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Research Article

Non-Isocyanate and Catalyst-Free Synthesis of a Recyclable Polythiourethane with Cyclic Structure

Shuang Wu, Ming Luo,* Donald J. Darensbourg,* Dandan Zeng, Yuhua Yao, Xiaobing Zuo, Xin Hu, and Dawei Tan

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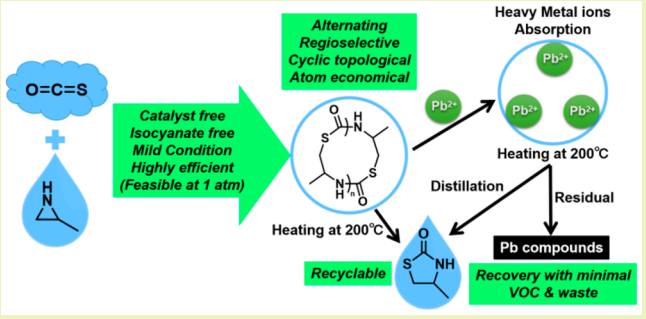
ABSTRACT: Polythiourethane is a promising heteroatom-containing polymeric material possessing outstanding properties such as high refractive index, biocompatibility, and good coordinating ability to heavy metal ions. However, examples of versatile polythiourethanes are relatively scarce as a result of the limited methods for their synthesis. Herein, we report an efficient non-isocyanate and catalyst-free strategy to synthesize polythiourethane from the highly alternating and regioselective copolymerization of carbonyl sulfide (COS) and 2-methyl aziridine. The copolymerization proceeded efficiently at room temperature and afforded copolymer in 95% selectivity and molecular weight of 15.2 kg/mol in 2 h. Furthermore, the reaction was efficient even at 1 atm of COS at room temperature. Remarkably, the copolymer possessed a cyclic topology, and it could be completely recycled into cyclic thiourethane by simply heating the bulk materials at 200 °C for 1.5 h. The copolymer was applied as a heavy metal absorption and recovery agent; lead ions in aqueous solution were adsorbed by the copolymer, and both were eventually separated and recovered in the form of lead compounds and cyclic thiourethanes, respectively. Hence, this study provides a sustainable and atom-economical method for synthesizing polythiourethane and a green method to recover hazardous metals with minimal waste and VOC emission.



KEYWORDS: *Cyclic polymer, Recyclable polymer, Carbonyl sulfide, Aziridine, Heavy metal recovery*

INTRODUCTION

Introducing heteroatoms (such as sulfur and nitrogen) into polymer structures, depending on the kind of functional groups, can endow enhanced or special characteristics to the materials. These include enhanced thermal and mechanical properties such as higher toughness and thermal stability,[1−4] metal absorption capability,[5−7] self-healing or reprocessable abilities,[7−10] and crystalline and optical properties.[11−21] Polythiourethanes are typical heteroatom-containing polymers containing both sulfur and nitrogen atoms in their structures. Unlike their oxygen analogue polyurethanes, detailed studies related to the synthesis of polythiourethanes are relatively scarce.[22−35] In fact, polythiourethanes find their utilization in optical materials, coatings, and medical technology because of their enhanced properties such as refractive index, adhesive strength, biocompatibility, and mechanical characteristics.[22−24] Polythiourethanes can be synthesized by a type of base-catalyzed nucleophilic addition of dithiols to diisocyanates (Scheme 1).[25−28] Obviously, the raw material dithiols and diisocyanates are very toxic and not always chemically stable. Alternatively, the polyaddition of bifunctional five-membered cyclic dithiocarbonates with diamines was also used to synthesize polythiourethane derivatives with thiol groups in the polymer chains (Scheme 1).[29−35] However, the *in situ* generated thiol groups always lead to the formation of cross-linked polymers by auto-oxidation cross-linking of thiols to form disulfide linkages, and thereby polythiourethanes with well-defined structures are unable to be achieved. Furthermore, the synthesis and purification of the cyclic dithiocarbonate monomers are elaborate.

Nitrogen-containing functional groups widely exist in natural products and bioactive compounds. Introducing nitrogen into polymeric structures during polymer synthesis is not always straightforward, but aziridines provide an efficient route to this end. Aziridines are a nitrogen analogue of epoxides and have a highly strained three-membered ring structure. Aziridines and their derivatives have been very useful intermediates in the preparation of a large variety of nitrogen-containing compounds and polymers such as oxazolidones, polyamines, poly(*β*-peptoid)s, and poly(urethane-amine)s.[36−58] However, unsubstituted aziridines are very nucleophilic, and when in

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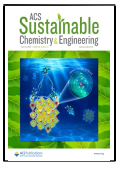
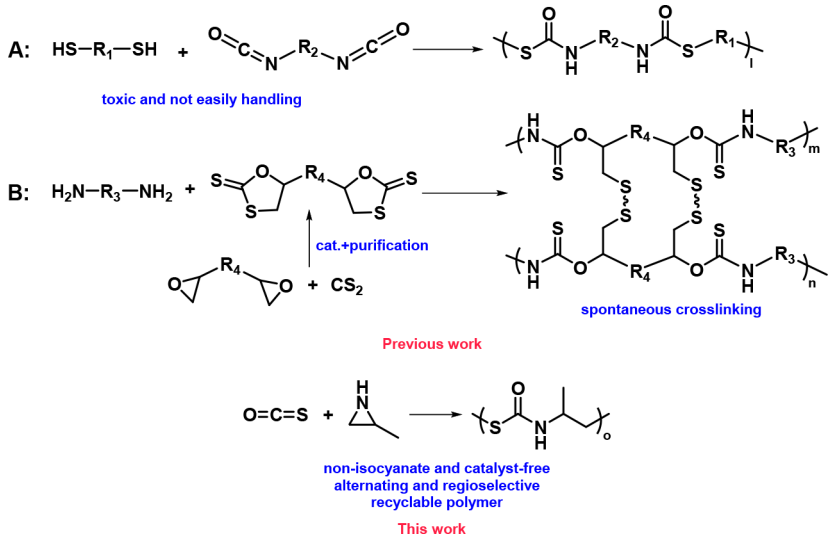
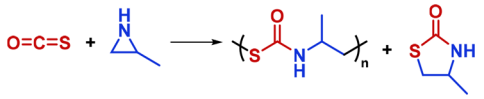


Scheme 1. Previously Reported Methods to Synthesize Polythiourethanes[a]



[a](A) Polyaddition of dithiols to diisocyanates. (B) Polyaddition of bifunctional cyclic dithiocarbonates with diamines. Bottom: copolymerization of COS and 2-methyl aziridine in this work.

