

Poly(thiocarbonate) Synthesis from Carbonyl Sulfide (or Carbon Disulfide), Diol, and Dichlorides: A Step Growth Route to PE-like Sulfur-containing Polymers

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 Electronic Supplementary Information

Abstract The facile synthesis of high-valued polymers from waste molecules or low-cost common chemicals presents a significant challenge. Here, we develop a series of degradable poly(thiocarbonate)s from the new step-growth polymerization of diols, carbonyl sulfide (COS, or carbon disulfide, CS₂), and dichlorides. Diols and dichlorides are common chemicals, and COS (CS₂) is released as industrial waste. In addition to abundant feedstocks, the method is efficient and performed under mild conditions, using common organic bases as catalysts, and affording unprecedented polymers. When COS, diols, and dihalides were used as monomers, optimized conditions could completely suppress the oxygen-sulfur exchange reaction, enabling the efficient synthesis of well-defined poly(monothiocarbonate)s with melting points ranging from 48 °C to 101 °C. These polymers, which have a structure similar to polyethylene with low-density in-chain polar groups, exhibit remarkable toughness and ductility that rival those of high-density polyethylene (melting point: 90 °C, tensile strength: 21.6±0.7 MPa, and elongation at break: 576%). Moreover, the obtained poly(monothiocarbonate)s can be chemically degraded by alcoholysis to yield small-molecule diols and dithiols. When CS₂ was used in place of COS, a pronounced oxygen-sulfur exchange reaction occurred. By optimizing reaction condition, it was found that polymers with —S(C=O)S— and —S(C=S)S— as the main repeating units exhibited high thermal stability and crystallinity. Thus, a new approach for regulating the structure of polythiocarbonates *via* the oxygen-sulfur exchange reaction is developed. Overall, the polymers hold great potential for green materials due to their facile synthesis, readily available feedstocks, excellent performance, and chemical degradability.

Keywords Poly(thiocarbonate)s; Step-growth polymerization; COS (CS₂); Oxygen-sulfur exchange reaction

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INTRODUCTION

Sulfur plays a fundamental role in polymer chemistry^[1] particularly through its incorporation into diverse characteristic sulfur-containing functional groups that impart unique chemical and physical properties to the resulting molecules or materials.^[2–4] Beyond traditional applications in rubber vulcanization and sulfuric acid production, sulfur-containing polymers have garnered considerable attention for their distinctive functionalities, including high refractive indices,^[5] strong affinity for heavy metals,^[6] and the ability of sulfur atoms to form dynamic covalent

bonds.^[3,7,8] Over the past decade, significant advances have been made in the synthesis of sulfur-containing polymers, including polythioamides,^[4,9,10] poly(thiocarbonate),^[11,12] polythioesters,^[13,14] polythioureas,^[6,15,16] polydisulfide,^[1,17,18] poly(thiourethane)^[19] and so on. Among them, polythiocarbonates, as sulfur-containing analogs of polycarbonates, exhibit significantly stronger crystallizability compared to their corresponding polycarbonate counterparts.^[20]

The synthesis of the poly(thiocarbonate)s is shown in Fig. 1. Traditionally, these polymers have been synthesized *via* condensation of dithiols with phosgene,^[21] or diols with thiophosgene (route a in Fig. 1),^[22] which are not environmentally friendly synthetic routes because of the use of highly toxic reactants. Carbon disulfide (CS₂) can be copolymerized with epoxides directly to synthesize poly(thiocarbonate)s, a process first reported by Adachi *et al.* in the 1970s,^[23] utilizing diethyl zinc and various bases as catalysts. However, long reaction time, low molecular weights, byproduct formation of

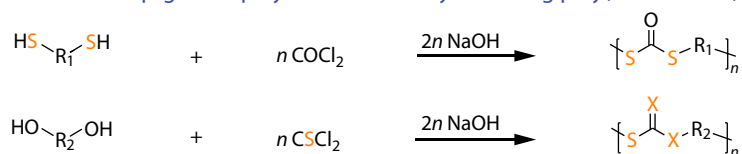
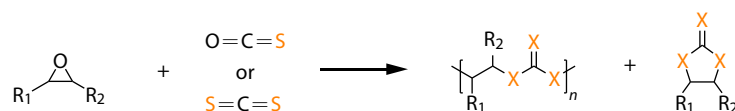
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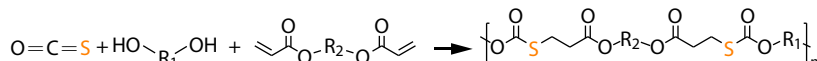
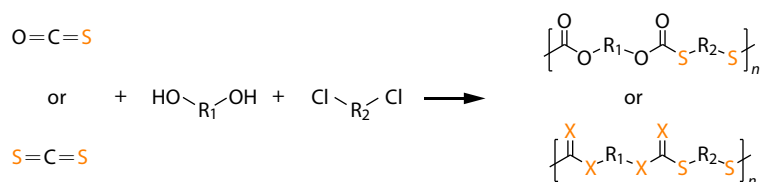
Invited Research Article for the Special Topic of “Depolymerizable Polymers”

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a. Common step-growth polymerization for synthesizing poly(thiocarbonates)

b. Chain copolymerization of COS (CS₂) and epoxides

c. Step-growth polymerization of diols, COS, and diacrylates

d. Step-growth polymerization of diols, COS (CS₂), and dichlorides (this work)

