

SUPPORTING INFORMATION

for

Crystalline and Elastomeric Poly(monothiocarbonate)s Prepared from Copolymerization of COS and Achiral Epoxide

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1. General information

All manipulations involving air- and/or water-sensitive compounds were carried out in glove box or under dry nitrogen using standard Schlenk techniques. Ethylene oxide (EO) and propylene oxide (PO) were distilled under a nitrogen atmosphere from CaH_2 prior to use. Carbonyl sulfide (99.995%) was purchased from Dalian Institute of Special Gases.

NMR ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 MHz type (^1H , 400 MHz; ^{13}C , 100 MHz) spectrometer. Their peak frequencies were referenced versus an internal standard (TMS) shifts at 0 ppm for ^1H NMR and against the solvent, DMSO-*d* at 39.5 ppm for ^{13}C NMR, respectively.

Gel Permeation Chromatography Molecular weights and molecular weight distributions of copolymers were measured by gel permeation chromatography (GPC) analysis at 35 °C and a flow rate of 1.0 mL/min, with DMF as the eluent, on a Agilent 1260 instrument coupled with an Agilent RI detector and equipped with four PL gel 5 m mixed-C columns. The sample concentration was about 0.1%, and the injection volume was 50 μL . The curve was calibrated using monodisperse polystyrene standards covering the molecular weight range from 580 to 460000 Da.

Differential Scanning Calorimetry (DSC) The analysis of DSC was carried out with a NETZSCH DSC 206 thermal analyzer.

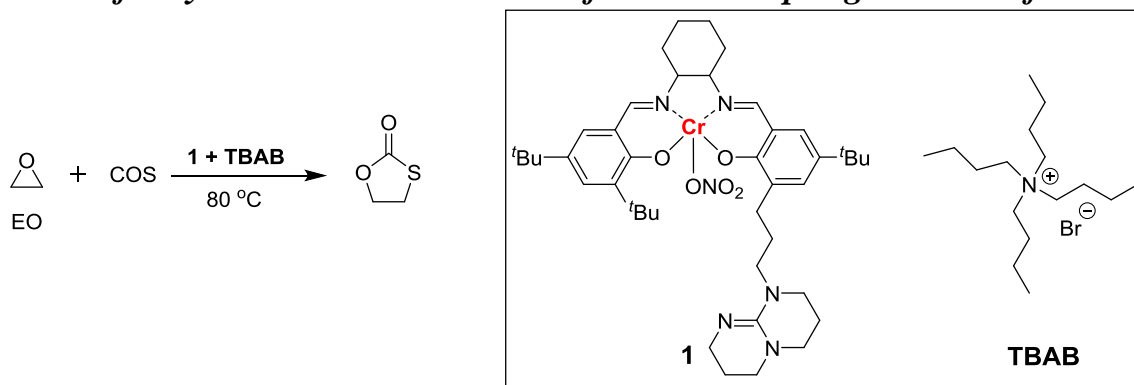
Electrospray Ionization Mass Spectrometry (ESI-MS) ESI mass spectrum of the copolymer in positive ion mode were carried out using a ESI Q-ToF (Waters, USA) mass spectrometer equipped with an orthogonal electrospray source (Z-spray) and referenced against the sample of $(m/z)^+ = 574.3182$ (Sample cone = 5 V).

Gas Chromatography Mass Spectrometry (GC-MS) The analysis of GC-MS was carried out with an Agilent 5977B-7890B.

Thermogravimetry (TGA) Thermo-gravimetric analyses of all resulted polymers were measured on Mettler-Toledo TGA/SDTA851e. The sample was heated at a rate of 10 °C/min.

Tensile Testing The dumbbell-shaped samples with a length of 75 mm, a width of 10.0 mm and a thickness of 2.0 mm were machined from a blend injector machine. The chamber with copolymer was heated to 110 °C and kept for 15 min at vacuum to make the polymer completely liquid. The fused polymer was injected into the mold. After the mold cooled to room temperature, it was opened and the resulting testbar polymer was isolated. The tensile tests were performed according to the ISO 37 standard on an INSTRON-5567A analyzer. The drawing rate was 10 mm/min for the tensile test.

