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Organocatalytic Ring-Opening (Co)polymerization of Six-Membered Monothiocarbonates for the Synthesis of Recyclable Poly(monothiocarbonate)s

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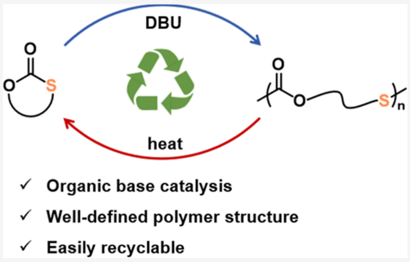
ABSTRACT: Developing chemically depolymerizable polymers (CDPs) that can revert back to monomers is of great significance for realizing a circular polymer economy. Poly(thiocarbonate)s, sulfur analogs of polycarbonates, are a rather under-investigated group of sulfur-enriched polymers with high potential as CDPs. Here, we report a recyclable poly(monothiocarbonate) obtained via organocatalytic ring-opening polymerization of a six-membered cyclic monothiocarbonate. The resulting polymer exhibited a melting point up to 127 °C and a Young's modulus of 305 MPa with a tensile stress of 23.2 MPa at 8.8% strain, while the analogue polycarbonate derived from trimethylene carbonate is amorphous with a low modulus (<100 MPa) under ambient temperature. Moreover, a successful copolymerization of 1,3-oxathian-2-one and 5,5-dimethyl-1,3-oxathian-2-one provided an access to precise tunability of thermomechanical performance of the poly(monothiocarbonate)s.



■ INTRODUCTION

The polymer wastes, particularly plastics, being discarded in landfills or leaked into the environment, are incessantly accumulated and highly persistent in the environment, which causes not only severe environmental problems, but also waste of resources.[1] An attractive strategy to address this issue is to develop polymers with closed-loop life recycles, particularly polymers that can undergo chemical recycling to monomer (CRM), thus creating a circular polymer economy.[2,3] An ideal CRM, involving a pyrolysis process rather than hydrolysis in an acidic or basic environment, requires a low ceiling temperature (T_c), which is defined as the temperature at which the rates of polymerization and depolymerization are equal, which occurs when the change in Gibbs free energy (ΔG_p) is zero. Accordingly, T_c could be calculated by Van't Hoff equation, $T_c = \Delta H_p^\circ/(\Delta S_p^\circ + R\ln[M]_{eq})$, ΔH_p° and ΔS_p°: enthalpy change and entropy change at standard polymerization conditions, $[M]_{eq}$: equilibrium monomer concentration.[3,4] Polymerization is favored at temperatures below T_c and depolymerization is favored above T_c. Specially, $T_c = \Delta H_p^\circ/\Delta S_p^\circ$ when $[M]_{eq}$ is designated as 1 M. On the other hand, a successful CRM needs to consider depolymerization kinetics, as the reactive chain end for depolymerization is usually blocked (like a proton), which will enhance the thermal stability of the polymer to far above its T_c. Chemical treatment such as adding a catalyst can frequently more cleanly initiate the depolymerization under moderate conditions, yet the cost of the catalyst, its reusability, and energy consumption need to be thoroughly evaluated. To date, a variety of cyclic monomers possessing low T_c have been explored for use in CRM, including cyclic (thio)esters,[5−25] cyclic (thio)carbonates,[26−35] cycloolefins,[36,37] phthalaldehydes,[38] cyclic acetals,[39] and others.[40,41]

Notably, in 2016, Chen et al.[5] achieved a breakthrough in ring-opening polymerization (ROP) of γ-butyrolactone (γ-BL) and produced polyester (PBL) with complete chemical recyclability, but the low polymerization temperature (−30 to −60 °C) limits the industrial viability. Later on, they developed a fused-ring γ-BL derivative termed as 3,4-T6GBL exhibiting a more negative ROP enthalpy change, which enables its excellent polymerizability under mild conditions and also retains the full chemical recyclability of γ-BL.[7] Interestingly, in 2021, Hong et al.[6] reported a new monomer γ-thionobutyrolactone (TnBL) made by introducing a sulfur atom into γ-BL. Although the ROP of TnBL became completely irreversible due to the S/O isomerization during polymerization, the resultant polythioester showed a drastic improvement in thermal and mechanical properties than PBL.

