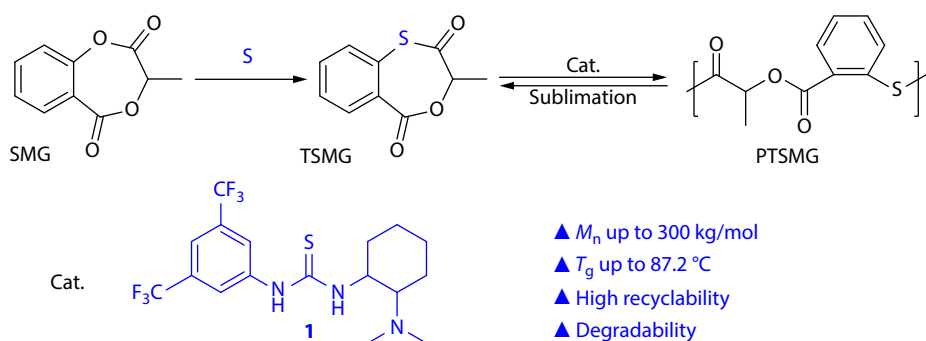
In this study, thiosalicylic methyl glycolide (TSMG) monomer containing a thiophenol ester bond was successfully synthesized via a one-pot method using biologically sourced 2-bromopropionyl bromide and thiosalicylic acids. Poly(thiosalicylic methyl glycolide) (PTSMG) with a higher

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Scheme 1 Synthesis of high molecular weight recyclable PTSMG by catalyst **1**.

molecular weight was successfully synthesized *via* the catalytic ROP of TSMG using thiourea-based bifunctional catalyst **1** (Scheme 1). Thiosalicylic acid-based copolyesters have excellent thermal/mechanical properties, degradability, and closed-loop recyclability. PTSMG can be depolymerized to monomer TSMG under vacuum at 85 °C with PEO as a non-volatile solvent, with a recovery selectivity of up to 98%.

EXPERIMENTAL

General Methods

Unless otherwise specified, all the ROP catalysis experiments were conducted under a dry nitrogen atmosphere. All syntheses and manipulations of the air/moisture-sensitive materials were performed under a dry nitrogen atmosphere in a glove-box or using standard Schlenk techniques.

Materials

Toluene, hexane, and THF were distilled from sodium benzophenone prior to use. CH_2Cl_2 (DCM) and acetonitrile were dried by refluxing with CaH_2 . Chloroform-*d* was purchased from J&K Scientific, Ltd., Beijing, China, and carefully dried over activated molecular sieves. Thiosalicylic acid, 3,5-bis(trifluoromethyl)phenylisothiocyanate, 2-dimethylaminomethylaniline, *N,N*-dimethylcyclohexylamine, 2-bromopropionyl bromide, methyl thiosalicylate, hexafluorobenzene and poly(ethylene glycol) (PEG=PEO) ($M_n \approx 1.0 \times 10^4$) were purchased from Energy Chemical Co., Ltd. 1-[3,5-Bis(trifluoromethyl)phenyl]-3-[(1*R*,2*R*)-(-)-2-(dimethylamino)cyclohexyl]thiourea was purchased from Bide Pharmatech Co., Ltd. The artificial seawater was purchased from Guangzhou Howei Pharma Tech Co., Ltd. 1 mol/L Phosphate buffer (PBS) was purchased from Pinggen Experimental Equipment Co., Ltd. 0.1 mol/L NaOH aqueous solution was made in the laboratory. All other chemicals were commercially available and were used after appropriate purification.

General Polymerization Procedure of Thiosalicylic Methyl Glycolide (TSMG) Catalyzed by TBACl in DCM

A typical polymerization procedure was illustrated by the synthesis of PTSMG ($[\text{Cat}]_0:[\text{I}]_0:[\text{TSMG}]_0=1:4:400$; Table S1 in the electronic supplementary information, ESI, entry 9). First, a mixture of the catalyst (0.025 mmol) and methyl thiosalicylate (0.1 mmol) was prepared in 2.5 mL of DCM with a catalyst concentration of 0.01 mol/L ($[\text{Cat}]_0:[\text{I}]_0=1:4$). Then, 0.5 mL of the solution of prepared catalyst (0.0025 mmol) and initiator (0.01 mmol) mixed solution, TSMG 0.5 mmol (104 mg) was dissolved in 1 mL of DCM and stirred for 5 h at room temperature, an

aliquot was withdrawn to determine monomer conversion by $^1\text{H-NMR}$ spectroscopy. Finally, the polymer was precipitated by adding *n*-pentane (5 mL). A white solid was obtained by recrystallization from DCM/*n*-pentane mixed solvent. The collected polymer sample was further dried in a vacuum oven at 50 °C for 8 h to a constant weight for GPC and $^1\text{H-NMR}$ analysis.