2. Synthesis of ethylene monothiocarbonate from the coupling reaction of COS and EO



A 50 mL autoclave equipped with a magnetic stirrer was heated to 120 °C under vacuum for 8 h, cooled under vacuum to room temperature and moved to a dry box. Complex **1** (7.9 mg, 0.01 mmol), tetrabutyl ammonium bromide (16.1 mg, 0.05 mmol) and ethylene oxide (4.4 g, 100 mmol, 10000 equiv) were added in the autoclave. The autoclave was placed in a bath at 80 °C, and pressurized to COS (7.2 g). After 1 h, the autoclave was cooled and the pressure was slowly vented. A small amount of the resultant copolymer was removed from the autoclave for ^1H NMR analysis (the cyclic product selectivity is >99%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 4.54 (t, $J = 4.8$ MHz, 2H), 3.67 (t, $J = 4.8$ MHz, 2H).

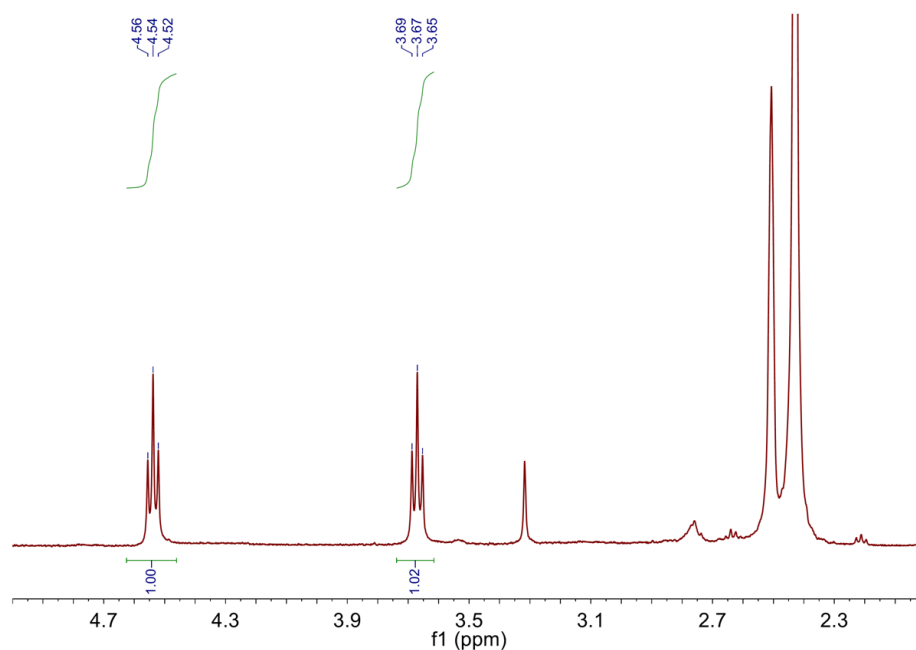


Figure S1. ^1H NMR spectrum of cyclic ethylene monothiocarbonate in $\text{DMSO}-d_6$.

3. *NMR spectra of poly(ethylene monothiocarbonate) from the copolymerizaiton at 110 °C*