- General method
- Readily available monomers
- Desired properties
- Simple polymerization conditions
- Scalability
- High efficiency

Fig. 1 Strategies for the synthesis of poly(thiocarbonate)s.

cyclic (thio)carbonates, and oxygen-sulfur exchange reaction (O—S ER) has been demonstrated by researchers, including Darensbourg,^[24,25] Werner,^[26] Plajer,^[27,28] Buchard,^[29] our group,^[30–33] and others (route b in Fig. 1). The synthesis of poly(thiocarbonate)s *via* the chain growth copolymerization of carbonyl sulfide (COS) and epoxides (route b in Fig. 1) was first reported by our group.^[34–38] Nevertheless, these synthetic methods are still limited by the formation of cyclic (thio)carbonates, which can only introduce identical spacer groups on both sides of the thiocarbonate moiety, and the tunability of the distribution density of thiocarbonate groups along the polymer backbone is limited by the available types of epoxide monomers, resulting in a uniform polymer backbone structure. Recently, Hu *et al.*^[39] reported multicomponent tandem polymerization using CS₂, dithiols, and alkyl dihalides as monomers, enabling the synthesis of poly(trithiocarbonate)s with systematically tunable structures, as well as high molecular weights and yields. In 2023, we discovered that COS can bridge diacrylates and diols to undergo a step-growth polymerization reaction (route c in Fig. 1).^[40–42] In this process, the thiocarbonate anion generated from the reaction between the diol and COS acts as a nucleophile, attacking the double bond of the diacrylate and thereby affording poly(ester-thiocarbonate) through a nucleophilic addition process. The resulting polymers possessed both thiocarbonate and ester linkages in the main chain, providing structural diversity and tunability.

Herein, we describe the step-growth polymerization of COS, diols, and dichlorides to yield a series of poly(thiocarbonate)s (route d in Fig. 1). Based on the nucleophilicity of the

thiocarbonate anion formed by the reaction of alcohols and COS in the presence of an organic base, a nucleophilic substitution reaction can be achieved in the presence of dichlorides. The resulting polymers contained only thiocarbonate linkages as functional groups in the main chain, enabling the construction of poly(monothiocarbonate)s directly from COS. As expected, originating from the in-chain thiocarbonate group, the obtained polymers possessed degradability and exhibited exceptional mechanical properties comparable to commodity HDPE with a low density of in-chain thiocarbonate polar groups. In addition, this synthetic method could be extended to CS₂ (route d in Fig. 1). Diols and dihalides are common and diverse chemicals used in industry. COS is regarded as an industrial waste gas, is produced in large quantities from abundant carbon monoxide and elemental sulfur, and is widely used as a fumigant for grain storage.^[43] Its flammability and toxicity upon inhalation pose significant challenges for its transportation and storage. In recent years, COS has emerged as a promising monomer for the synthesis of sulfur-containing polymers.^[36,37,44,45] Meanwhile, CS₂ is an inexpensive and widely used chemical, with an annual global production of approximately 2 million tons, and is industrially synthesized from readily available sulfur and carbon.^[46] From both environmental and polymer science perspectives, the utilization of COS and CS₂ as monomers for the production of high-performance sulfur-containing polymers is of considerable significance. In this study, we regulated the polymer structure more arbitrarily (route d). The method is highly efficient, facile, scalable, can be performed under mild polymerization conditions, and uses readily available monomers.

EXPERIMENTAL

General Considerations

^1H - and ^{13}C -nuclear magnetic resonance spectroscopy (NMR) spectra were recorded using a Bruker Advance DMX 400 MHz spectrometer. Chemical shift values were referenced to the solvent signal (residual proton resonances for ^1H -NMR spectra and carbon resonances for ^{13}C -NMR spectra).

The molar mass and polydispersity of the polymers were measured by gel permeation chromatography (GPC) at 35 °C using a Waters 1515 isocratic pump, a model 2414 differential refractometer GPC instrument with trichloromethane (CHCl_3) as the mobile phase, and Waters Styragel HR3 and HR4 7.8×300 mm columns. The flow rate of CHCl_3 was 1.0 mL/min. Linear polystyrene polymers with narrow molar mass distributions were used as the standards to calibrate the apparatus.

The decomposition temperatures (T_d) of the polymers were determined using a TA Q50 instrument (TA Instruments). The sample was heated from 40 °C to 600 °C at a rate of 10 °C/min under nitrogen atmosphere. The temperature at which the mass loss was 5% was considered as $T_{d,5\%}$.

Differential scanning calorimetry (DSC) measurements of polymers were carried out on a TA Q200 instrument at a heating/cooling rate of 10 °C/min. The data reported were from the second heating cycle.

Wide-angle X-ray scattering diffraction (WAXD) measurements were performed using a Rigaku Ultima IV instrument.

Tensile tests were performed on an Instron 3343 instrument at a crosshead speed of 20 mm/min on the compression-molded tensile testing specimens. Extension-to-break tests were performed with three replicates per material to report the average values and standard deviations for each set.