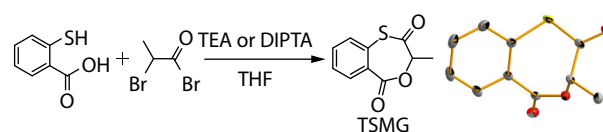
Polymerization Procedure of TSMG Catalyzed by **1**

A typical polymerization procedure was illustrated by the synthesis of PTSMG ($[\text{1}]_0:[\text{TSMG}]_0=1:50$; Table S2 in ESI, entry 2). First, bifunctional catalyst **1** (4 mg, 0.01 mmol) and 1 mL of DCM were placed in the feeding tube, and TSMG (104 mg, 0.5 mmol) was transferred to the reaction tube. The feed and reaction tubes were sealed together and placed in a low-temperature reactor (−30 °C). After 10 min, the solution in the feed tube was transferred to the reaction tube. After 1.5 h of reaction time, benzoic acid was added to quench the reaction. Monomer conversion was determined by $^1\text{H-NMR}$ spectroscopy. The polymer was precipitated by adding 5 mL of *n*-pentane and recrystallized with DCM and *n*-pentane to obtain a white solid. The collected polymer samples were dried to a constant weight in a vacuum oven at 50 °C. Finally, the polymers were characterized and analyzed.

Synthesis and Characterization of TSMG

Thiosalicylic acid (2 g, 0.013 mol) and triethylamine (TEA) or *N,N*-diisopropylethylamine (DIPEA) (0.027 mol) were transferred to a 250 mL constant pressure funnel, and 100 mL of anhydrous THF dissolved in raw material was added. 2-Propionyl bromide (3 g, 0.014 mol) and 100 mL of anhydrous THF were transferred to a 500 mL round-bottomed flask, placed in an ice bath under argon for approximately 1 h, and stirred for approximately 8 h after returning to room temperature (Scheme 2). The white solid was removed by filtration and the reaction liquid was concentrated and subsequently dissolved in ethyl acetate. The organic phase was quickly washed with saturated aqueous sodium chloride solution (3×30 mL), dried with anhydrous MgSO_4 , concentrated, and recrystallized with ether to obtain a white solid TSMG (1.0 g, 38% yield), and sublimed under vacuum at 80 °C to obtain a white solid.

TSMG $^1\text{H-NMR}$ (400 MHz, chloroform-*d*, δ , ppm): 7.94 (d,



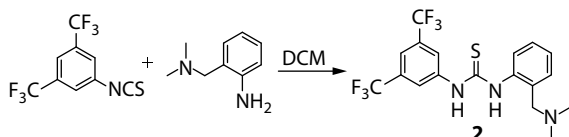
Scheme 2 Synthesis of TSMG.

$J=7.7$ Hz, 1H, Ar—H), 7.62–7.47 (m, 3H, Ar—H), 5.01 (q, $J=6.4$ Hz, 1H, —CHCH₃), 1.54 (d, $J=6.4$ Hz, 3H, —CHCH₃). ¹³C-NMR (101 MHz, Chloroform-d, δ , ppm): 195.49 (Ar—C=O), 167.71 (Ar—C=O), 132.95 (Ar—C), 132.62 (Ar—C), 132.38 (Ar—C), 131.39 (Ar—C), 129.77 (Ar—C), 128.75 (Ar—C), 75.17 (—CHCH₃), 14.88 (—CHCH₃). HRMS (ESI): m/z calculated for C₁₀H₈O₃S; [M + Na]⁺ 231.0086; observed: 231.0081.

Synthesis and Characterization of Bifunctional Organic Catalyst 2

3,5-Bis(trifluorophenyl) methyl isothiocyanate (4 mmol, 1.08 g) was added to a dry mixture of DCM (20 mL) and 2-dimethylaminomethyl aniline (600 mg, 4 mmol) and stirred at room temperature, and the reaction was monitored by TLC (Scheme 3). After the reaction was complete, the mixture was concentrated under a vacuum. The mixture was purified using a silica gel chromatography column (DCM/MeOH) to obtain a light yellow solid (1.38 g, 82%).

Bifunctional organic catalyst **2**: ¹H-NMR (600 MHz, DMSO-d₆, δ , ppm): 10.50 (s, 2H, —NH), 8.23 (s, 2H, Ar—H), 7.83–7.71 (m, 2H, Ar—H), 7.29 (dd, $J=22.6$, 7.3 Hz, 2H, Ar—H), 7.14 (t, $J=7.5$ Hz, 1H, Ar—H), 3.41 (s, 2H, —CH₂—), 2.05 (s, 6H, —CH₃).



Scheme 3 Synthesis of bifunctional organic catalyst **2**.

RESULTS AND DISCUSSION

Synthesis of TSMG and Screening of Monomer ROP Conditions

To introduce thiophenol ester bonds into the polymer, TSMG was synthesized *via* a one-pot method using commercial thiosalicylic acid and amino acid-derived 2-bromopropionyl bromide. NMR spectroscopy (Figs. S1 and S2 in ESI), single-crystal X-ray diffraction (Table S6 in ESI), and high-resolution mass spectrometry (ESI) analyses confirmed the chemical structure of TSMG. Because of the structural similarity between TSMG and salicylic methyl glycolide (SMG), tetrabutylammonium halide was first attempted as a catalyst to catalyze the ROP of TSMG, according to our previous work.^[30] First, the ROP of TSMG was catalyzed with tetrabutylammonium chloride (TBACl) as a catalyst and methyl thiosalicylate as an initiator. The reaction was carried out in tetrahydrofuran (THF) at a ratio of 1:4:100 for [TBACl]₀: [I]₀: [TSMG]₀, and the monomer conversion reached 97% after 2 h at room temperature (Table S1 in ESI, entry 1). However, a large amount of solid precipitated from the reaction solution, and the ¹H-NMR spectrum shows multiple peaks at 5.60 ppm (Fig. S5 in ESI). This may be due to the strong basicity of the chloride ions in TBACl to TSMG, which causes a severe side reaction that produces small molecules insoluble in THF. When weaker basic tetrabutylammonium bromide (TBABr) and tetrabutylammonium iodide (TBAI) were used to catalyze the polymerization reactions (Table S1 in ESI, entries 2 and 3) with conversions of approximately 88% after 4 h and 8 h, respectively, the gel permeation chromatography (GPC) spectra of the resulting PTSMG show bimodal GPC traces and broad molecular weight dispersi-