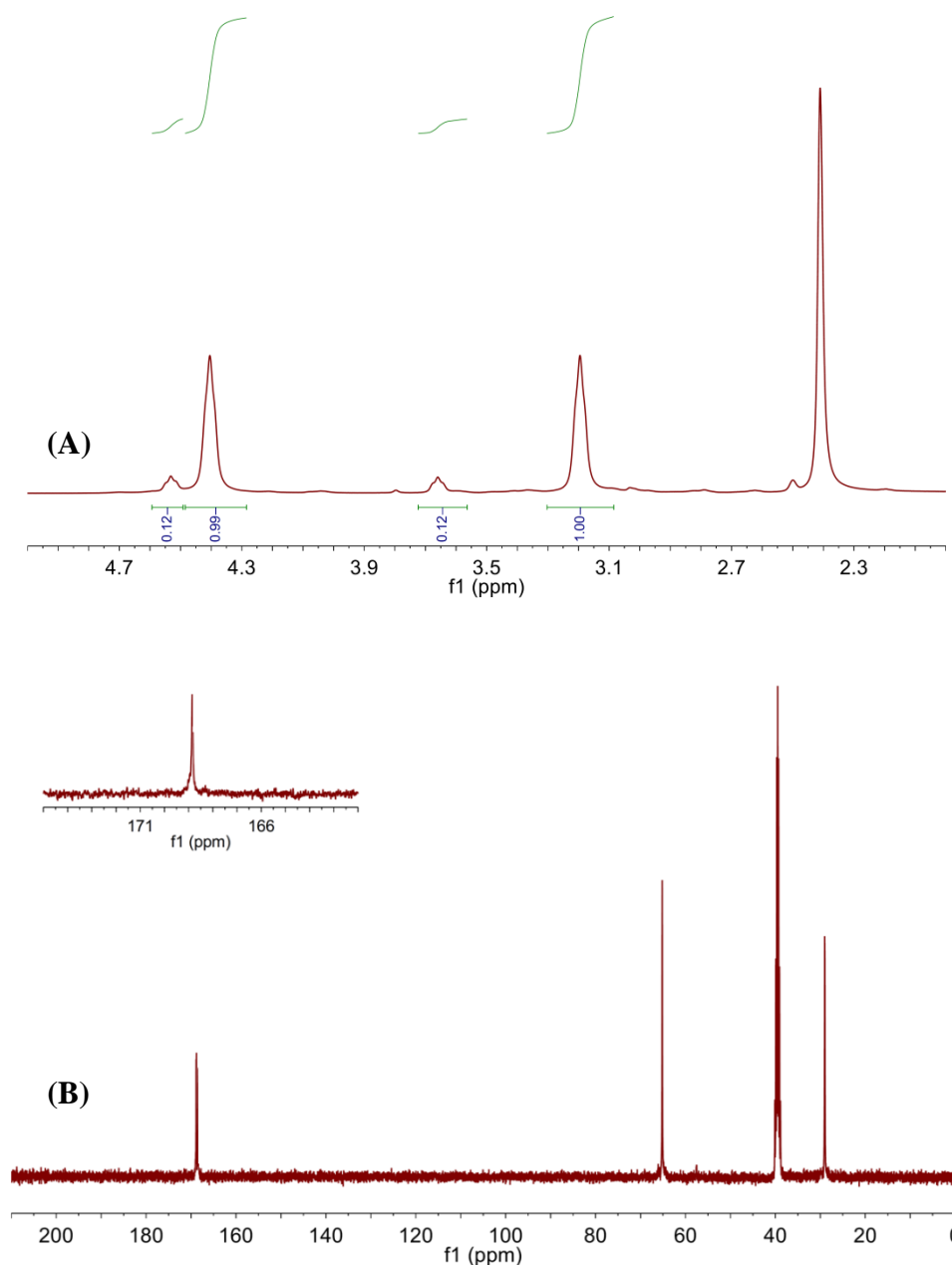


Figure S2. (A) ^1H NMR spectrum of the crude poly(ethylene monothiocarbonate) (400 MHz, $\text{DMSO}-d_6$) (entry 7, Table 1) and (B) ^{13}C NMR spectrum of the purified poly(ethylene monothiocarbonate) (100 MHz, $\text{DMSO}-d_6$, 80 °C) (entry 7, Table 1).