In the case of six-membered cyclic esters, such as δ-valerolactone (δ-VL) and dilactone, the moderate ring strain leads to a higher ceiling temperature of the polyesters, thereby reducing their depolymerizability.[10,42] A successful strategy has been proposed for regulating the ring strain by adjusting the structure and position of the substituents on the δ-VL ring.[9−15,43] Another attractive method is to simply replace

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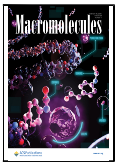


Scheme 1. (a) ROP of MTC Catalyzed by *tert*-BuOK. (b) Alternating Oxetane/COS Copolymerization Catalyzed by a (Salen)CrCl/[PPN]Cl Catalytic System. (c) This Work: Ring-Opening (co)polymerization of Six-Membered Monothiocarbonates Catalyzed by Organic Base

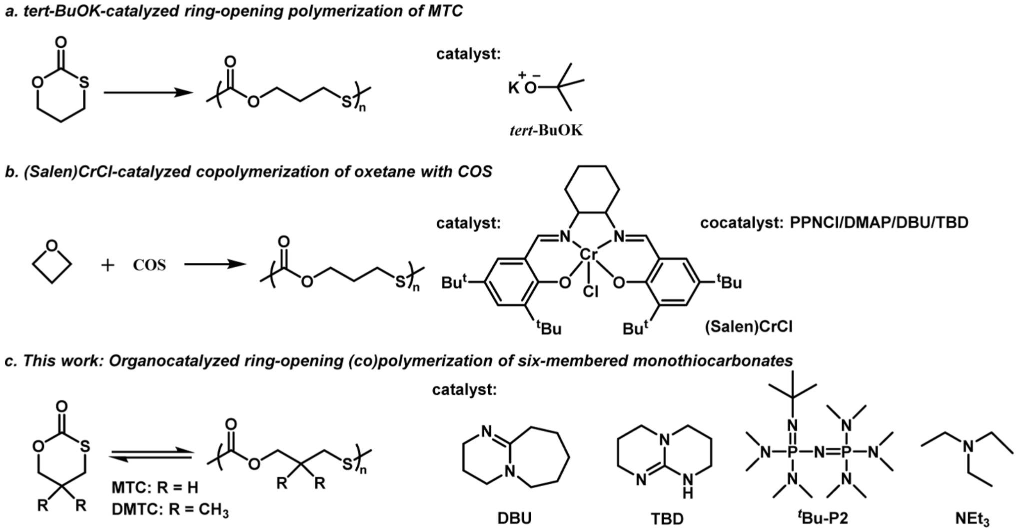


Table 1. ROP of MTC and DMTC[a]

entry	monomer	catalyst	$[M]/[I]/[Cat]$	solvent	temp. (°C)	time (h)	conv.[b] (%)	M_n (kg/mol)[c]	$Đ$[c]
1	MTC	NEt_3	500/2/1	bulk	30	12	11	3.0	2.05
2	MTC	TBD	500/2/1	bulk	30	12	11	6.9	2.13
3	MTC	^{t}Bu-P2	500/2/1	bulk	30	12	14	5.9	2.48
4	MTC	DBU	500/2/1	bulk	30	12	47	8.2	1.95
5	MTC	DBU	500/2/1	bulk	130	4	95		
6	MTC	DBU	500/2/1	DMF	60	12	69	3.5	1.74
7	MTC	DBU	500/2/1	NMP	60	12	86	10.6	2.67
8	MTC	DBU	500/2/1	toluene	60	12	>99	13.6	2.49
9	MTC	DBU	500/2/1	toluene	60	12	>99	14.4	2.39
10	DMTC	DBU	40/2/1	bulk	25	3	94	5.5	1.39
11	DMTC	DBU	500/2/1	bulk	25	12	94	24.0	1.44
12	DMTC	DBU	1000/2/1	bulk	25	18	89	43.9	1.41

[a] Conditions: initiator (I) = BnOH, $[M]_0 = 4$ M for entries 6 to 8, $[M]_0 = 8$ M for entry 9. [b] Conversion of monomer, determined by ^{1}H NMR spectroscopy. [c] Determined by GPC in $CHCl_3$ (for entries 1 to 9) or THF (for entries 10 to 12), calibrated with polystyrene standards.

oxygen atoms with sulfur atoms in the cyclic monomers recently reported by the groups of Lu,[24] Chen,[44] Tao,[22] and Dusselier.[21] For example, Tao et al.[22] demonstrated that an oxygen-to-sulfur substitution in dilactones could accelerate ring-closure during depolymerization due to the decreased ring-strain. Meanwhile, the resultant poly(dithiolactone)s exhibit distinctive characteristics, including controllable molecular weight (up to 100.5 kDa) and atactic stereostructures, yet with high crystallinity.