ty (Figs. S6A and S6B in ESI). The appearance of bimodal peaks in the GPC traces may indicate that there are multiple initiation and growth pathways in the polymerization reactions. To verify this hypothesis, the ROP of TSMG was catalyzed by TBABr in the absence of an initiator, and 85% of the monomers were polymerized within 10 h with extremely poor controllability (Table S1 in ESI, entry 4). This shows that TBABr can directly initiate ROP of TSMG, accompanied by severe transesterification. Meanwhile, it was found that without tetrabutylammonium halide as a catalyst, methyl thiosalicylate could directly initiate the ROP of TSMG in THF at room temperature with 28% conversion after 10 h (Table S1 in ESI, entry 5); however, the ROP of TSMG did not occur in DCM (Table S1, entry 6). In the MALDI-TOF mass spectrum of the resulting PTSMG (Table S1 in ESI, entry 5), a set of primary peaks at $208.23n + 168.21 + 23$ can be assigned to n (TSMG) + methyl thiosalicylate + Na⁺, and a series of weak peaks cyclic polymers was found (Fig. S7 in ESI). Because methyl thiosalicylate can directly initiate the ROP of TSMG in THF, whereas it does not react in DCM, subsequent experiments will use DCM as the reaction solvent to exclude the ROP initiated by methyl thiosalicylate. When DCM was utilized as a solvent, the molecular weight of PTSMG did not increase linearly (Table S1 in ESI, entries 7 and 8; Figs. S6D and S6E in ESI) (Table S1 in ESI, entries 9 and 10) using TBACl/Br/I as a catalyst and methyl thiosalicylate as an initiator. Therefore, tetrabutylammonium halide cannot catalyze the ROP of TSMG in a controlled manner because of the existence of several chain growth paths, which can be attributed to the fact that the thiophenol ester bond is more vulnerable to nucleophilic attack due to its relatively strong electrophilicity; thus, both methyl thiosalicylate and tetrabutylammonium halide can directly initiate polymerization.^[31–33]

With the aim of improving one main chain growth path *via* synergistic activation of both the initiator and catalyst and suppressing the individual path of the initiator or catalyst, classical single-molecule bifunctional organocatalysts (**1** and **2**) were used to mediate the synthesis of PTSMG.^[16,33–35] However, in the presence of initiator, the controllable ROP of TSMG could not be achieved *via* changing catalyst, catalyst-to-initiator ratio, and reaction temperature during the catalytic process (Table S2; Figs. S6C and S9 in ESI). The ROP of TSMG faces great challenges because of the stronger electrophilicity (compared to the thioester bonds) of the thiophenol ester bond.^[36,37] We have tried several catalytic systems for the ROP of TSMG, but none can effectively suppress side reactions such as transesterification and back-biting reactions.

Interestingly, when no initiator was used, the polymerization proceeded well at a low temperature of −30 °C, and the conversion of the monomers reached 97% in 2 h using **1** as a catalyst. Furthermore, the number average molecular weight measured by GPC could reach 203.5 kDa with narrow molecular weight dispersity ($\bar{D}=1.59$) (Table S2, entry 2; Fig. S9A in ESI). Therefore, the ROP of TSMG can be directly catalyzed using **1**. In 2021, Tao *et al.* reported effective single-molecule anion-binding catalysis, which was applied to successfully synthesize high-molecular-weight poly(mandelic acid) (150.0 kDa) *via* the ROP of *O*-carboxyanhydride (OCA).^[33] This unique anion dynamic binding promoted efficient chain growth, and the thiourea moiety stabilized the anion while reducing the alkalinity and nucleophilicity of the anion-transporting species through synergistic decarboxylation, resulting in bet-

ter inhibition of side reactions (such as transesterification and back-biting reactions).

Synthesis of High Molecular Weight PTSMG

Based on the above results, in order to synthesize high-molecular-weight PTSMG, catalyst **1** was directly applied to catalyze the ROP of TSMG in DCM. The conversion of TSMG reached 94% at $-30\text{ }^{\circ}\text{C}$ for 1.5 h at a $[\text{TSMG}]_0/[\mathbf{1}]_0$ ratio of 25:1. The molecular weight of PTSMG, measured by GPC, was close to the NMR molecular weight, and the molecular weight dispersity of the polymer was narrow ($\bar{D}=1.68$) (Table 1, entry 1). In the $^1\text{H-NMR}$ spectrum of the PTSMG polymer, the chain end group of thiophenol is clearly observed at 4.71 ppm (the sulfhydryl signal in methyl thiosalicylate was located at 4.71 ppm in $^1\text{H-NMR}$ spectra) (Table 1, entry 1, Table S2, entry 1; Fig. 1, Figs. S8, S10 and S19 in ESI), indicating that the polymer PTSMG was obtained. In addition, the M_n of PTSMG increased linearly with the monomer conversion while $\bar{D}$ (1.20–1.42) remained low (Table S3, Fig. S11 in ESI), which indicated that the side reactions were weak (e.g., cyclization, transesterification). Moreover, the molecular weight of PTSMG increased linearly with the $[\text{TSMG}]_0/[\mathbf{1}]_0$. When the ratio exceeded 100, the molecular weight of PTSMG was stabi-

lized at approximately 300 kDa (Table 1, entries 2–4; Fig. 2).