Table 1. Catalyst-Free Copolymerization of COS and MeAz under Different Reaction Conditions



entry[a]	solvent	COS (MPa)	T (°C)	time (h)	conversion[b] (%)	copolymer selectivity[c] (%)	M_w[d] (kg/mol)	$Đ$[d] (M_w/M_n)
1		2	20	2	>99	71	11.7	1.91
2	THF	2	20	2	>99	95	15.2	1.68
3	DCM	2	20	2	>99	70	14.0	2.12
4	acetonitrile	2	20	2	>99	68	3.5	2.03
5	ethyl acetate	2	20	2	>99	78	4.1	2.11
6	toluene	2	20	2	>99	82	4.2	2.18
7	ethanol	2	20	2	>99	85	3.4	2.05
8	DMF	2	20	2	>99	52	4.4	2.30
9	DMAc	2	20	2	>99	43	3.4	2.23
10	THF	2	40	2	>99	94	14.0	1.95
11	THF	2	60	2	>99	86	14.4	2.10
12	THF	2	20	0.5	72	95	10.1	1.69
13	THF	2	20	1	88	95	12.1	1.86
14	THF	2	20	1.5	95	95	14.0	1.78
15	THF	1.5	20	2	>99	96	8.5	1.64
16	THF	1	20	2	>99	95	5.9	1.46
17	THF	1 atm	20	5 min	55	96	0.7	1.11

[a]Reactions were carried out in different solvents in a 10 mL autoclave; 0.3 mL of MeAz was added. [b]Conversion of MeAz, which was determined by ^{1}H NMR spectroscopy. The integral of the methane proton (1.78 ppm) of monomer (MeAz) and the total integral of the methane protons (3.81 and 3.86 ppm) of polymer and cyclic products were used to calculate the monomer conversion. The alternating structure of all the copolymers were determined by ^{1}H NMR spectroscopy. [c]Estimated on the basis of ^{1}H NMR spectroscopy. The copolymer selectivity is the molar ratio of the copolymer versus cyclic product. [d]M_w and $Đ$ were determined by GPC in DMF based on polystyrene standard samples.

polymer synthesis, electrophilic attacks of Lewis acids (or protons) on aziridine monomers will lead inevitably to branched chains or homopolymerized polyimine linkages. Most aziridine-involved polymerization systems focus on homopolymerization of substituted, functionalized aziridines, but the synthesis of aziridine-derived copolymers with highly alternating selectivity and high molecular weights is still a challenge and has been rarely reported.[48−51] For instance, aziridines were used to prepare aliphatic polyurethanes by copolymerization with carbon dioxide (CO_2); efforts have been made by employing various catalytic systems or supercritical CO_2, but as far as we know, no fully alternating aziridine−CO_2 copolymers have been achieved.[52−58] Carbonyl sulfide (COS), a sulfur analogue of CO_2, is widely released from volcano eruptions and industrial processes. Excessive industrial activities cause the increase of COS's concentration in the atmosphere to become an aerial pollutant.[59] Recently, successful copolymerization of COS with epoxides has provided a variety of well-defined polymonothiocarbonates, indicating that COS is an excellent building block for synthesizing sulfur-containing polymers.[12−17,60−68] We expect to construct sulfur and nitrogen-containing polythiourethanes

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through the copolymerization of COS and aziridines (Scheme 1), and we speculate that the weaker acidity of COS compared to CO_2 may be beneficial to weaken the homopolymerization of aziridines and achieve well-defined and alternating aziridine−COS copolymer.

Inspired by our previous successful copolymerization of propylene oxide with COS,[16] we investigated the copolymerization of COS with 2-methyl aziridine (MeAz), which is the nitrogen analogue of propylene oxide. In this work, we report an efficient non-isocyanate and catalyst-free strategy to synthesize polythiourethane from the highly alternating and regioselective copolymerization of COS and MeAz. This process is very active and can proceed smoothly at room temperature even at just 1 atm of COS. The analysis of the detailed linkage structures suggests that the resulted copolymer has an alternating cyclic topology. To the best of our knowledge, this is the first example of COS-involved copolymerization feasible at only 1 atm and also the first COS-based cyclic polymer. The synthesized polythiourethane can be recyclable back into cyclic thiourethane upon heating at 200 °C for 1.5 h. Moreover, the thiourethane group endows the copolymer with sensitive and selective coordination with heavy metal ions such as mercury, lead, and cadmium ions. Herein, we have taken advantage of both the thermal depolymerization characteristics and metal binding ability of this polythiourethane to absorb and recover lead ions with minimal waste and VOC emission.