4. DSC curves of poly(ethylene monothiocarbonate)

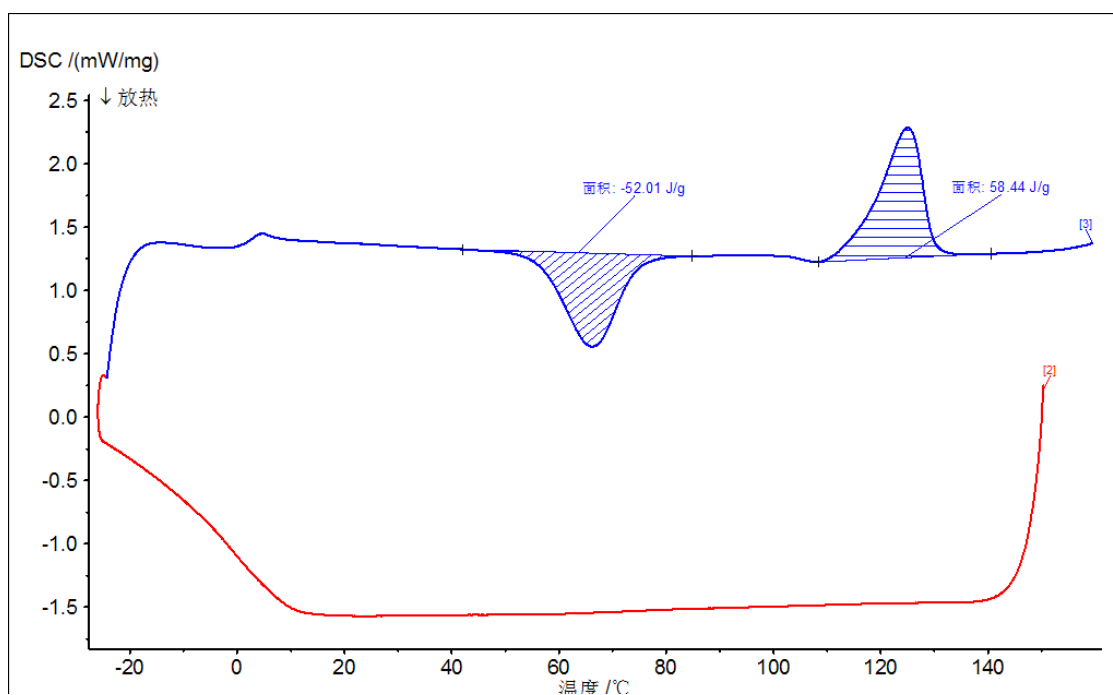


Figure S3. DSC curves of poly(ethylene monothiocarbonate) with a M_n of 193.3 kg/mol (entry 9, Table 1). Under N_2 atmosphere, the sample was annealed at 150 °C for 10 min and cooled to -20 °C at a rate of -15 °C/min (red line), then heated to 160 °C at a rate of 10 °C/min (blue line).