Mechanism of Catalyst **1** for the ROP of TSMG

It has been reported that thiourea groups can activate monomers by hydrogen bonding during the ROP of monomers.^[33] Therefore, in order to demonstrate the interaction between catalyst **1** and TSMG, $^1\text{H-NMR}$ comparison experiments were performed. When 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea (**TU**) and TSMG were mixed in CDCl_3 at a ratio of 1:1 for about 10 min, the proton of the $-\text{NH}$ groups of **TU** were shifted from 5.94/7.63 ppm to 6.09/8.10 ppm, which hints at hydrogen bonding interaction between TSMG and **TU** (Fig. 3).^[33] When **TU** alone was used to catalyze the polymerization of TSMG (Table 1, entry 6), polymerization did not occur, indicating that **TU** cannot open TSMG by hydrogen bonding alone in the absence of basic groups. When *N,N*-dimethylcyclohexylamine (**DMCHA**) was used to catalyze the ROP reaction alone, the monomer conversion of TSMG was 93% within 30 min, and the molecular weight of PTSMG was 281.4 kDa, but the molecular weight dispersity was wide ($\bar{D}=2.06$) (Table 1, entry 7). This indicates that **DMCHA** can catalyze the ROP of TSMG directly, but its controllability is poor,

Table 1 Synthesis of high molecular weight PTSMG catalyzed by **1**.

Entry	Cat.	$[\text{Cat.}]_0/[\text{M}]_0$	$T\text{ (}^{\circ}\text{C)}$	$t\text{ (h)}$	Conv. ^b (%)	$M_{n,\text{calcd}}^c\text{ (g/mol)}$	$M_{n,\text{NMR}}^d\text{ (g/mol)}$	$M_{n,\text{obsd}}^e\text{ (g/mol)}$	$\bar{D}^e$
1	1	1/25	-30	1.5	94	4900	1.31×10^5	1.091×10^5	1.68
2	1	1/50	-30	2	97	1.01×10^4	— ^f	2.035×10^5	1.59
3	1	1/100	-30	2	94	1.96×10^4	— ^f	3.002×10^5	1.46
4	1	1/200	-30	9	77	3.20×10^4	— ^f	2.990×10^5	1.45
5	1	1/200	-30	16	97	4.04×10^4	— ^f	3.087×10^5	1.54
6	TU	1/25	-30	1.5	0	—	—	—	—
7	DMCHA	1/25	-30	0.5	93	4800	— ^f	2.814×10^5	2.06

^a Conditions: Reactions were carried out under a dry nitrogen atmosphere in DCM, $[\text{M}]=1\text{ mol/L}$, monomer = TSMG; ^b Determined by $^1\text{H-NMR}$ spectroscopy; ^c Calculated from the molecular weight of $M_{n,\text{TSMG}} \times [\text{TSMG}]_0/[\mathbf{1}]_0 \times \text{conversion yield}$; ^d Determined from the relative integration of the signals for the main-chain methine units and chain ends; ^e Experimental M_n and $\bar{D}$ determined by GPC in THF against polystyrene standards; ^f The $M_{n,\text{NMR}}$ cannot be calculated because the chain ends signal is very weak.

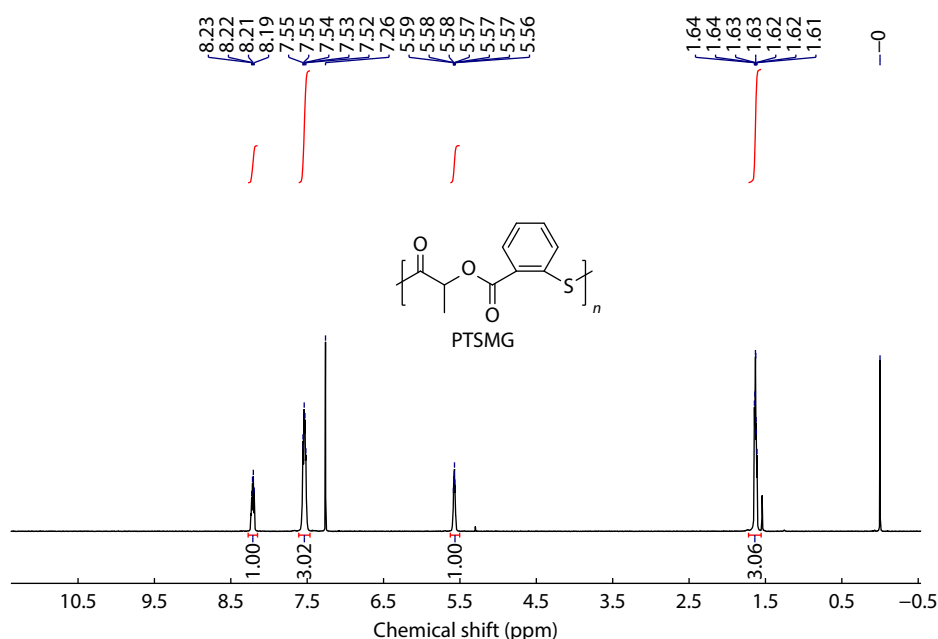


Fig. 1 $^1\text{H-NMR}$ spectrum of PTSMG prepared by **1**.