RESULTS AND DISCUSSION

Catalyst-Free Copolymerization of COS and MeAz. In order to examine the effectiveness of the spontaneous copolymerization of COS and MeAz, we first carried out the reaction without adding any catalysts or solvent at ambient temperature (entry 1, Table 1). MeAz was fully converted at 20 °C in 2 h, and the reaction was very efficient at providing a polythiourethane with a molecular weight (M_w) of 11.7 kg/mol with a polydispersity of 1.91. Both copolymer and cyclic product were observed, and the copolymer selectivity was 71% on the basis of the ^{1}H NMR spectrum of the crude product (Figure S1). This represents an excellent example of the selective and catalyst-free synthesis of a polythiourethane from COS and MeAz. Hence, in an effort to investigate factors affecting copolymer selectivity and molecular weight, the reactions were performed in common solvents such as tetrahydrofuran (THF), dichloromethane (DCM), acetonitrile, ethyl acetate, toluene, ethanol, *N*,*N*-dimethylformamide (DMF), and *N*,*N*-dimethylacetamide (DMAc) at ambient temperature. For the optimization of the solvent (entries 2−9 in Table 1), the pressure of COS was set at 2 MPa with a reaction time of 2 h. The reaction performed in THF exhibited an increase in both molecular weight and copolymer selectivity as compared to the results in solventless conditions, providing a copolymer in 95% selectivity (Figure S2) and M_w of 15.2 kg/mol with a polydispersity of 1.68. The molecular weight also increased when DCM was used (entry 3, Table 1) in comparison with solventless conditions, but it resulted in a slightly broader polydispersity and showed no increase in copolymer selectivity. The molecular weights of the copolymers significantly decreased when the other solvents were employed (entries 4−9, Table 1), and the copolymer selectivity was lower than that carried out in THF. We speculate that the positive effect of THF mainly comes from its relatively weak polarity. Actually, it is quite common that the polarity of solvents significantly affects the synthesis of nitrogen- and sulfur-containing five-membered ring compounds;[69] almost no cyclic products were produced in weakly polar solvents such as THF and tetrachloromethane. In contrast, high yields of cyclic products were obtained in strongly polar solvents such as ethanol and *t*-butanol.[69] Just as in this work, less polar THF and DCM exhibited better inhibition of the production of cyclic byproducts. The optimum solvent chosen was THF, and then, we investigated the effects of reaction temperature, time, and COS pressure on the reaction results. Upon increasing the reaction's temperature from 20 to 40 and 60 °C (entries 10 and 11), the copolymer selectivity decreased to 94% and 86%, respectively, with a slight decrease and fluctuation in molecular weights. The generation of more cyclic products indicated that the copolymer selectivity slightly decreased at higher temperatures. Therefore, the optimum reaction temperature was chosen as 20 °C. The conversion and molecular weight decreased along with the shortening of the reaction time (entries 12−14). MeAz was almost completely converted in 1.5 h; i.e., its conversion reached 95%, and the molecular weight was 14.0 kg/mol, indicating that this copolymerization could completely finish in a time between 1.5 and 2 h under these conditions. The pressure of COS also had a significant effect on the copolymerization; that is, the molecular weights sharply decreased when the pressure was set at 1 and 1.5 MPa, and other conditions remained unchanged (entries 15 and 16). Therefore, using THF as the solvent at 20 °C affords the optimum reaction condition for this copolymerization process. It is worth noting that the copolymerization of COS and MeAz showed remarkable activity even at only 1 atm of COS (entry 17). See the Supporting Information for experimental details and reaction process photos (Figure S20). The reaction was performed at 20 °C in THF in a flask; the viscosity of the system increased rapidly, and the solution became turbid with time. We ended the reaction after 5 min when the stirring bar was stopped by the viscous solution. The characterization of the crude product showed that this atmospheric copolymerization afforded a copolymer in a 96% selectivity with a molecular weight of 700 g/mol and a polydispersity of 1.11. As far as we are aware, this appears to be the first reported COS-involved copolymerization at 1 atm of COS and ambient temperature.

The main-chain sequence of the resulting copolymer was confirmed by ^{1}H and ^{13}C NMR spectroscopy (Figure 1). In the ^{1}H NMR spectrum of the afforded copolymer in DMSO-d_6, the resonance of the methine proton in the thiourethane linkage appeared at 3.81 ppm due to the electron-withdrawing effect of the nitrogen atom. Meanwhile, the resonance of the methylene proton in the thiourethane linkage appeared at 2.87 ppm. In addition, the proton signal of the N*H* groups was found downfield at 8.15 ppm, and all signals were assigned with the integration ratio being in accord with the protons' molar ratio. No other signals assignable to the imine linkage[57] (resulting from homopolymerization of MeAz) were observed, demonstrating that the copolymer possesses an alternating structure. To further validate the alternating structure of the copolymer, matrix assisted laser desorption ionization time-of-flight mass (MALDI-TOF-MS) spectrometry was employed to confirm the polymeric chain sequence. As shown in Figure S21, a group of high-intensity equidistant peaks of 1228.354, 1345.375, and 1462.404 m/z show a molecular mass interval of 117.02 m/z, which agree well with the molecular mass of the assumed repeating thiourethane unit. Accurate chain structure

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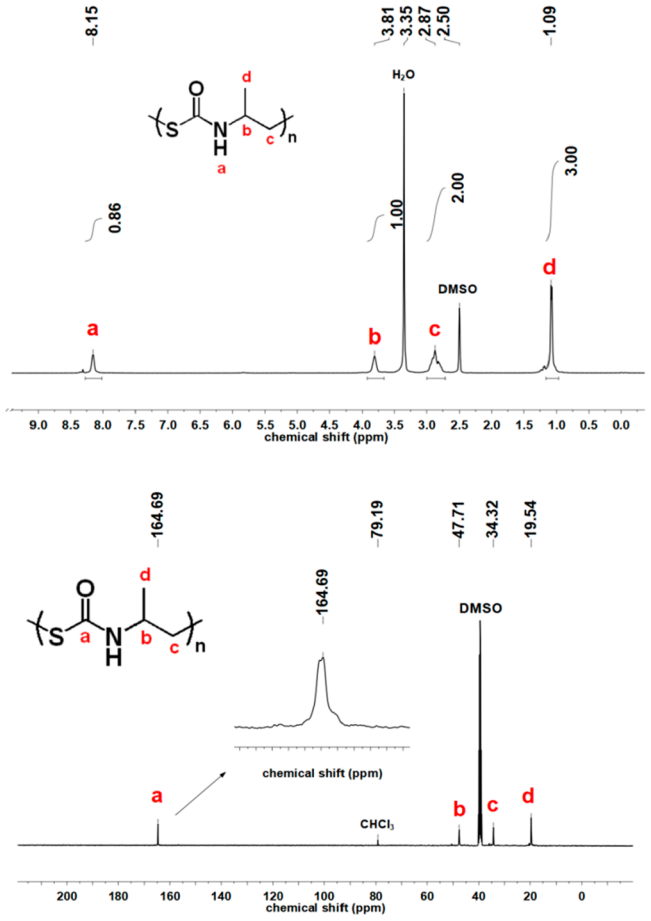
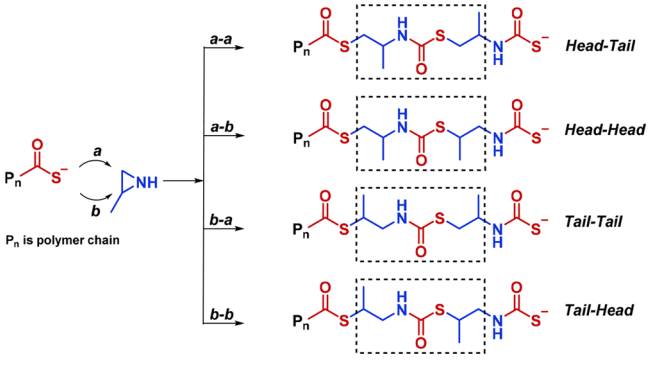