As with six-membered cyclic esters, the six-membered cyclic carbonates, such as trimethylene carbonate (TMC) and its derivatives, have been known for a long time to undergo equilibrium polymerizations.[45] In particular, ROP of TMC can reach high molecular weights in neat conditions to produce amorphous poly(trimethylene carbonate), a soft material suitable for in vivo use.[33,46] However, the formation of oligomers and decarboxylated side products upon depolymerization limits the practicality of CRM.[47] A natural and reasonable hypothesis comes to be that the six-membered cyclic thiocarbonates (6CTC), as sulfur analogues of TMC, may realize a balance between the polymerization and depolymerization abilities; meanwhile, introducing sulfur atoms into polymers can enhance their optical and mechanical properties, as well as increase their crystallinity.[48−51] Early works made by Endo[52−56] focused mainly on the controlled cationic/anionic ROP of a series of cyclic thiocarbonates (mono- or dithio-substituted) with five-to seven-membered rings, but the recyclability of the polymer was not investigated. Moreover, an S/O isomerization was observed during the ROP of cyclic thiocarbonates in which the carbonyl oxygen atom was replaced with the sulfur atom.[53−56] It is worth noting that the ROP of 1,3-oxathian-2-one (labeled as MTC) initiated by *tert*-BuOK, the simplest 6CMTC, yields a semicrystalline poly(monothiocarbonate) possessing a melting point (T_m) up to 116 °C[52] (Scheme 1a). In 2016, Zhang and Darensbourg et al.[57] reported a similar poly(monothiocarbonate), which was synthesized by the copolymerization of oxetane and COS in the presence of a (salen)CrCl/cocatalyst system (Scheme 1b). The studies mentioned above all employed metal catalysts and did not explore the depolymerization behavior of polymers. Fortunately, we recently[58] provided a convenient and reliable method for the synthesis of 6CMTC by the cycloaddition of carbonyl sulfide (COS) with 1,3-halohydrin, which enables the synthesis of poly(monothiocarbonate)s with different sub-