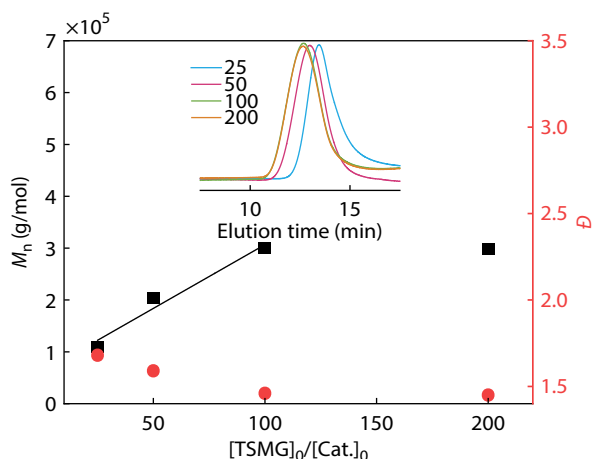


Fig. 2 Plots of the relationship between M_n and $\bar{D}$ of polymer versus $[\text{TSMG}]_0/[\text{I}]_0$ ratios, and representative GPC traces of the PTSMG.

which may be caused by the indiscriminate attack of the thiophenol chain ends on the thiophenol ester bond in TSMG and PTSMG in the absence of **TU** stabilizing anions. To demonstrate that catalyst **1** can directly initiate the ROP of TSMG, the purified PTSMG was end capped with catalyst **1**, which can be verified by the displacement of the fluorine atom signal from 63.54 ppm to 63.42–63.45 ppm (Fig. S12 in ESI).

Therefore, the catalytic synthesis of high-molecular-weight PTSMG by catalyst **1** can be attributed to two reasons: (1) the low initiation efficiency of the tertiary amine in catalyst **1** generates thiophenol chain ends with strong attacking ability, and the ROP of TSMG has a slow initiation and fast growth process. (2) The thiourea group in catalyst **1** controls the end of the thiophenol chain around the catalyst through hydrogen bonding while activating the monomers, thus promoting the thiophenol chain end to attack the activated monomers instead of the thiophenol ester bond on the poly-

mer chain, reducing side reactions such as transesterification and back-biting.^[33] Hillmyer *et al.* demonstrated that the ring-opening site of the monomer is on the phenolic ester bond in the ROP of SMG. To prove that the ring-opening site of TSMG is located on the thiophenol ester bond, catalytic experiments were performed with $[\textbf{1}]_0:[\text{I}]_0:[\text{TSMG}]_0$ in a ratio of 1:10:10. According to $^1\text{H-NMR}$ spectrum, a new set of quadruple peaks appeared at 5.66 ppm (Fig. S13 in ESI). The new product was purified by column chromatography and characterized using NMR spectroscopy and ESI-HRMS (Figs. S14 and S15 in ESI). By careful comparison of the $^1\text{H-NMR}$ spectra, the peak at 4.70 ppm was assigned to the thiophenol proton at the chain end, which is similar to the thiophenol proton signal of methyl thiosalicylate at 4.71 ppm. The structure of 1-((2-(methoxycarbonyl)phenyl)thio)-1-oxopropan-2-yl 2-mercaptobenzoate (MPTOYM) indicated that the active thiophenol chain end opens TSMG at the thiophenol ester bond. Therefore, the ROP of TSMG catalyzed by catalyst **1** has a high regional selectivity.

Combined with the above experimental results, we propose a possible catalytic mechanism (Fig. 4): (1) Catalyst **1** activates TSMG to form A through hydrogen bonding; (2) the tertiary amine group in catalyst **1** attacks the carbonyl carbon in the thiophenol ester bond, and the monomer is opened. After ring opening, the thiophenol terminal interacts with the thiourea group to form species B. At this point, it is critical that the chain ends are stabilized by the neighboring thiourea moiety. (3) Thiophenol anions attack TSMG, which is activated by the thiourea group. (4) This process is repeated to complete the ROP. (5) The polymer was quenched with alcohol.

Study of Closed-loop Recyclability, Thermal/Mechanical Properties and Hydrolytic Degradation of PTSMG

Depolymerization of polymers into starting monomers is an effective strategy to solve the problem of plastic pollution.^[11] Recently, Tao *et al.* reported that it is feasible to improve the