Figure 1. ^{1}H (top) and ^{13}C NMR (bottom) spectra (DMSO-d_6) of the product of entry 2 in Table 1.

analysis will be discussed later. The ^{13}C NMR (Figure 1) resonance of the methine carbon appeared at 47.71 ppm, and the signals of the methylene and methyl carbons were observed at 34.32 and 19.54 ppm, respectively. The carbon resonance of the carbonyl (C═O) was found downfield at 164.69 ppm.

As shown in Scheme 2, there are four possible different diad microstructures of the backbone of polythiourethane, head-to-tail, head-to-head, tail-to-head, and tail-to-tail. Because of the steric hindrance of the methyl group of MeAz, propagation predominantly occurred at the less hindered methylene carbon; thus, the sequential *a*−*a* attack led to the head-to-tail structure as the major product. This is evident from the

Scheme 2. Pathways for the Formation of Four Different Diad Microstructures



carbonyl region in the ^{13}C NMR spectrum of the copolymer (Figure 1), where the carbonyl carbon afforded a single peak signal, indicating that this copolymerization exhibited high regioselectivity in the formation of the polymer's structure. This high regioselectivity was also supported by ^{1}H NMR (Figure 1); as the thiourethane structure is asymmetric, the protons on the four possible different diad microstructures were in totally different chemical environments, and thus, their resonance signals would appear at different chemical shifts instead of the current concise ones.

The resulting copolymer exhibited relatively good solubility in common polar organic solvents, such as DMF, DMAc, and dimethyl sulfoxide at ambient temperature. However, the copolymer was found to be insoluble in DCM, THF, diethyl ether, methanol, ethanol, or water. The thermal properties of the copolymer (entry 2, Table 1) were measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), whose curves are shown in Figure 2. The

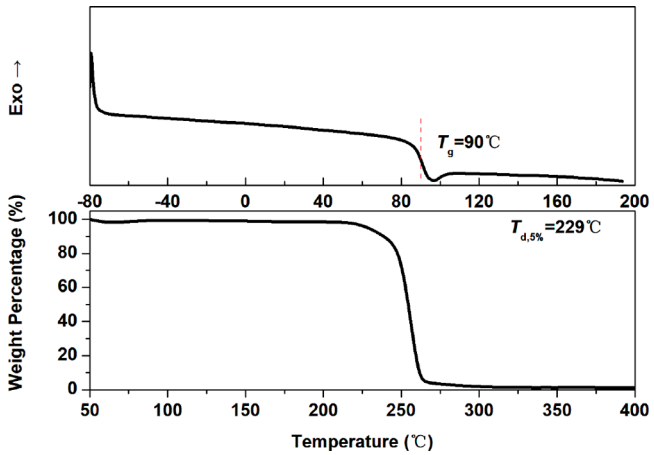


Figure 2. DSC (top) and TGA (bottom) curves of the COS−MeAz copolymer.

copolymer displayed an initial decomposition temperature at 5% weight loss ($T_{d,5\%}$) of 229 °C under a nitrogen atmosphere. The glass transition temperature (T_g) of the copolymer was found to be 90 °C from the second heating curve. The complete DSC curve is shown in Figure S23; a strong endothermic peak was observed around 170 °C on the first heating curve. First, we suspected that it was a melting peak, but no exothermic crystallization peak was observed on the cooling curve; meanwhile, no endothermic peak was observed around 170 °C on the second heating curve. We believe that this copolymer is amorphous instead of crystalline based on the DSC result, although the powder X-ray diffraction (XRD) (Figure S24) observation exhibited slight crystalline signs for the copolymer. These solubility and thermal properties are the result of a highly alternating polar thiourethane structure of this COS-based polythiourethane. These properties are quite different from those of the MeAz−CO_2 copolymer, which contained a high portion of imine linkages and exhibited thermally induced reversible transitions in water around the lower critical solution temperatures.[54]

Investigation of the Copolymerization Mechanism. The MALDI-TOF-MS spectrum (Figure 3) mainly consisted of two series of molecular ion peaks, which presumably correspond to two cyclic polythiourethanes with no chain ends. The group of red-labeled peaks corresponds to cyclic