Polymerization Experimental Procedure

Polymerization of 1,10-decanediol, COS and 1,10-dichlorodecane

A 10 mL autoclave with magnetic stirrer was first dried in an oven at 110 °C overnight, then immediately placed into the glovebox chamber. After being kept under vacuum for 1–2 h, the reaction vessel was moved into a glovebox under a nitrogen atmosphere. 1,10-Decanediol (0.35 g, 2.0 mmol, 1.0 equiv.) was added to the reactor. 1,10-Dichlorodecane (0.42 mL, 2.0 mmol, 1.0 equiv.) was then added into the vessel. After that, catalyst, for example, DBU (0.66 mL, 4.4 mmol, 2.2 equiv.) and DMF (1.0 mL) was added into the reactor. The reactor was sealed and charged with set amounts of COS (0.27 g, 4.4 mmol, 2.2 equiv.). The reaction was carried out at 90 °C for 24 h. Subsequently, the reactor was cooled in an ice-water bath. The residual gas was then vented slowly. The crude product was quenched with HCl in ethanol (1 mol/L). The crude product was dissolved in CHCl_3 and precipitated using cold ethanol. The product was collected via centrifugation and dried under vacuum at 45 °C until a constant weight.

Polymerization of 1,10-decanediol, CS_2 and 1,10-dichlorodecane

A 10 mL pressure-resistant glass tube equipped with a magnetic stir bar was dried overnight in an oven at 110 °C and then promptly transferred to a glovebox. After standing under vacuum for 1–2 h, the reaction vessel was moved into a glovebox

under a nitrogen atmosphere. Subsequently, 1,10-decanediol (0.35 g, 2.0 mmol, 1.0 equiv.) and 1,10-dichlorodecane (0.42 mL, 2.0 mmol, 1.0 equiv.) were added to the pressure tube in sequence, followed by the addition of DBU (0.66 mL, 4.4 mmol, 2.2 equiv.), DMF solvent (1.0 mL), and CS_2 (0.24 mL, 4.0 mmol, 2.0 equiv.). The tube was then sealed and the reaction was carried out at 60 °C for 5 h. Upon completion, the tube was cooled in an ice-water bath, and the residual gas was slowly released. The crude product was quenched with a 1 mol/L ethanolic hydrochloric acid solution, dissolved in chloroform, and precipitated in cold ethanol. The product was finally collected via filtration and dried under vacuum at 45 °C to constant weight.

RESULTS AND DISCUSSION

Diols-COS-dichlorides Polymerization

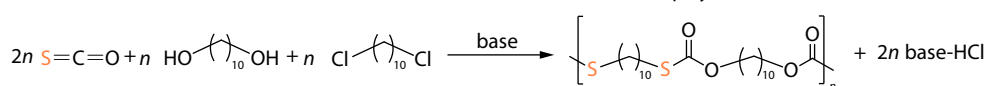
A variety of diols and dichlorides with different carbon numbers were used. The nine diols used were 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, 1,10-decanediol, 1,12-dodecanediol, 1,14-tetradecanediol, 1,18-octadecanediol, 1,20-eicosanediol, and 1,22-docosanediol. The four dichlorides used were 1,3-dichloropropane, 1,4-dichlorobutane, 1,6-dichlorohexane, and 1,10-dichlorodecane. All monomers were commercially available and used as purchased without purification.

We first examined the step polymerizations of 1,10-decanediol, COS and 1,10-dichlorodecane, as model reactions under various conditions. A range of commercially available basic catalysts have been used for this reaction, including organic bases such as 1,8-diazabicyclo[5.4.0]undecane-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), as well as inorganic bases such as K_2CO_3 , Cs_2CO_3 , NaH_2PO_4 , Na_2HPO_4 , and Na_3PO_4 .

To determine the optimal reaction conditions, 1,10-decanediol and 1,10-dichlorodecane were allowed to react with COS under various reaction conditions, and the results are shown in Table 1. Compared to the results from 60, 80 and 100 °C (Table 1, entries 14–16 and 17), the molecular weight and polymer polydispersity index were the optimal at 90 °C in 1 mL of DMF within 24 h, thus generating the poly(thiocarbonate) **P7** with a number-average molecular weight (M_n) of 21.5 kDa and a polydispersity index ($\mathcal{D}$) of 3.2 (Table 1, entry 11).

In addition, M_n of poly(thiocarbonate) was highly dependent on the solvent. In the case of tetrahydrofuran, toluene, and acetonitrile, M_n of the poly(thiocarbonate)s was relatively low, only 2.4–3.3 kDa (Table 1, entries 18–20). A similar solvent dependence was observed in the cycloaddition reaction of CO_2 with 1,3-diols.^[47,48] High polar solvents such as DMF, DMSO, and NMP had better polymerization effects (Table 1, entries 11, 21, and 22). It seemed that the higher polarity of the solvent was beneficial to the formation of poly(thiocarbonate)s. On this basis, one hypothesis could be that high-polarity solvents were conducive to the dissolution of polymers, which resulted in the improvement of molecular weight. Similarly, in the absence of solvent, the M_n of the polymer was only 4.8 kDa (Table 1, entry 23). Furthermore, the monomer concentration also affects the M_n of the polymer. The optimal monomer concentration was 2 mol/L (Table 1, entries 6 and 11–13).