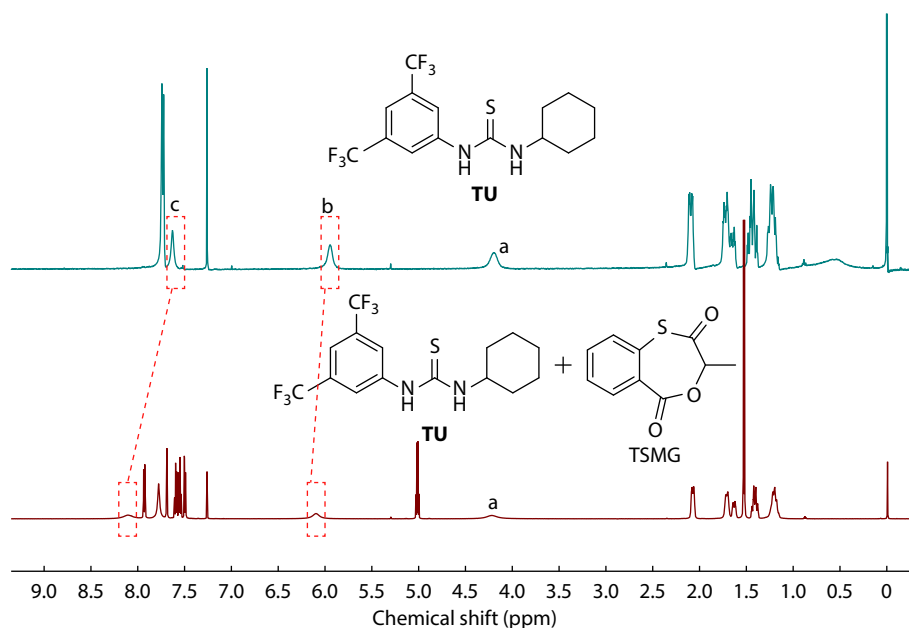


Fig. 3 $^1\text{H-NMR}$ spectra of a mixture of TSMG and **TU** in CDCl_3 at 25 °C.

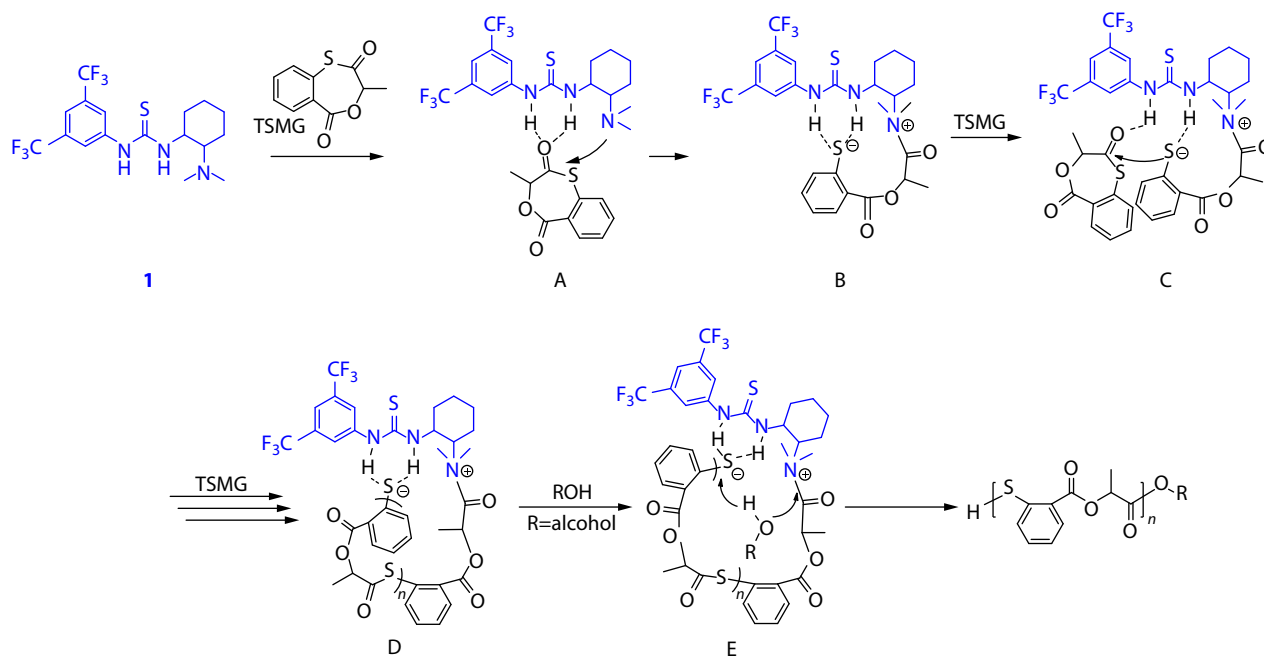


Fig. 4 Diagram of possible pathways for ROP of TSMG catalyzed by catalyst **1**.

closed-loop recovery of polymers by oxygen-sulfur substitution of cyclic ester monomers.^[16,26] Closed-loop recovery of PTSMG was attempted due to the fact that TSMG contains thiophenol ester bonds and a structure similar to SMG.^[27] According to density functional theory (DFT), the ring strain energy of SMG and TSMG monomers are 7.97 and 2.82 kcal/mol, respectively (Fig. S20 in ESI). The ring strain energy of TSMG is lower than that of SMG, which indicates that the depolymerization of PTSMG makes it easier to obtain TSMG. Therefore, closed-loop recovery of PTSMG was first attempted in toluene. TSMG was recovered in 82.5% yield when *t*-BuOK was added as a depolymerization catalyst (Table S4, entry 1, in ESI). When the reaction time was extended to 36 h, the recovery yield of the monomer did not increase significantly (84.5%) (Table S4, entry 2; Fig. S16 in ESI). It can be seen that the recovery of PTSMG in toluene is not ideal. Vacuum sublimation recovery of polymers can quickly separate monomers and is favorable for improving the recovery rate of monomers.^[12,13] Thus, the vacuum sublimation method was used to recover TSMG. The recovery yield of PTSMG increased to 94.5%, and the recovery selectivity of TSMG was 98% after depolymerization at 85 °C for 24 h under catalyst-free conditions

with PEO as a non-volatile solvent (Table S5; Fig. S17 in ESI). The introduction of sulfur atoms seems to improve the closed-loop recovery selectivity of TSMG (compared to the closed-loop recovery of SMG), and the lower recovery temperature also reduces the energy consumption (Fig. S18 in ESI).