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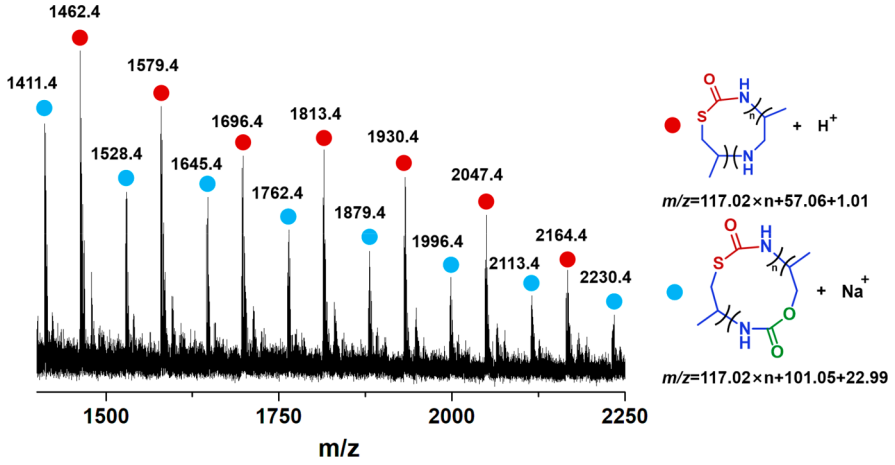
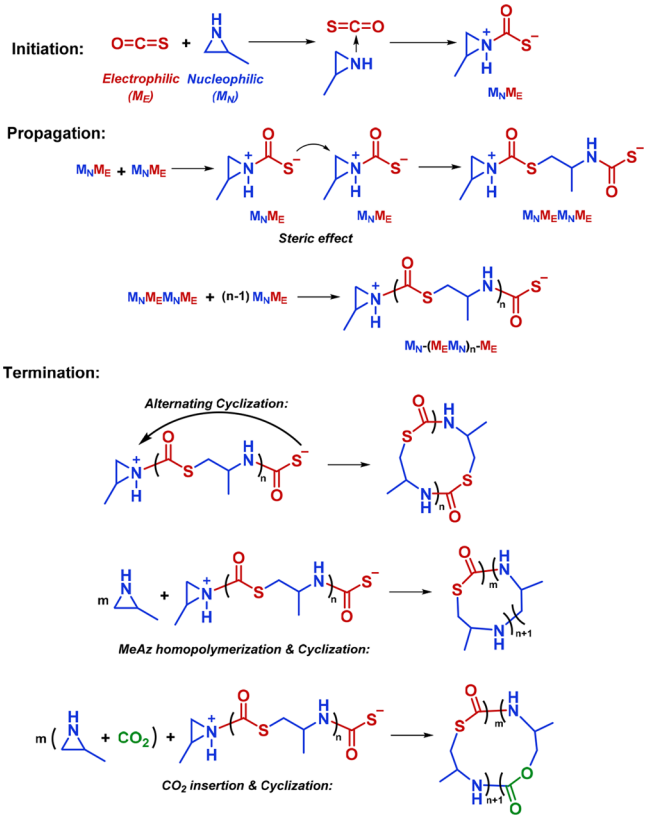


Figure 3. MALDI-TOF-MS spectrum (m/z = 1400−2250) of the product of entry 2 in Table 1.

polythiourethane with alternating thiourethane linkages and one imine (MeAz) linkage; because of the protonation of this individual imine linkage, the cyclic polythiourethane traveled with a proton. While the other group of blue-labeled peaks were assigned to cyclic polythiourethane with alternating thiourethane linkages and one urethane linkage, it traveled with a sodium ion. We believe that this copolymerization reaction undergoes a spontaneous zwitterionic copolymerization mechanism. As shown in Scheme 3, the nucleophilic monomer (M_N) MeAz and electrophilic monomer (M_E) COS spontaneously react to form zwitterionic intermediates (M_NM_E) without any initiator or catalyst. Subsequently, the copolymer chain propagates gradually with the interactions between the intermediates. At last, chain termination occurs via intramolecular backbiting to yield a cyclic copolymer. If no side reactions occurred, a copolymer with a fully alternating structure would be provided. However, when the insertion of excess MeAz occurred, an alternating polythiourethane with extra imine linkages would be formed, as the red-labeled peaks show in Figure 3. Similarly, when CO_2 in the atmosphere participated in chain propagation and copolymerized with MeAz to form urethane linkages, then the copolymer with excrescent urethane linkages would be afforded, as the blue-labeled peaks show in Figure 3. The synthesis of high-molecular-weight polymers with cyclic topology has always been a synthetic challenge, for the topological constraint imposed by cyclization leads to special properties.[70−84] Nonetheless, zwitterionic polymerization has been proven to be an effective method for synthesizing cyclic polymers.[80−84] However, most of the reported cyclic polymers such as polylactide, polysiloxane, and poly(α-peptoid) synthesized via zwitterionic polymerization merely involved the homopolymerization of a single-component monomer.[80−84] That is, there are scarcely reported cyclic polymers with alternating structures prepared by copolymerization of two-component monomers like that observed in this work. As far as we know, this is the first reported COS-based alternating cyclic polymer.

Scheme 3. Plausible Mechanism of the COS/MeAz Copolymerization



Thermal Depolymerization of the COS−MeAz Copolymer. We notice that the carbon yield in the copolymer's TGA curve (Figure 2) was extremely low, and there was no residue in the crucible after the TGA test. Thus, we speculate that the copolymer depolymerized into small molecules. We carried out a decomposition experiment of the copolymer in a sealed tube, and a light yellow clear liquid was obtained at 200 °C after 3 h. The liquid compound was confirmed to be the cyclic thiourethane (4-methylthiazolidin-2-one) by NMR (Figure 4) and liquid chromatography−mass spectrometry (LC−MS) (Figure S25). Thiazolidin-2-ones are important compounds in both pharmaceutical and synthetic organic chemistry.[85,86] This indicates that the COS−MeAz copolymer can be completely recycled by thermally depolymerizing it into a valuable small molecule. The whole process of the copolymerization and depolymerization of COS and MeAz is sustainable and atom-economical.

In order to study the kinetics and mechanism of the depolymerization process, we carried out the characterization of the GPC and NMR of the decomposition products obtained

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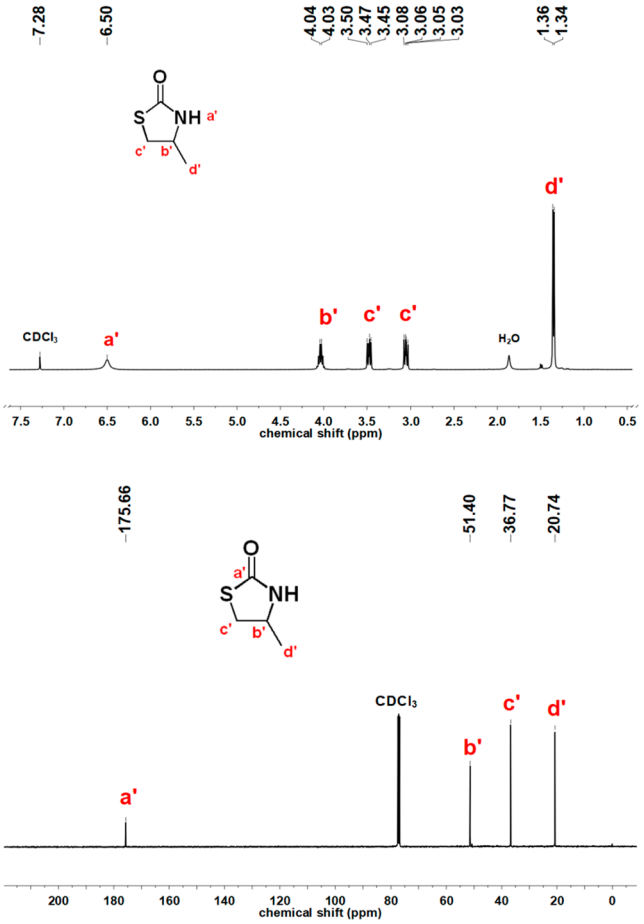