No poly(thiocarbonate)s were detected when inorganic base catalysts were used (Table 1, entries 1–5), probably be-

Table 1 1,10-Decanediol, COS, and 1,10-dichlorodecane polymerization.^a

Entry	Catalyst (equiv.)		Solvent (mL)		<i>T</i> (°C)	<i>t</i> (h)	<i>M</i> _n ^b (kDa)	<i>Đ</i> ^b
1	K ₂ CO ₃	2.2	ACN	2	60	16	—	—
2	Cs ₂ CO ₃	2.2	ACN	2	60	16	—	—
3	NaH ₂ PO ₄	2.2	ACN	2	60	16	—	—
4	Na ₂ HPO ₄	1.1	ACN	2	60	16	—	—
5	Na ₃ PO ₄	0.7	ACN	2	60	16	—	—
6	DBU	2.2	DMF	2	90	24	13.3	2.6
7	DBN	2.2	DMF	2	90	24	5.2	2.6
8	TBD	2.2	DMF	2	90	24	3.3	3.0
9	DBU	2.0	DMF	2	90	24	12.2	2.3
10	DBU	1.6	DMF	2	90	24	5.0	2.0
11	DBU	2.2	DMF	1	90	24	21.5	3.2
12	DBU	2.2	DMF	3	90	24	23.8	3.5
13	DBU	2.2	DMF	4	90	24	10.5	4.4
14	DBN	2.2	DMF	2	60	16	5.6	2.8
15	DBN	2.2	DMF	2	90	16	9.2	3.8
16	DBU	2.2	DMF	1	80	24	10.5	4.2
17	DBU	2.2	DMF	1	100	24	2.2	2.2
18	DBU	2.2	toluene	2	60	16	2.4	3.3
19	DBU	2.2	THF	2	60	16	3.4	2.8
20	DBU	2.2	ACN	2	60	16	3.3	3.2
21	DBU	2.2	DMSO	1	90	24	11.1	3.1
22	DBU	2.2	NMP	1	90	24	11.2	2.5
23	DBU	2.2	—	—	90	24	4.8	3.1

^a Reaction conditions: [1,10-decanediol]:[1,10-dichlorodecane]:[COS] = 1:1:2.2 = 1:1:2.2. ^b Number-average molecular weight (*M_n*) and polydispersity index (*Đ* = *M_w*/*M_n*) determined by GPC in CHCl₃ at 35 °C using linear polystyrene standards.

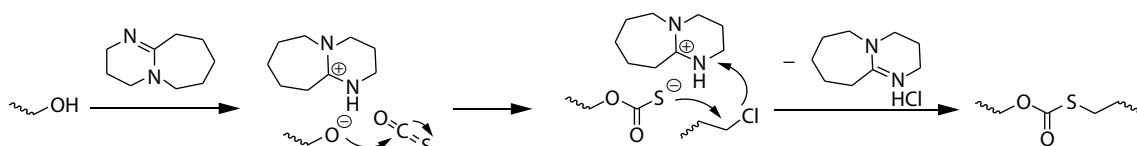
cause of the release of CO₂ from the combination of carbonate and hydrochloric acid. Gnanou *et al.*^[49] reported Cs₂CO₃-promoted polycondensation of CO₂ with diols and dihalides for the synthesis of miscellaneous polycarbonates. However, carbonate is unsuitable for catalyzing the diol-COS-dihalides reaction. As for phosphates, their insufficient basicity may hinder the effective activation of diols or COS, and their poor solubility, potential side reactions with COS, as well as the steric hindrance and structural rigidity of phosphate anions, may all contribute to their failure to form effective intermediates. DBU, DBN, and TBD are common organic-based catalysts. These organic bases were found to effectively increase the catalytic activity for the diol-COS-dichloride reaction, thus generating the corresponding poly(thiocarbonate)s in good to excellent yields. DBU showed superior catalytic performance (Table 1, entries 6–8).

We further investigated the role of organic bases in the reaction. When a substoichiometric amount of DBU was used, a lower molecular weight was detected (Table 1, entries 6, 9, and 10). In particular, when the DBU amount was below 2.0 equiv., the *M_n* dropped sharply from 13.3 kDa at 2.2 equiv. of DBU to 5.0 kDa at 1.6 equiv. (Table 1, entries 6 and 10). This

suggests that DBU is more likely to participate in the reaction as a reactant rather than as a catalyst. DBU was combined with the removed hydrochloric acid to regulate the acid-base environment of the reaction system.

Based on these results, a plausible reaction pathway for the formation of poly(thiocarbonate)s is shown in Fig. 2. In the initial step, the base DBU interacts with the alcohol and enhances the nucleophilicity of the oxygen atom, which subsequently reacts with COS to selectively produce the thiocarbonate anion. The thiocarbonate anion undergoes a nucleophilic substitution reaction with chloride to form a monothiocarbonate linkage. Meanwhile, HCl generated during nucleophilic substitution reacts with DBU to form a DBU-HCl salt. Thus, DBU not only activated the alcohol for nucleophilic attack but also acted as an acid acceptor.