When tested and analyzed by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA), PTSMG demonstrated a high glass transition temperature ($T_g=87.2$ °C), which is significantly higher than the T_g of most aliphatic polythioesters.^[12,16,26,27] Similar to PSMG, there was no melting peak during the cycle heating process. Compared to the 5% weight loss temperature ($T_{d,5\%}$) of PSMG, the $T_{d,5\%}$ of PTSMG is lower at 236 °C, which may be caused by the more easily broken thiophenol ester bond (Figs. 5a and 5b).^[8] The mechanical properties of PTSMG with different molecular weights were evaluated using a mechanical testing machine. When the molecular weight of PTSMG increased from 159.7 kDa to 300.2 kDa, the elongations at break (ϵ_B) keep similar with values of $2.2\pm0.5\%$ and $2.5\pm0.6\%$, the tensile strength at break (σ_B) of PTSMG increases clearly from 23.3 ± 1.1 MPa to 33.2 ± 1.3 MPa (Fig. 5c), which is consistent

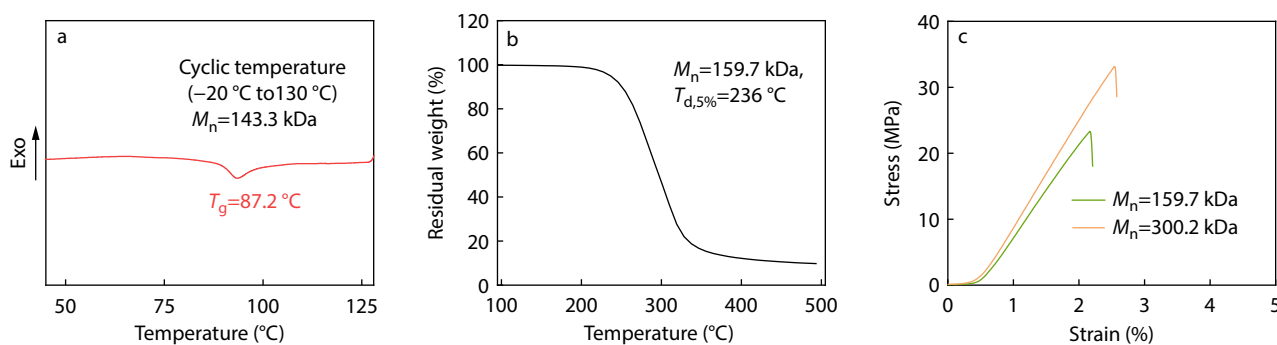


Fig. 5 (a) DSC second heating scan thermogram (10 °C/min) for PTSMG; (b) TGA thermogram of PTSMG; (c) Stress-strain curves of PTSMG.

with the trend reported in literature. The brittleness and moderate fracture strength of PTSMG may have been caused by the benzene ring (rigid group).

The chain structure of PTSMG is similar to that of PSMG, which contains an easily broken thiophenol ester bond, which may result in good hydrolytic degradation.^[8,14] The hydrolysis degradation experiments of PTSMG were conducted in phosphate buffered aqueous solution (1 mol/L PBS, pH 7.4), artificial seawater (pH 7.4) and 0.1 mol/L NaOH aqueous solutions, which simulated the degradation conditions of PTSMG *in vivo*, in ocean, and industrial composting systems, respec-

tively. In addition, in order to complete the hydrolysis degradation experiment quickly and accurately, the degradation temperature of the polymer was set at 50 °C. When degraded in artificial seawater, the PTSMG sample ($M_n=300.2$ kDa) slowly changed from transparent to white opaque with increasing degradation time, which was caused by the expansion of the water absorption of the sample. When the degradation time was 79 days, the sample was degraded into a massive structure, and 69% of its weight was lost during this time (Fig. 6d). The GPC traces show that the molecular weight of the sample decreased rapidly after 38 days (Fig. 6a). The degradation