Figure 4. ^{1}H (top) and ^{13}C (bottom) NMR spectra ($CDCl_3$) of the cyclic thiourethane.

at a fixed temperature of 200 °C for different heating times, and the results are shown in Table 2. A plot of the copolymer's selectivity and M_w versus heating time is shown in Figure 5.

Table 2. Results of the Depolymerization of the COS/MeAz Copolymers

entry[a]	time (min)	copolymer selectivity[b] (%)	M_w[c] (g/mol)	$Đ$[c] (M_w/M_n)
1	0	95	15200	1.68
2	15	93	822	1.05
3	30	88	807	1.04
4	45	85	815	1.03
5	60	67	816	1.03
6	75	40	815	1.03
7	90	<1		

[a]The thermal degradation reactions were carried out in sealed 10 mL PTFE tubes. 50 mg of copolymer was added in each tube and heated in an oven. The tubes were quickly cooled down to room temperature after heating, and the copolymer and cyclic products were all sealed in the tubes and had no loss. [b]Estimated on the basis of ^{1}H NMR spectroscopy. The copolymer selectivity is the molar ratio of the copolymer versus cyclic product. The integrals of the methine proton (3.81 ppm) of copolymer and methine and methene protons (3.86 and 3.46 ppm) of cyclic product were used to calculate the selectivities. Please see Figure S1 for a detailed description. [c]M_w and $Đ$ were determined by GPC in DMF based on polystyrene standard samples.

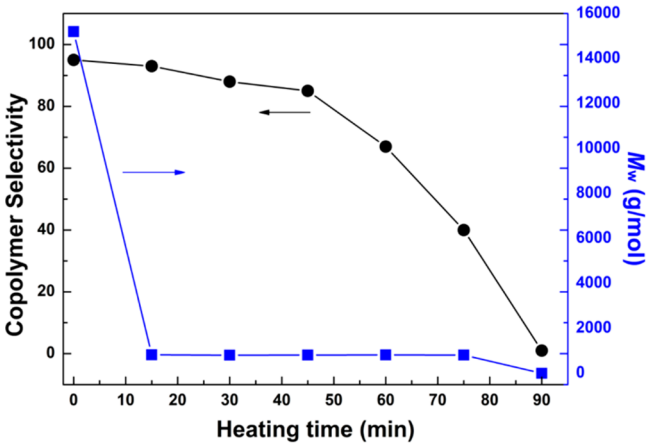

Figure 5. Plot of copolymer selectivity and M_w versus heating time.

The extent of depolymerization was determined on the basis of ^{1}H NMR spectroscopy by observing the disappearance of the methylene and methine protons in the polymer chain and the appearance of these same protons in the cyclic product (Figure 6). The copolymer selectivity showed an overall trend

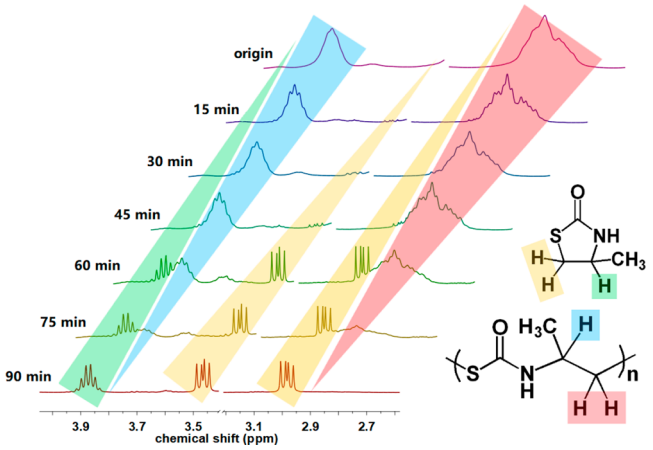

Figure 6. ^{1}H NMR (DMSO-d_6) spectra of the depolymerization products from different heating times. For clarity, the spectra were zoomed, and the peaks for H_2O were eliminated.

of a slow decrease and then a rapid decrease with the heating time. However, the molecular weights of the copolymers did not follow the same trend like copolymer selectivity. Notably, the molecular weight decreased sharply from 15.2 kg/mol to approximately 800 g/mol in a short time (about 15 min) and then remained stable around 800 g/mol for a relatively long time. Following heating for more than 90 min, all copolymers depolymerized to cyclic thiourethanes. It seemed that the high-molecular-weight copolymers rapidly depolymerized into oligomers at the very beginning of depolymerization. The oligomers whose molecular weights are around 800 g/mol (degree of polymerization is around 6−7) exhibited better thermal stability than the original copolymers, and these oligomers gradually depolymerized into cyclic thiourethanes under heating. A similar example was reported by Melchiors et al. in exploring the thermal depolymerization of poly[(*R*)-3-hydroxy butyrate] to the corresponding cyclic trimer.[87]

The MALDI-TOF-MS spectrum (Figure S22) of the degradation products showed that the molecular weights of