With the optimal conditions in hand, the substrate scope of the reaction was investigated, and the results are summarized in Fig. 3. The diols and dichlorides are commercially available. All substrates successfully produced the corresponding poly(monothiocarbonate)s. With these diols and dichlorides, we synthesized polymers **P1–P15** with *M_n* of 1.9–27.7 kDa and *Đ* of 1.4–4.1, in the presence of DBU as the

**Fig. 2** A plausible reaction pathway to the generation of thiocarbonate in the presence of DBU.

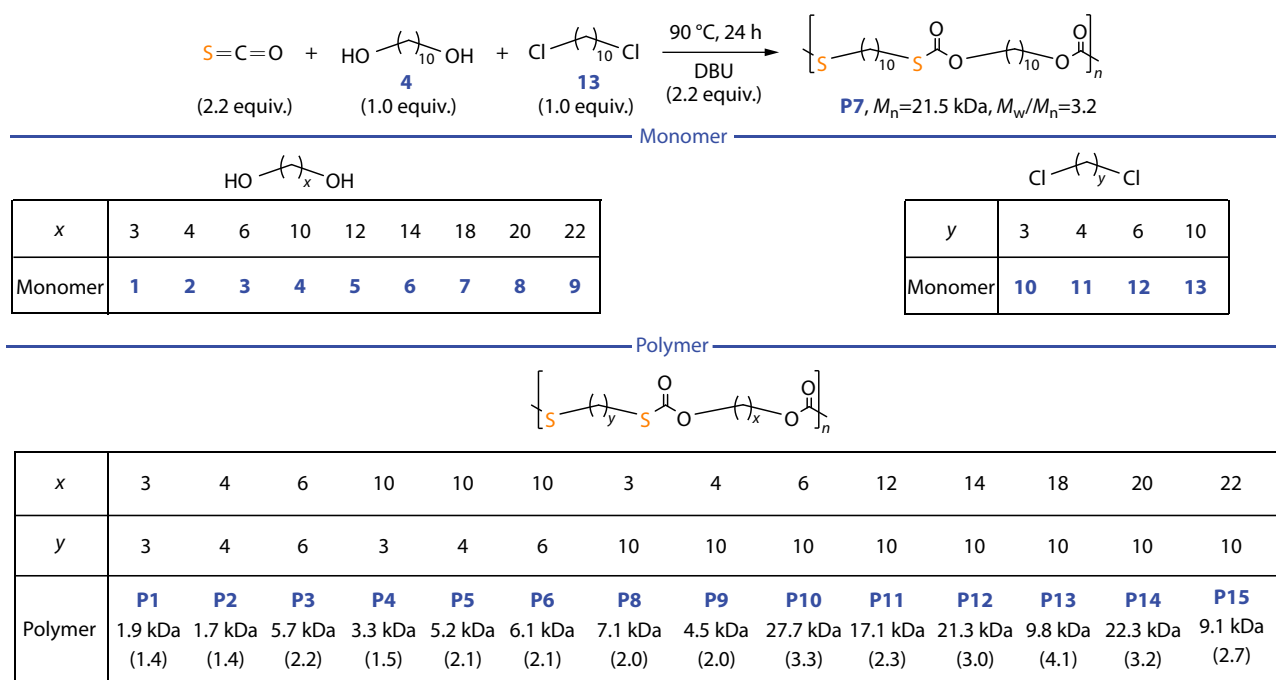


Fig. 3 Polymers are synthesized from diols, dihalides, and COS. M_n and $\bar{D}$ values are determined by GPC in CHCl_3 , calibrated with polystyrene standards. NMR spectra and GPC curves of the obtained polymers are shown in Figs. S1–S38 (in the electronic supplementary information, ESI).

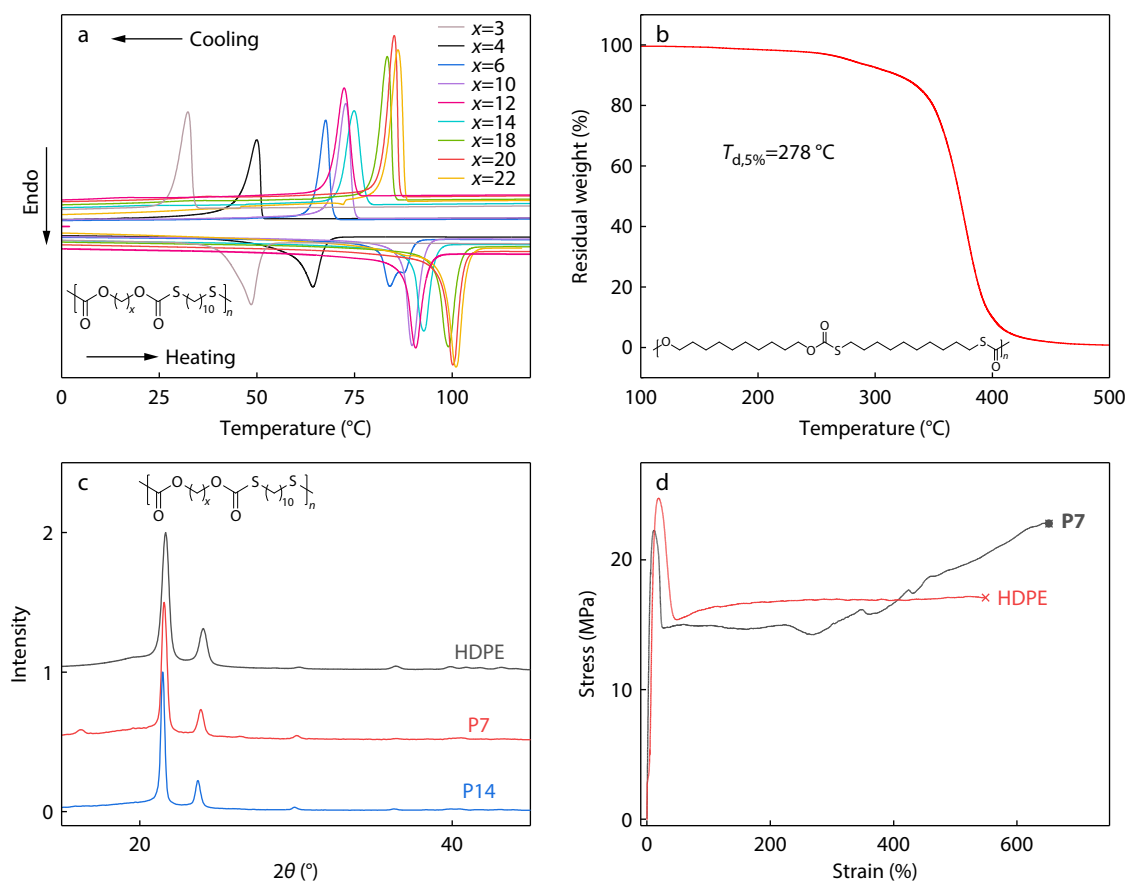
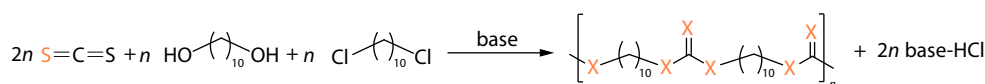