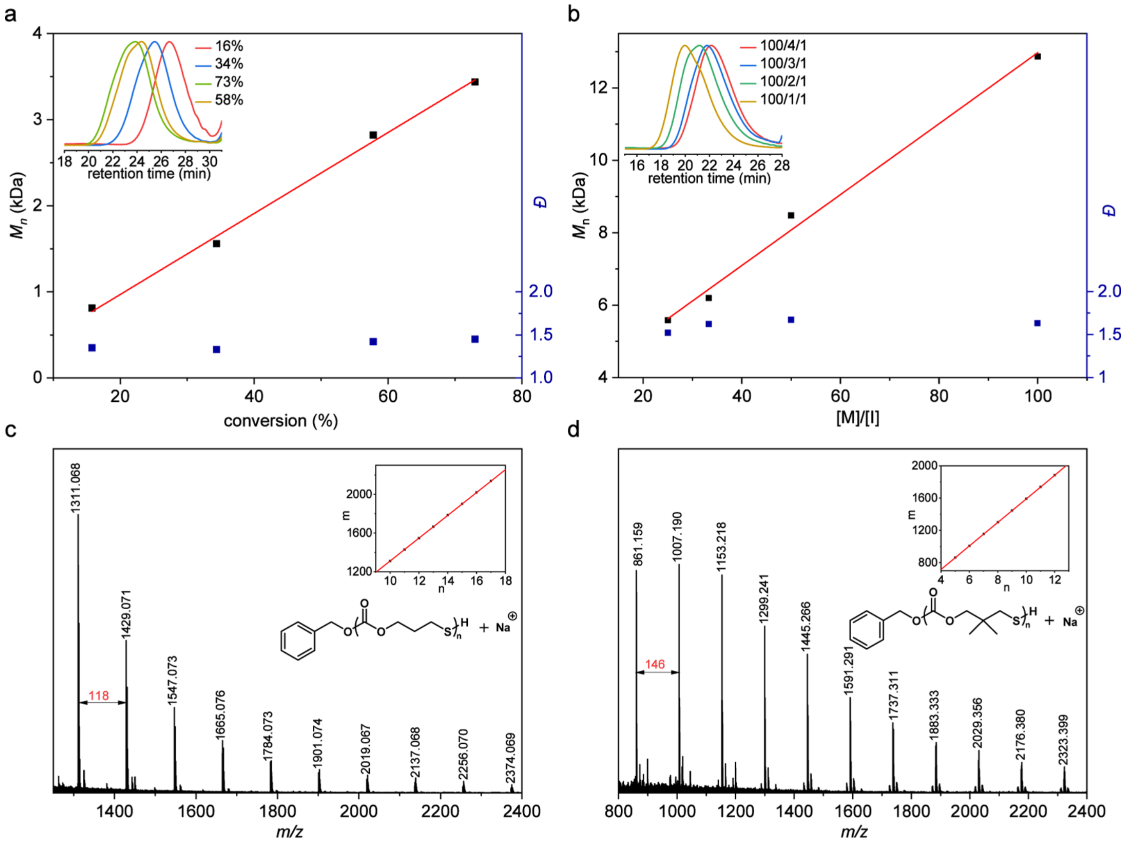


Figure 1. ROP of DMTC. (a) M_n and $Đ$ vs Conversions of DMTC at a $[M]_0/[I]_0/[\mathrm{Cat}]_0$ ratio of 100/1/1, toluene, 25 °C; (inset) overlay of SEC profiles at different DMTC conversions. (b) M_n and $Đ$ vs $[M]_0/[I]_0$ ratio; (inset) overlay of SEC profiles at different $[M]_0/[I]_0$ ratios. (c) MALDI-TOF-MS of PMTC. (d) MALDI-TOF-MS of PDMTC.

stituents. Based on this, we made some progress by replacing the halohydrins with more inexpensive and readily available diols.

In this work, we aimed to obtain poly(monothiocarbonate)s with the capacity of CRM through the organocatalytic ROP of 6CMTCs (Scheme 1c). Two specific monomers, 1,3-oxathian-2-one (MTC) and 5,5-dimethyl-1,3-oxathian-2-one (labeled as DMTC), were explored on the (co)polymerization characteristics as well as the thermal and mechanical performances of the resultant (co)polymers.

■ RESULTS AND DISCUSSION

Ring-Opening Polymerization of Cyclic Monothiocarbonates. The initial ROP of MTC performed in bulk at 30 °C for 12 h with benzyl alcohol as the initiator and an organic base as the catalyst leads to low conversions (<15%) and low molecular weights in the cases of ^{t}Bu-P2, TBD, and NEt_3, while DBU reached a conversion of about 47%, as determined by ^{1}H nuclear magnetic resonance (NMR) analysis of the reaction mixture (Table 1, entries 1−4). In fact, the solution became heterogeneous induced by precipitation of the polymer during the polymerization, which was consistent with the early report by Endo.[52] By raising the reaction temperature to 130 °C (higher than the literature T_m of 116 °C), the MTC conversion greatly increased up to 95% within 4 h in the presence of DBU (Table 1, entry 5). However, the resultant polymer was hardly soluble in common solvents such as tetrahydrofuran, dichloromethane, and *N*,*N*-dimethylformamide, which caused difficulty in determining the molecular weight. Nonetheless, DBU was chosen as the catalyst for further investigation of the (co)polymerization behaviors of MTC and DMTC.

Solution ROP of MTC with $[M]_0$ = 4 M proceeded more efficiently in toluene at 60 °C, achieving a conversion of over 99% within 12 h, whereas conversions of 69% and 86% were observed in DMF and NMP, respectively (Table 1 entries 6−8). Unexpectedly, PMTC still precipitated during the solution polymerization, accounting for the significant discrepancy between the molecular weight of 13.6 kDa measured by GPC and the theoretical molecular weight of 29.6 kDa, as well as the broad molecular weight distribution. Unlike MTC, ROP of DMTC in bulk reached high conversions at 25 °C, affording a unimodal polythiocarbonate with a relatively low molecular weight distribution $Đ$ (M_w/M_n) < 1.45. The molecular weights of the polymers increased from 24.0 to 43.9 kDa by increasing the ratio of monomer/initiator from 250/1 to 500/1 (Table 1 entries 11 and 12). Encouraged by these promising results, we conducted a more detailed study of the polymerization reaction of DMTC. With a feed ratio of $[M]_0/[I]_0/[\mathrm{Cat}]_0$ = 100/1/1, the M_n values of PDMTC grew linearly with monomer conversion, while $Đ$ was relatively low (<1.5) (Figure 1a). On the other hand, the variation of M_n showed an approximately linear relationship with $[M]_0/[I]_0$ ratios, while maintaining unimodal distribution, though a slight increase of $Đ$ at lower $[M]_0/[I]_0$ ratios was observed (Figure 1b, see also Table S1).