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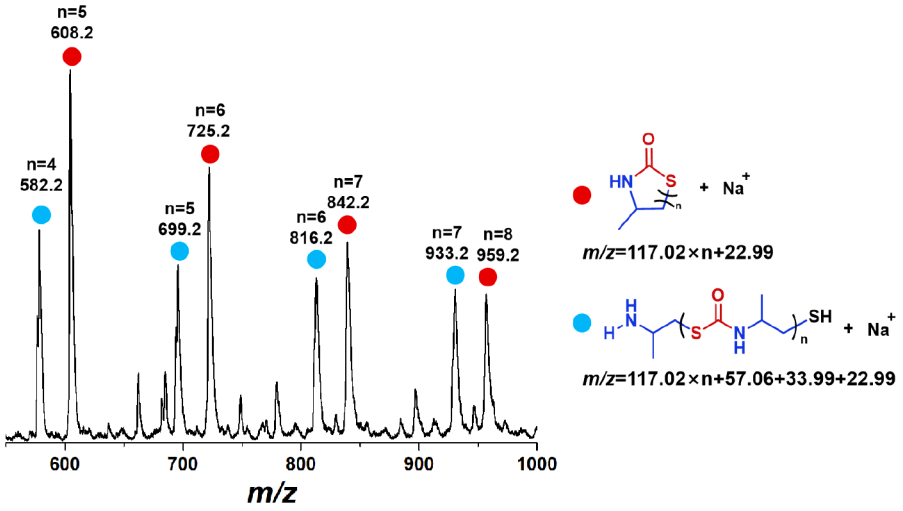
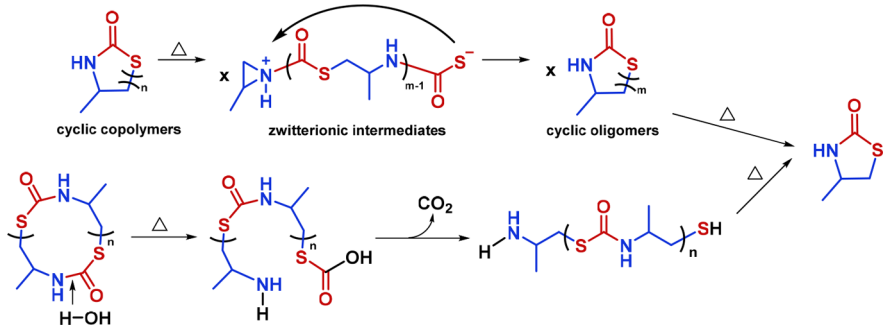


Figure 7. MALDI-TOF-MS spectrum (m/z = 550−1000) of the product of entry 5 in Table 2.

Scheme 4. Plausible Mechanism of Depolymerization of the COS−MeAz Copolymer



the oligomers were mainly around 600−800, which were generally consistent with GPC. The MALDI-TOF-MS spectrum (Figure 7) consisted of two series of molecular ion peaks. That is, the group of red-labeled peaks corresponds to cyclic alternating polythiourethanes, while the other group of blue-labeled peaks was assigned to linear alternating polythiourethane with one more MeAz linkage and end groups of $-NH_2$ and −SH. On the basis of the above results, we propose two plausible depolymerization routes as shown in Scheme 4. In the first case, a large amount of short-chain zwitterionic intermediates are produced when the cyclic copolymers are heated and scissioned; simultaneously, a large number of cyclic oligomers are generated via the backbiting of these zwitterionic intermediates. In the other case, water molecules interact with the heated copolymers when the linkages break at the C−N bond; terminal $-NH_2$ and −SCOOH are produced instantly. Upon releasing a CO_2 molecule from the unstable −SCOOH, a terminal −SH is obtained.

Application of Polythiourethane for Heavy Metal Absorption and Recovery. Sulfur-containing polymers have proven to be effective for absorbing heavy metal ions.[5−7] However, most studies only focus on the absorption of the metal ion and rarely consider the sustainability of the subsequent separation and recovery of the metal from the polymers. In fact, in most cases the polymers need to be heated at high temperature or incinerated in order to obtain the metal compounds, but in this way the polymer can no longer be recovered and becomes volatile organic matter (VOC) or carbon residue. Polymers are unrecoverable; on one hand, this leads to higher costs of metal recovery, and on the other hand, decomposed polymers might become environmental pollutants. Considering the special thermal recovery characteristics of the COS−MeAz copolymer, we first investigated the absorption efficiency of the copolymer for some metal ions and then further studied the separation of polymer and metal after absorption.

In this test, aqueous solutions of metal chloride salts (LiCl, $CoCl_2$, $HgCl_2$, $PbCl_2$, $NiCl_2$, $CdCl_2$) were stirred in the presence of COS−MeAz copolymers at ambient temperature for 12 h. Initially, copolymers were suspended in the solution and subsequently precipitated to the bottom due to the higher density of the metal ions/polymers complex. After the precipitates were removed by centrifugation, the concentrations of metal ions were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results are shown in Table 3. At first we investigated the copolymers' effectiveness and selectivity for absorbing the lithium ion and cobalt ion in order to recover expensive cobalt from the spent lithium ion battery. Unfortunately, the removal efficiency and selectivity for the cobalt ion were unsatisfactory (entries 1 and 2, Table 3), indicating that the thiourethane group does not strongly coordinate with cobalt ions. Subsequently, we employed the copolymers to absorb some biotoxic metal (mercury, lead, and cadmium) ions. Adding copolymer into $HgCl_2$ solution could reduce the concentration of Hg^{2+} sharply from 5.82 to 0.76 g/L after 12 h of stirring, absorbing 86.9% of Hg^{2+}, indicating that the copolymer is an efficient Hg^{2+} absorbent. Meanwhile, the copolymer also exhibited relatively

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Table 3. Absorption of the Copolymer for Metal Ions

entry[a]	metal ion	C_0 (g/L)	C_f (g/L)	removal efficiency (%)
1	Li^+	5.43	5.26	3.1
2	Co^{2+}	5.75	5.59	2.8
3	Hg^{2+}	5.82	0.76	86.9
4	Pb^{2+}	5.17	3.11	39.8
5	Cd^{2+}	5.42	4.08	24.7
6[b]	Pb^{2+}	10.68	7.55	29.3

[a]Carried out in aqueous solutions of different metal chloride compounds, the solutions were prepared with an aim concentration of 60 mg/L, and C_0 is the real concentration measured by ICP. Copolymer (20 mg) was added into 4 mL of solution. C_f is the concentration of the clear liquid after filtration. Removal efficiency = $(C_0 - C_f)/C_0 \times 100\%$. [b]This reaction was performed at 50 °C.