Fig. 4 (a) DSC curves of **P7–P15**. (b) TGA curve of **P7**. (c) WAXD patterns of **P7**, **P14** and HDPE. (d) **P7** exhibits high tensile strength comparable to HDPE.

Table 2 1,10-Decanediol, CS₂, and 1,10-dichlorodecane polymerization.^a

Entry	Solvent	T (°C)	t (h)	[OSS]:[SOS]: [SSS]:[OOS] ^b	M _n ^c (kDa)	Đ ^c
1	DMF	90	23	0:10:14:3	8.7	2.6
2	DMF	60	4	9:1:10:1	7.7	2.2
3	DMF	60	5	20:4:18:3	18.5	1.8
4	DMF	80	5	3:13:10:2	37.9	2.0
5 ^d	DMF	60	5	10:0:13:1	22.8	1.8
6	ACN	60	17	20:16:20:3	27.3	1.6
7	DMSO	60	17	13:20:20:3	22.0	1.7
8 ^d	DMF	90	5	0:8:10:1	—	—
9	DMF	60	23	3:7:6:1	44.3	3.1
10 ^d	ACN	60	5	14:0:6:1	33.2	2.6
11	DMF	70	5	12:8:17:3	4.9	4.7
12	ACN	60	5	11:0:4:1	2.9	4.3
13 ^e	DMF	60	5	17:0:14:1	3.2	5.0
14 ^f	DMF	90	23	0:8:7:1	—	—
15	DMF	RT	—	20:0:5:1	3.0	3.9
16	DMF	40	18	25:0:11:2	3.4	4.7
17 ^g	DMF	60	5	25:0:25:4	3.3	4.6

^a Reaction conditions: [Diol]:CS₂:[Dihalide]:DBU = 1:2:1:2.2, [Diol] = 1 mol/L. ^b [OSS]:[SOS]:[SSS]:[OOS] ratios determined by ¹H-NMR analysis of the products. ^c M_n and Đ determined by GPC in CHCl₃ at 35 °C using linear polystyrene standards. ^d [Diol]:CS₂:[Dihalide]:DBU = 1:2.2:1:2.2. ^e [Diol]:CS₂:[Dihalide]:DBU = 1:4:1:2.2. ^f catalyst is DBN. ^g [Diol]:CS₂:[Dihalide]:DBU = 1:2:1:2. NMR spectra and GPC curves of the obtained polymers are shown in Figs. S67–S83 in ESI.

merization of diols, CS₂, and dihalides. During this process, the oxygen-sulfur exchange reaction (O—S ER) occurs. Using the reaction of 1,10-decanediol, CS₂, and 1,10-dichlorodecane as an example, the resulting polythiocarbonate contained four types of repeating units: (—O(C=S)S—), (—S(C=O)S—), (—S(C=S)S—), and (—O(C=O)S—), which are denoted as [OSS], [SOS], [SSS], and [OOS], respectively. The polymer structure and molecular weight were influenced by the reaction conditions. To systematically investigate the effects of various parameters (temperature, reaction time, catalyst, and solvent) on the polymerization outcome, a detailed study was conducted. The results are presented in Table 2.

First, the effect of temperature on the polymerizations of 1,10-decanediol, CS₂, and 1,10-dichlorodecane was investigated. As shown in entries 3, 5, 12, and 13 of Table 2, when the reaction was conducted at 60 °C for 5 h, the main repeating units of the resulting polythiocarbonate were [OSS] and [SSS], regardless of variations in monomer ratio or solvent type. This result indicates that the solvent and monomer ratio have minimal influence on the polymer structure, which is further supported by the comparison of entries 5 and 10, 6 and 7, as well as 3, 12, and 13.