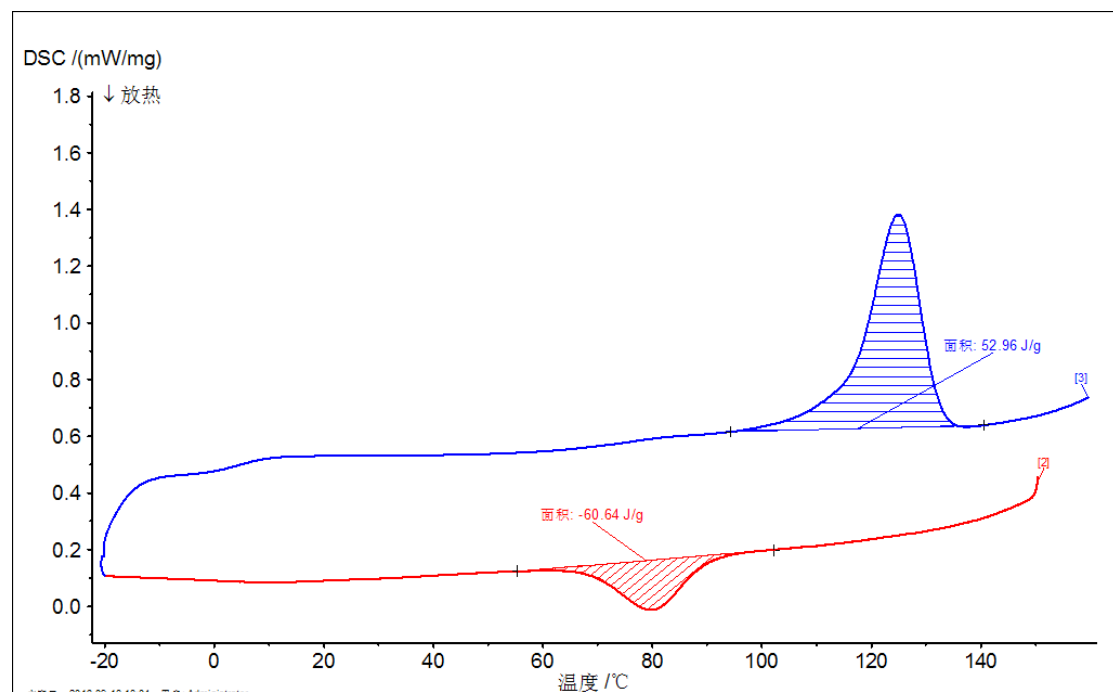


Figure S4. DSC curves of EO/COS copolymer with a M_n of 193.3 kg/mol (entry 9, Table 1). Under N_2 atmosphere, the sample was annealed at 150 °C for 10 min and cooled to -20 °C at a rate of -2.5 °C/min (red line), then heated to 160 °C at a rate of 10 °C/min (blue line).

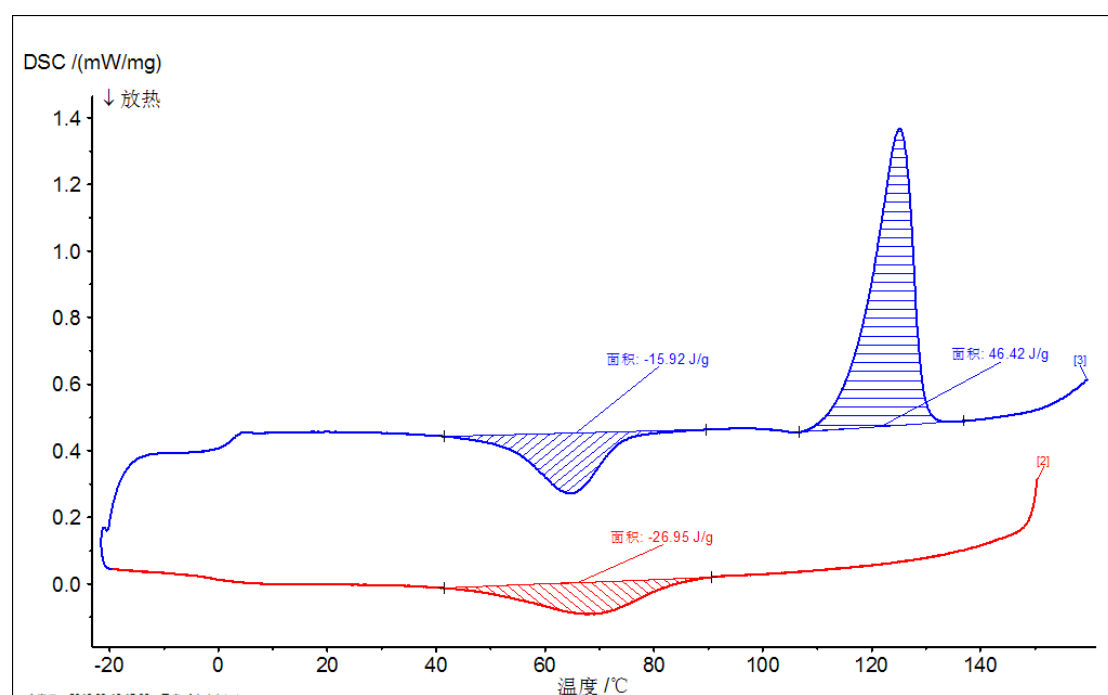


Figure S5. DSC curves of EO/COS copolymer with a M_n of 193.3 kg/mol (entry 9, Table 1). Under N_2 atmosphere, the sample was annealed at 150 °C for 10 min and cooled to -20 °C at a rate of -5 °C/min (red line), then heated to 160 °C at a rate of 10 °C/min (blue line).