good effectiveness for absorbing Pb^{2+} and Cd^{2+}; their removal efficiencies were 39.8% and 24.7%, respectively. Lead is one of the most hazardous metals to human health found in water, especially for children even at low concentration.[88] Furthermore, it is widely used as the main raw material of lead−acid batteries. Nowadays, the lead−acid battery still occupies a large share of the battery market and is widely used in automotive and domestic applications. We expected to take advantage of the special depolymerization and absorption characteristics of this copolymer to accomplish the complete absorption and recovery process of Pb^{2+}. As shown in Figure 8, 500 mg of

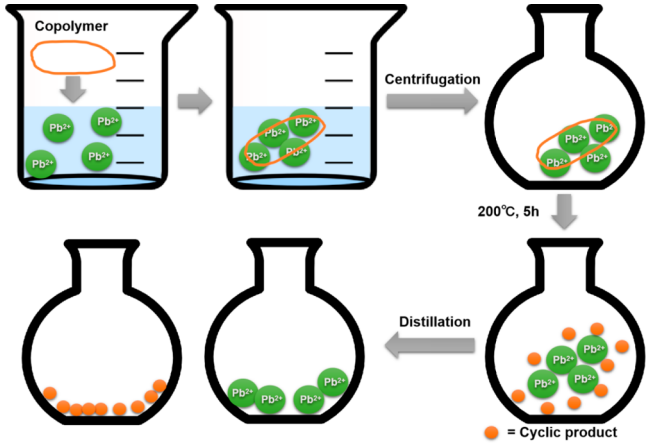

Figure 8. Schematic diagram of the facile lead absorption and recovery process.

copolymer (newly prepared as entry 2 in Table 1) was added into 100 mL of a saturated aqueous solution of $PbCl_2$, and the mixture was stirred at 50 °C for 12 h. The precipitated solid was obtained by centrifugation, after which the solid was heated at 200 °C for 5 h, providing a black turbid liquid. We speculated that the liquid was a mixture of cyclic thiourethane and lead compound; thus, distillation under reduced pressure was carried out to separate them into a clear liquid and black solid. The clear liquid was confirmed by ^1H NMR (Figure S19) to be cyclic thiourethane. X-ray photoelectron spectroscopy (XPS) was employed to characterize the black solid and indicated that the black solid mainly contained three elements of oxygen, lead, and chlorine (Figure S48). According to the XPS spectra and elemental quantification of Pb 4f as shown in Figure S49, it can be seen that lead element contained two valence states of +4 and 0, which might result from the disproportionation reaction of Pb^{2+} in the absorption and recovery process. Combined with the XPS results of chlorine (Figure S50), we speculate that lead was eventually recovered in the form of elemental lead and tetravalent lead compound.[89] Calculations based on the result (entry 6, Table 3) indicated that 313 mg of lead was absorbed by using 500 mg of copolymer, and they were eventually recovered in the form of lead compounds and valuable cyclic thiourethane. The whole absorption and recovery process is sustainable and atom-economical, offering a greener method to recover hazardous metal with minimal waste and VOC emission.

CONCLUSIONS

In conclusion, we have reported the synthesis of alternating and regioselective polythiourethane from the spontaneous copolymerization of COS and MeAz. This copolymerization provides an efficient non-isocyanate and catalyst-free strategy to synthesize polythiourethane. The reaction proceeded smoothly at room temperature with tetrahydrofuran as the solvent to efficiently afford polythiourethane in 95% selectivity and with a molecular weight of 15.2 kg/mol and a polydispersity of 1.68. This reaction exhibited excellent activity; that is, 55% monomer was converted in 5 min at room temperature at just 1 atm of COS, affording the corresponding copolymer in 95% selectivity. This work also examined the detailed and accurate linkage structures of the copolymer and indicated that it has an alternating cyclic topology; meanwhile the plausible mechanisms of zwitterionic copolymerization and formation of cyclic topology were proposed. This polythiourethane was completely recyclable back to cyclic thiourethane in the pure state upon heating the bulk polymer at 200 °C for 1.5 h. A plausible depolymerization mechanism was proposed as the copolymer first rapidly depolymerized to low-molecular-weight oligomers and then slowly depolymerized to cyclic thiourethane. We took advantage of the special thermal depolymerization characteristics of this polymer for heavy metal ion absorption and recovery. Through an absorption and thermal depolymerization process, 313 mg of lead was absorbed by using 500 mg of copolymer, and they were both eventually recovered as lead compounds and cyclic thiourethane. Overall, the results reported herein established that the copolymerization and depolymerization of COS and MeAz is very sustainable and atom-economical. Furthermore, its application in heavy metal recovery offers a greener method to recover hazardous metal with minimal waste and VOC emission.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.0c00435.

NMR and MALDI-TOF-MS spectra, GPC, DSC, and XRD curves of the copolymers; NMR and LC−MS spectra of the cyclic products; video screenshots of the atmospheric copolymerization progress; and XPS spectra of the black solid in lead recovery (PDF)

AUTHOR INFORMATION

Corresponding Authors

Ming Luo − *School of Materials Engineering, Changshu Institute of Technology, Changshu, Jiangsu 215500, China;* orcid.org/0000-0002-6166-0681; Email: tianyaguzhao@zju.edu.cn

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Donald J. Darensbourg − *Department of Chemistry, Texas A&M University, College Station, Texas 77843, United States;* orcid.org/0000-0001-9285-4895; Email: djdarens@chem.tamu.edu

Authors

Shuang Wu − *School of Materials Engineering, Changshu Institute of Technology, Changshu, Jiangsu 215500, China*

Dandan Zeng − *School of Materials Engineering, Changshu Institute of Technology, Changshu, Jiangsu 215500, China*

Yuhua Yao − *School of Materials Engineering, Changshu Institute of Technology, Changshu, Jiangsu 215500, China*

Xiaobing Zuo − *School of Materials Engineering, Changshu Institute of Technology, Changshu, Jiangsu 215500, China*

Xin Hu − *School of Materials Engineering, Changshu Institute of Technology, Changshu, Jiangsu 215500, China;* orcid.org/0000-0001-8113-8631

Dawei Tan − *School of Materials Engineering, Changshu Institute of Technology, Changshu, Jiangsu 215500, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acssuschemeng.0c00435

Notes

The authors declare no competing financial interest.

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