A more detailed analysis of the polymer structures obtained at different temperatures revealed the following: at 80 °C and above, [SOS] and [SSS] were the dominant structures (Table 2, entries 1, 4, 8, and 14). Under the reaction conditions of 70 °C (Table 2, entry 11), the main repeating units were [OSS], [SOS], and [SSS], indicating a more pronounced O—S ER at this temperature, resulting in a more complex polymer structure. When the temperature was 60 °C or below, the polythiocarbonate consists mainly of [OSS] and [SSS] units (Table 2, entries 15 and 16). These results demonstrate that temperature regulation can serve as an effective method for

controlling the structural composition of polymers.

According to the results shown in entries 6 and 12, as well as entries 2, 3, and 9 in Table 2, the reaction time also influences the polymer structure. At a reaction temperature of 60 °C, the polymer structure exhibited minimal changes over shorter reaction times (such as 4 or 5 h), with [OSS] and [SSS] being the predominant repeating units. However, as the reaction time was extended to 15 h or longer, the proportion of [SOS] units in the polymer increased significantly, indicating that the O—S ER became more pronounced with prolonged reaction time. At higher reaction temperature conditions (90 °C, Table 2, entries 1 and 8), the effect of reaction time on polymer structure was relatively minor, with temperature acting as the dominant factor. Therefore, it can be concluded that at lower temperatures, the reaction time plays a more significant role in modulating the polymer structure, whereas at elevated temperatures, the temperature becomes the primary influencing factor.

The effects of different organic base catalysts (DBU and DBN) on polymerization were also investigated. The results indicated that the type of organic base had little effect on the polymer structure but significantly influenced the molecular weight of the resulting polymer (Table 2, entries 1 and 14). Notably, the polymer obtained in entry 14 possessed a high molecular weight and strong crystallinity, making it difficult to dissolve completely in the solvent. Thus, its molecular weight could not be accurately determined. In addition, the influence of the amount of the DBU catalyst on the reaction was studied. The results show that when the amount of DBU was less than 2.2 equiv., the molecular weight of the polymer decreased significantly: for example, when 2.2 equiv. of DBU were used, the polymer had a M_n of 18.5 kDa (Table 2, entry 3), while reducing the DBU amount to 2.0 equiv. resulted in a M_n of only 3.3 kDa (Table 2, entry 17). These results further confirm that DBU not only acts as a catalyst, but also serves as

a proton acceptor, binding with the HCl generated during the nucleophilic substitution process to form a DBU-HCl salt, thereby facilitating the progress of the reaction. This reaction mechanism is consistent with that observed for the nucleophilic substitution process during the polymerization of diols, COS, and dihalides.

In this study, the observed O—S ER occurred during step-growth polymerization involving CS₂. Previously reported mechanisms of O—S ER associated with CS₂ have been described in the context of chain-growth polymerization.^[24,52] Therefore, there may be mechanistic differences between the two processes, although certain similarities may also exist. The proposed mechanism is as follows. The intermediate formed by the reaction of an alcohol with CS₂ readily undergoes decarboxylation in the presence of an organic base (particularly at high base concentrations), generating intermediates such as COS, CO₂, and thiols. These intermediates can

then participate in cross-polymerization reactions, ultimately leading to the occurrence of the O—S ER. There is much more to discover about this, about these reactions.

The polymer obtained in entry 4 of Table 2 exhibited σ_B of 20.2 MPa and ε_B of 606% (Figs. 6e, S84 and S85 in ESI), demonstrating excellent mechanical properties. All of the resulting polythiocarbonates were crystalline polymers. To characterize their thermal stability and crystallinity, TGA and DSC analyses were conducted on the polymers with three different structural types. The results are as follows: the polymer with [SOS] and [SSS] as the main repeating units exhibited $T_{d,5\%}$ of 230 °C and T_m of 91 °C (Figs. 6d and 6c); the polymer with [OSS] and [SSS] as the main repeating units showed $T_{d,5\%}$ of 160 °C and T_m of 64 °C (Fig. 6d and 6a); and the polymer with [SOS], [OSS], and [SSS] as the main repeating units had $T_{d,5\%}$ of 198 °C and T_m of 68 °C (Fig. 6d and 6b). These results