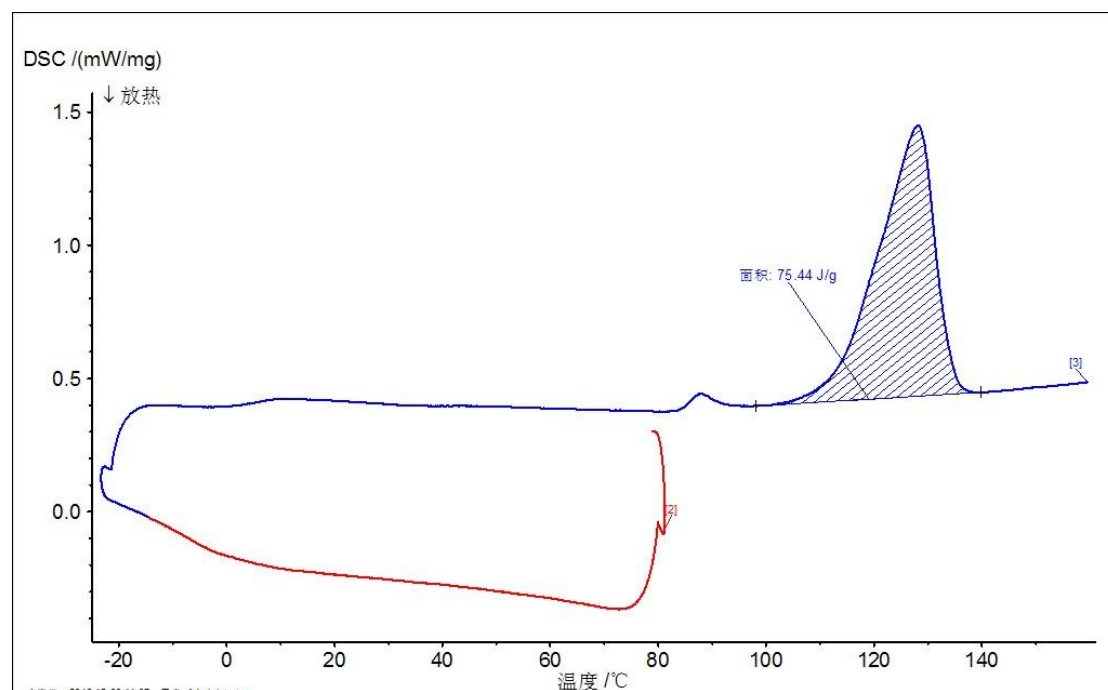
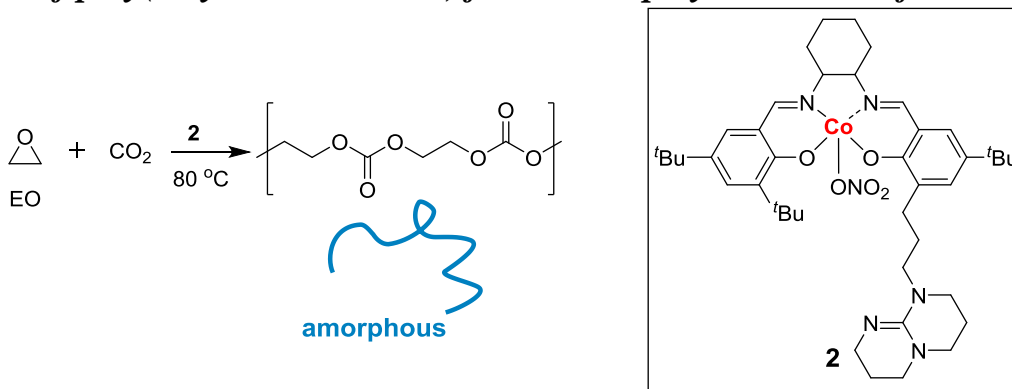


Figure S6. DSC curves of EO/COS copolymer with a M_n of 193.3 kg/mol (entry 9, Table 1). Under N_2 atmosphere, the sample was annealed at 80 °C for 10 min and cooled to -20 °C at a rate of -15 °C/min (red line), then heated to 160 °C at a rate of 10 °C/min (blue line).

5. Synthesis of poly(ethylene carbonate) from the copolymerization of CO₂ and EO



A 50 mL autoclave equipped with a magnetic stirrer was heated to 120 °C under vacuum for 8 h, cooled under vacuum to room temperature and moved to a dry box. Complex **2** (7.9 mg, 0.01 mmol) and ethylene oxide (4.4 g, 100 mmol, 10000 equiv) were added in the autoclave. The autoclave was placed in a bath at 80 °C, and pressurized to CO₂ (1.5 MPa). After 1 h, a small amount of the resultant copolymer was removed from the autoclave for ¹H NMR analysis (the polymer selectivity and carbonate linkages of the resulted copolymer are all >99%) and was also used for GPC analysis (*M_n* = 16.8 kg/mol, PDI = 1.18). The crude polymer was dissolved in a 20 mL CHCl₃/MeOH (5/1, v/v) mixture with 0.5% HCl solution and precipitated from methanol. This process was repeated 3-5 times to completely remove the catalyst, and white polymer was obtained by vacuum-drying. ¹H NMR (400 MHz, CDCl₃): δ 4.38 (m, 4H).