Furthermore, we examined the chain microstructures of both PMTC and PDMTC by NMR and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS). The −SC(O)O− unit of PMTC (Table

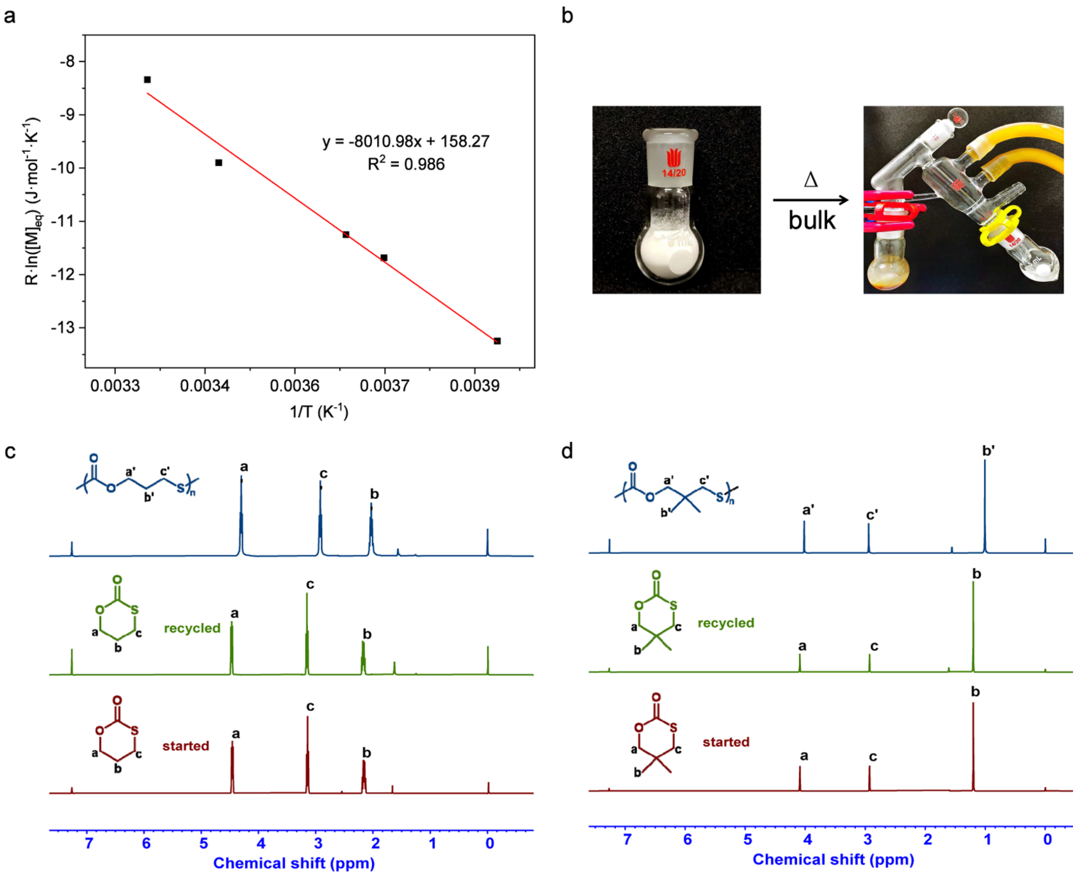


Figure 2. (a) Van't Hoff plot for the ROP of DMTC in the temperature range of 258 to 298 K; (b) thermal depolymerization of polymers to monomers via distillation. (c) Overlay of the ^{1}H NMR spectra in $CDCl_3$ of started DMTC (bottom), recycled DMTC (middle), and PDMTC (top). (d) Overlay of the ^{1}H NMR spectra in $CDCl_3$ of started MTC (bottom), recycled MTC (middle), and PMTC (top).

1, entry 7) and PDMTC (Table 1, entry 11) was clearly seen at 170.73 and 165.79 ppm in ^{13}C NMR, respectively, and no other carbonyl carbon signals were observed (Figure S3). Concurrently, each MALDI-TOF-MS spectrum of PMTC (Table 1, entry 4) and PDMTC (Table 1, entry 10) showed a single series of peaks with an interval of m/z 118.0 and 146.0, equivalent to the molecular weight of MTC and DMTC respectively, along with a $PhCH_2O-$ terminal group (Figure 1c,d).