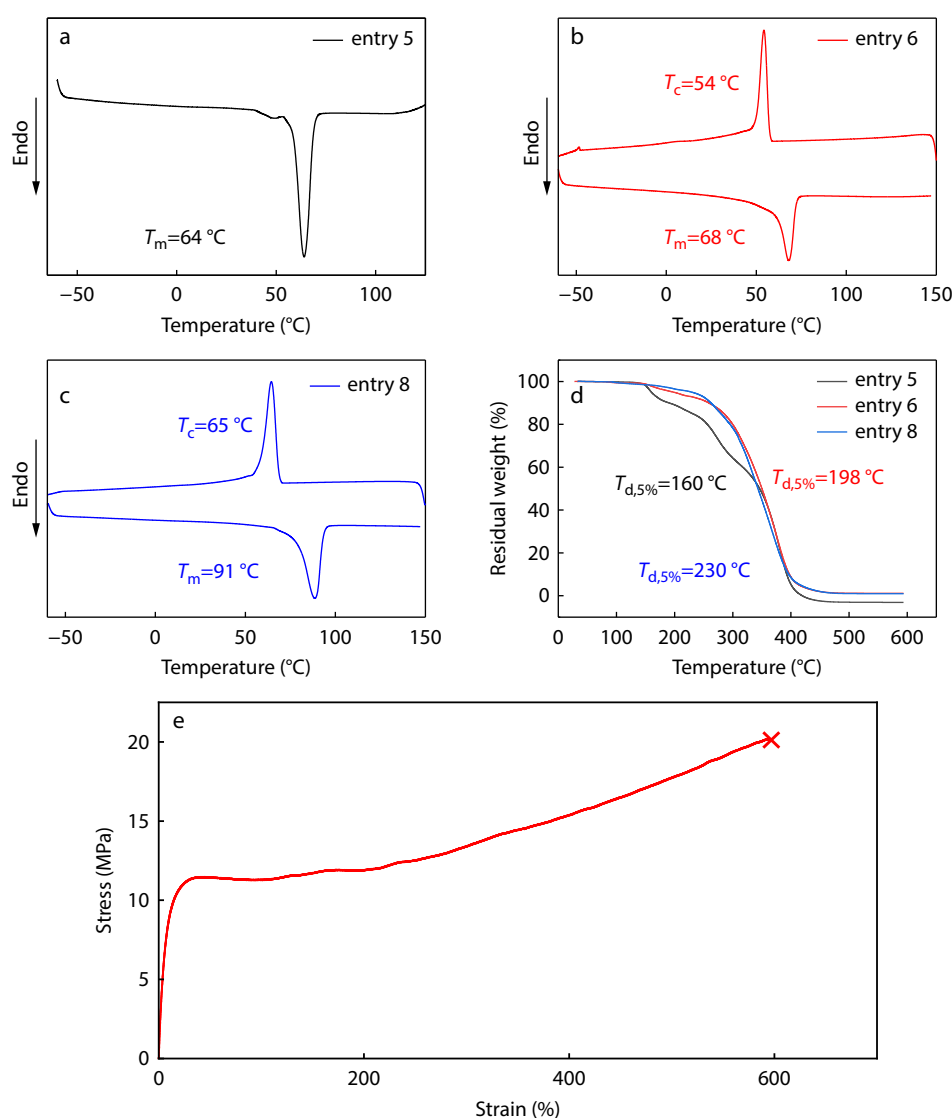


Fig. 6 (a) DSC curve of the polymer in Table 2, entry 5 (with [OSS] and [SSS] as the main structures); (b) DSC curve of the polymer in Table 2, entry 6 (with [SOS], [OSS] and [SSS] as the main structures); (c) DSC curve of the polymer in Table 2, entry 8 (with [SOS] and [SSS] as the main structures); (d) TGA curves of the polymer in Table 2, entries 5, 6 and 8; (e) Stress-strain curve of the polymerization product of 1,10-decanediol, CS₂, and 1,10-dichlorodecane (Table 2, entry 4).

indicate that a higher proportion of [SOS] and [SSS] repeating units in the polymer leads to improved thermal stability and crystallinity. This may be attributed to the fact that both the [SOS] and [SSS] structures are highly symmetric functional groups, which promote greater regularity in the polymer chains, thereby enhancing the crystallization ability and thermal stability of the polymer. Therefore, in the step-growth polymerization of diols, CS_2 and dihalides, the polymer structure and properties can be regulated by controlling the reaction conditions and utilizing the O—S ER. This type of reaction is vital for the efficient and facile synthesis of sulfur-containing polymers. Further studies on this type of reaction are underway in our group.

CONCLUSIONS

We demonstrated a new step-growth polymerization of COS (CS_2), diols, and dichlorides. This method uses readily available monomers of COS (CS_2), diols and dihalides, which is efficient, convenient, and scalable. The step-growth polymerization of COS, diols, and dichlorides catalyzed by organic bases efficiently yields structurally diverse poly(monothiocarbonate)s, with no chain units resulting from the O—S ER detected. When long-chain linear diols and dichlorides (such as 1,10-decanediol and 1,10-dichlorodecane) were used as monomers, the resulting polymers exhibited excellent mechanical properties comparable to those of commercial HDPE. This is attributed to the low-density thiocarbonate groups in the polymer backbone, which allow the long alkyl chains to crystallize in a manner similar to polyethylene. Furthermore, the obtained poly(monothiocarbonate)s could be chemically degraded *via* alcoholysis to yield small diol and dithiol molecules. In contrast, the step-growth polymerization of CS_2 , diols, and dichlorides catalyzed by organic bases is accompanied by an unavoidable O—S ER. By developing strategies that utilize this O—S ER, it is possible to obtain polythiocarbonates with diverse sequence structures and tunable properties. Using the polymerization of 1,10-decanediol, CS_2 , and 1,10-dichlorodecane as model system, we systematically investigated the effects of temperature, reaction time, catalyst type, and catalyst loading on polymer structure and molecular weight. Polymers with [SOS] and [SSS] as the main repeating units exhibited higher thermal stability and crystallinity. Synthetic methods have the advantages of high efficiency, facile synthesis, adjustable structure, and being carried out under mild conditions. The produced polymers are expected to become green materials with large raw material scale, easy synthesis, wide application, and excellent performance.

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/s10118-025-3392-9>.

Data Availability Statement

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

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