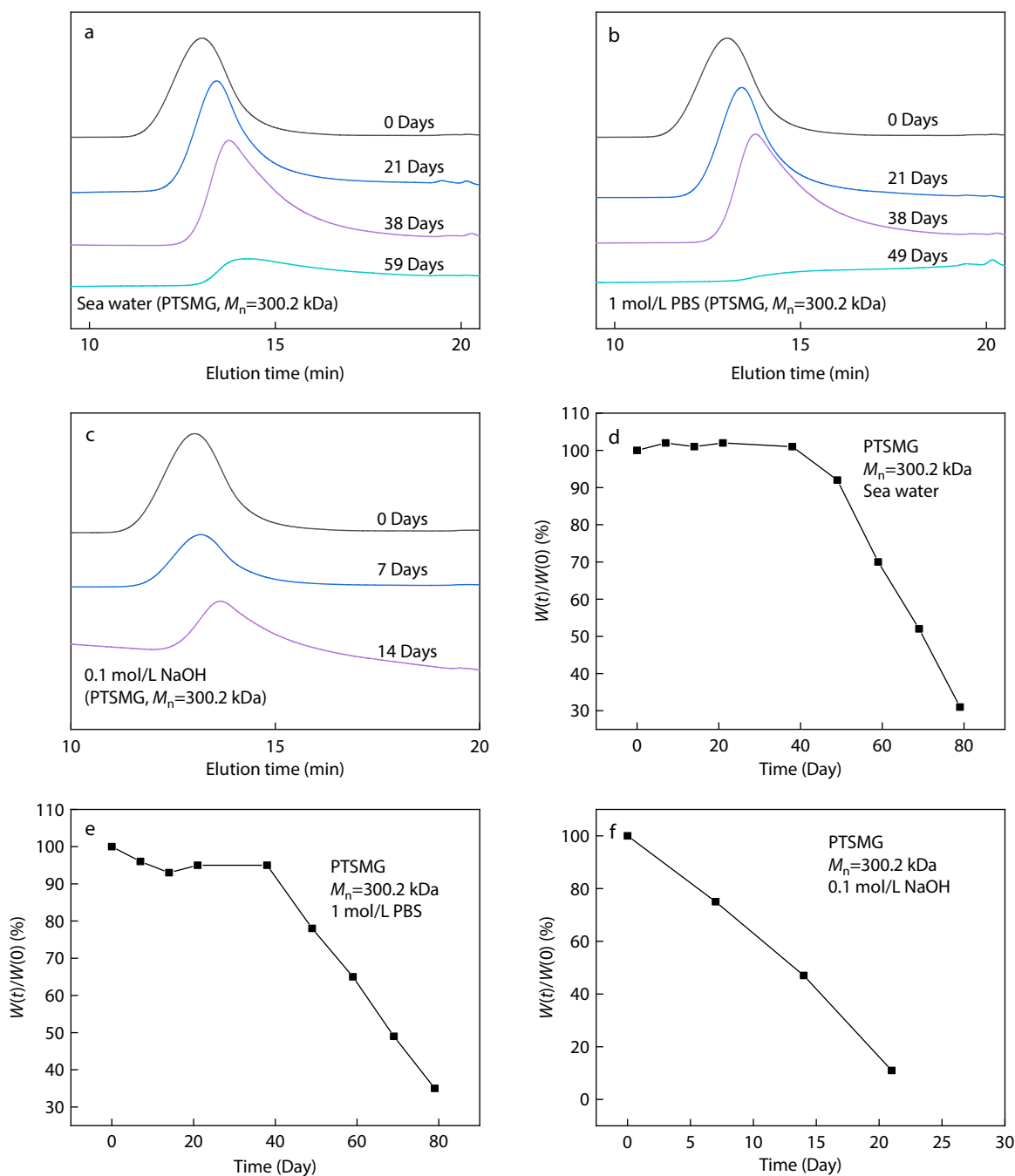


Fig. 6 (a–c) GPC traces of PTSMG in sea water, 1 mol/L PBS and 0.1 mol/L NaOH solution, respectively; (d–f) Investigation of hydrolytic degradation of PTSMG sample under 50 °C.

of the sample in 1 mol/L PBS was similar to that in seawater (Figs. 6b and 6e). With the extension of the degradation time after 40 d, the weights and molecular weights of the samples decreased rapidly after the induction period. After summing up the GPC trace and weightlessness data, it was concluded that PTSMG follows the bulk erosion model in artificial seawater and 1 mol/L PBS.^[9] When PTSMG was degraded in a sodium hydroxide aqueous solution, the mass of the sample continued to decline with increasing degradation time, and the weight loss reached 89% on day 21 (Fig. 6f). According to the GPC traces, M_n and $\bar{D}$ of the sample fluctuated slightly during degradation (Fig. 6c). Therefore, the hydrolytic degradation of PTSMG in 0.1 mol/L NaOH solution follows the surface erosion mechanism, which is consistent with the degradation behavior of other polyesters under similar conditions.

CONCLUSIONS

In this work, TSMG containing a thiophenol ester bond was designed and synthesized for the first time, and the synthesis of high molecular weight PTSMG with a molecular weight of up to 300.2 kDa ($\bar{D}$ =1.46) was achieved using **1** as a catalyst. A preliminary mechanism study showed that during the propagation process, the resulting anion group at the chain end is dynamically bound to the catalyst through hydrogen bonding, which can promote chain propagation and effectively inhibit side reactions (such as transesterification and back-biting reactions). The closed-loop recovery experiment showed that the recovery yield of PTSMG was 94.5%. DSC and mechanical test results showed that PTSMG has a high glass transition temperature (T_g =87.2 °C), and the σ_B of PTSMG can reach 33.2±1.3 MPa. Hydrolytic degradation results showed that PTSMG could be well degraded in artificial seawater, 1 mol/L PBS and 0.1 mol/L NaOH solution. PTSMG exhibited good recyclability and degradation properties. PTSMG can be recycled back to TSMG through a closed loop *via* sublimation. When PTSMG is discarded, it can be rapidly hydrolyzed and degraded in the environment. These two characteristics provide a feasible solution for the problem of plastic pollution.

Conflict of Interests

The authors declare no interest conflict.



Electronic Supplementary Information

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Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author upon reasonable request.

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