These results indicated that the organo-catalytic ROP of DMTC exhibits a controlled feature and affords regioregular poly(monothiocarbonate)s without an occurrence of oxygen−sulfur exchange reaction, while ROP of MTC is poorly controlled due to the polymer's low solubility in common solvent, which is most likely caused by its high degree of crystallinity.

■ CHEMICAL RECYCLABILITY OF PDMTC

The low solubility of PMTC makes it difficult to obtain reliable thermodynamic parameters of the ROP of TMC, while DMTC showed an equilibrium polymerization. Thus, the thermodynamic properties of DMTC ROP with DBU/BnOH were obtained by measuring the equilibrium monomer conversion (4 M in toluene, $[M]/[BnOH]/[DBU] = 100/1/1$) at different temperatures (i.e., −15 to 25 °C). A Van't Hoff plot is shown in Figure 2a (see also Figure S4), and the raw data of equilibrium conversion are listed in Table S2. Accordingly, the enthalpy (ΔH_p°) and entropy (ΔS_p°) changes were calculated as −8.01 kJ/mol and −18.3 J/(mol K), respectively. The ceiling temperature of DMTC polymerization was calculated T_c = 165 °C at $[M]_0$ = 1 M, while its carbonate analogue 5,5-dimethyl-1,3-dioxan-2-one exhibited a higher T_c of 212 °C (with *t*-BuOK in THF) estimated on the data reported by Endo.[45] This result again demonstrated that the ring strain of the monomer could be effectively reduced by a subtle O-to-S substitution. The chemical recyclability of PDMTC was then investigated under solid conditions. Neat DMTC was recycled with the yield of 82% by distillation under reduced pressure at 180 °C for 8 h (Figure 2c). Similarly, pure MTC was recovered with the yield of 70% at 210 °C for 10 h (Figure 2d).

Thermal and Mechanical Properties of the Poly(monothiocarbonate)s. The thermal properties of the resultant poly(monothiocarbonate)s were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Semicrystalline PMTC with a M_n of 8.2 kDa (Table 1, entry 4) exhibited a high T_m of 127 °C (Figure 3a) similar to the polymer derived from copolymerization of COS and oxetane reported previously by Zhang's group.[57] In comparison, a PDMTC with a M_n of 43.9 kDa (Table 1, entry 12) exhibited weaker crystalline ability as no melting endothermic peak was observed on the second heating but a low glass transition temperature (T_g) of −4.5 °C (Figure 3a). By storing the sample at room temperature for more than 24 h, a T_m of 67 °C with a melting enthalpy ΔH_m = 8.62 J/g was observed. Powder wide-angle X-ray diffraction (XRD) analysis also confirmed the crystalline nature of the poly(monothiocarbonate)s. For PMTC, five diffraction peaks

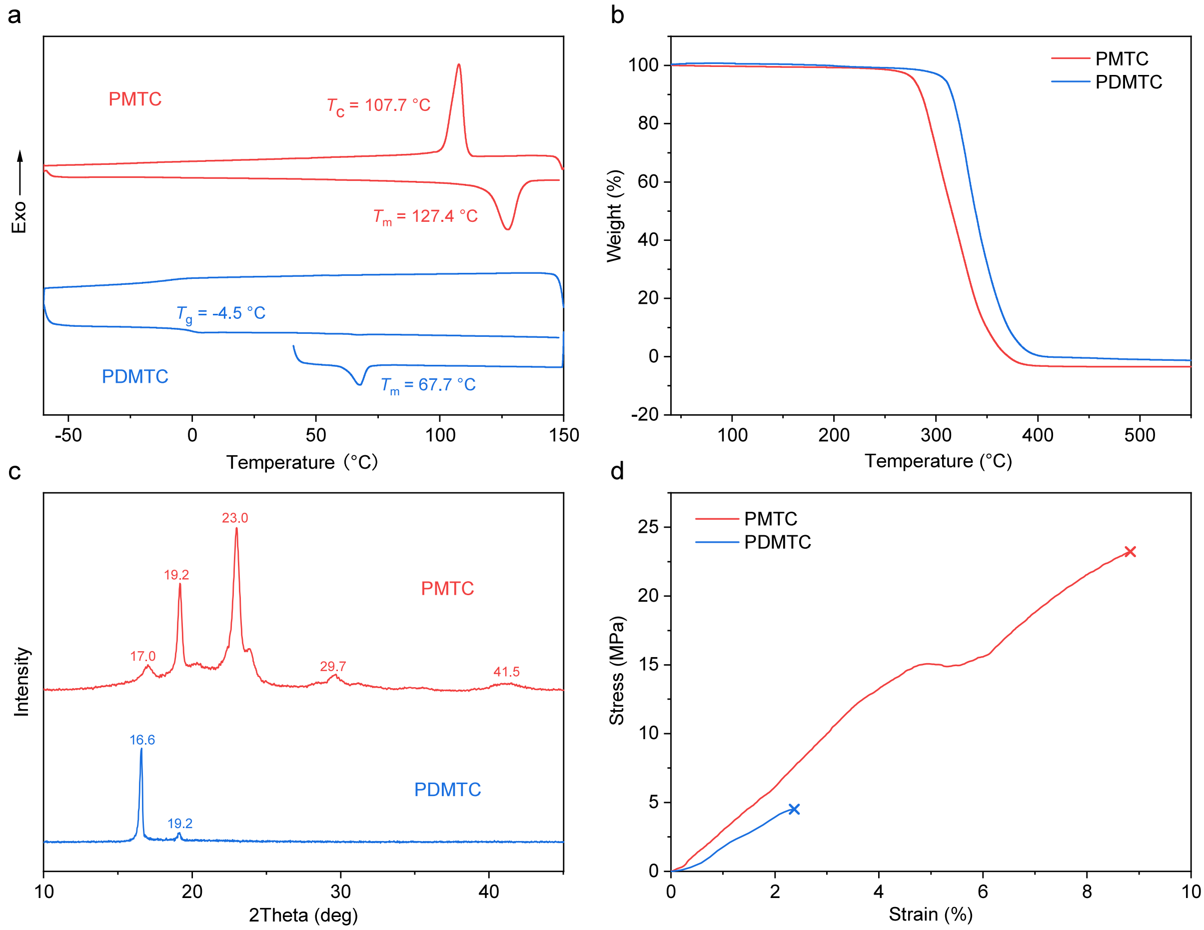


Figure 3. (a) DSC, (b) TGA, and (c) XRD analysis of PMTC (Table 1 entry 4) and PDMTC (Table 1 entry 12); (d) uniaxial tensile elongation analysis of the bulk PMTC (Table 1 entry 9) and PDMTC (Table 1 entry 12).

Table 2. Results of Copolymerization MTC with DMTC[a]

entry	[MTC]/[DMTC]	t (h)	M_n[b] (kg/mol)	$Đ$[b]	$[C_{MTC}]/[C_{DMTC}]$[c]	T_g[d] (°C)	T_m[d] (°C)	E[e] (MPa)	ε_B[e] (%)
1	4/1	24	13.7	1.39	4.59	−24.7	93.8	91.1	16.0
2	2/1	72	21.0	1.36	2.04	−24.2	68.0	23.4	61.9
3	1/1	72	20.1	1.35	1.13	−17.0			
4	1/2	72	18.7	1.35	0.48	−12.8			
5	1/4	48	15.3	1.36	0.24	−10.6			

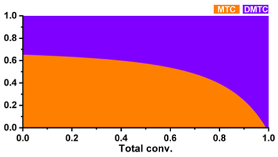
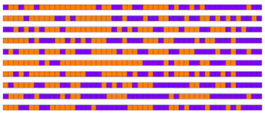
[a] Conditions: catalyst = DBU, initiator (I) = BnOH, [MTC + DMTC]/[I]/[Cat] = 200/1/1, 25 °C. [b] Determined by GPC in THF, calibrated with polystyrene standards. [c] Molar ratio, determined by ^{1}H NMR of purified products. [d] Glass transition temperature (T_g) and melting temperature (T_m) determined using DSC. [e] Young's modulus (E) and tensile stress at strain (ε_B) determined by tensile tests.

appeared at 2θ values of 17.0, 19.2, 23.0, 29.7, and 41.5°, among which two main peaks at 2θ values of 19.2 and 23.0° are relatively strong, while for PDMTC, only two peaks at 2θ values of 16.6 and 19.2° were observed. These results clearly demonstrated that the β-position dimethyl substituents greatly affected the stacking of the polymer chains. The TGA suggested that these polys(monothiocarbonate)s exhibit good thermal stability, with $T_{d,5\%}$ values of 282 °C for PMTC and 309 °C for PDMTC (Figure 3b). Uniaxial tensile elongation tests were performed on the samples of PMTC with a M_n of 14.4 kDa (Table 1, entry 9) and PDMTC of a M_n of 43.9 kDa (Table 1 entry 12). The samples for uniaxial tensile elongation tests were prepared by the hot pressing molding method. According to the tensile test, the PMTC possesses a Young's modulus (E) of 305 MPa, with a high tensile stress at break σ_B of 23.2 MPa at 8.8% strain (ε_B), while the PDMTC showed poor mechanical properties with E = 37.3 MPa, σ_B = 4.5 MPa, and ε_B = 2.3%. These results again reflected the big challenge to balance the depolymerization ability and physical performance.

Copolymerization of MTC and DMTC. The combination of soft and hard segments in one polymer chain is considered an effective method to enhance the mechanical properties of materials.[59,60] Considering this, an attempt was made to improve the physical properties of the obtained poly(monothiocarbonate)s through the copolymerization of MTC with DMTC.

The copolymerization reaction was conducted in a feed ratio of [MTC + DMTC]/[BnOH]/[DBU] = 200/1/1 at 25 °C in bulk. The copolymer structure and monomer reactivity ratio were characterized by ^{1}H NMR. Three models, specifically the Beckingham−Sanoja−Lynd (BSL) model, the Frey model, and

Table 3. Reactivity Ratios Calculated From Models of BSL, Frey, and Meyer−Lowry (M−L) (Left); the Copolymer Distribution Derived from Monte Carlo Simulation (Right)

Reactivity ratios			Illustrations of microstructions	
Model	r_1	r_2	Monomer fraction F plotted againist total conversion	Monte Carlo simulation of comonomer distribution
BSL	1.837	0.541		
Frey	1.737	0.576		
M-L	1.741	0.564		

the Meyer−Lowry (ML) model, were used to determine the reactivity ratios, and the calculated values are listed in Table 3 (Figures S6−S9). The reactivity ratios predicted by all three models fall within the range of 0.5−2, and the BSL model provides the best fit to the experimental data, indicating that the copolymerization reaction results in a random copolymer. Moreover, the random sequence structure of the copolymer (Table 2 entry 3) was also illustrated by Monte Carlo simulation (Table 3). In the early stage of copolymerization, the relatively high $r_{(\mathrm{MTC})}$-to-$r_{(\mathrm{DMTC})}$ ratio suggests that more MTC is consumed. As the polymerization proceeds, the amount of DMTC incorporated increases, with its proportion exceeding that of MTC. This result was confirmed by the crude ^{1}H NMR spectra obtained via interval sampling monitoring (Figure S5a). Furthermore, the DOSY NMR spectrum of the copolymer (Table 2 entry 3) confirmed that both monomers were incorporated simultaneously into a single polymer chain (Figure S5b).

The thermal and mechanical properties of the copolymers were further investigated. The T_m decreased from 93.8 to 68 °C with the content of MTC in the copolymer was reduced from 82% to 67%. When the DMTC content reaches 53% or higher, the copolymer becomes amorphous and does not have a melting peak. The T_g increased from −24.7 to −10.6 °C with the decrease in MTC content, approaching the T_g of PDMTC (Table 2, Figures S15−S19). Regarding mechanical properties, the introduction of DMTC increased the polymer's elongation at break but significantly reduced the elastic modulus and tensile strength. For example, the copolymer's ε_B reached 61.9%, while the σ_B and E decreased to 4.1 and 23.4 MPa, respectively (Table 2, entry 2, see also Figure S27). The other copolymers' mechanical properties were not assessed, as the low T_g made the samples inaccessible for characterization. Therefore, the thermal and mechanical properties of the poly(monothiocarbonate)s have been regulated through copolymerization.

■ CONCLUSIONS

In conclusion, we develop a recyclable poly(monothiocarbonate) via organic base-catalyzed ROP of six-membered cyclic monothiocarbonate. The poly(monothiocarbonate) exhibited a lower ceiling temperature as well as enhanced thermal and mechanical properties than its oxygen analogue polycarbonate. Furthermore, the random copolymerization of MTC and DMTC was demonstrated to effectively modulate the thermomechanical properties of the poly(monothiocarbonate)s. Our ongoing work is developing other cyclic thiocarbonate monomers (i.e., dithiocarbonates) and the corresponding polymer that can achieve a balance between recyclability and mechanical performance.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.4c03028.

> Experimental section, monomer synthesis, ROP of six-membered cyclic monothiocarbonate, thermodynamic study of ROP of DMTC, chemical recycling to monomer of polymers under bulk thermal, analysis of reactivity ratios, copolymerization of MTC of DMTC, and WAXD curves of crystalline copolymers (PDF)

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Notes

The authors declare no competing financial interest.

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