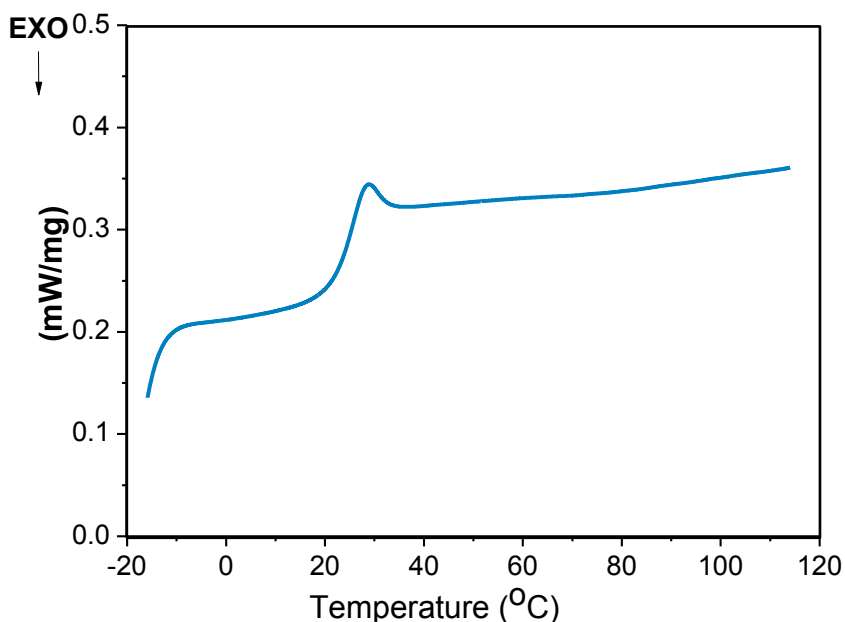
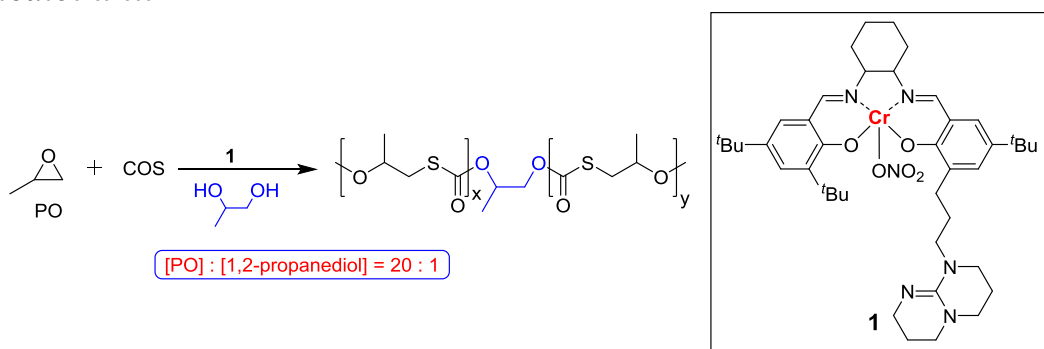


Figure S7. DSC thermograms of poly(ethylene carbonate) with a *M_n* of 16.8 kg/mol

6. Synthesis of the poly(propylene monothiocarbonate) oligomer bearing 1,2-propanediol unit



To a stirred mixture of complex **1** (0.005 mmol, 1 equiv.) was dissolved in propylene oxide (50 mmol, 10000 equiv.) to form a red-brown solution in a nitrogen atmosphere. When the mixture solution was added 1,2-propanediol (2.5 mmol) and 1,2-dimethoxyethane (7 mL), an aliquot was then taken from the mixture to calibrate 1,2-propanediol by GC-MS (Figure S8A). Then the mixture was charged into a pre-dried 50 ml autoclave equipped with a magnetic stirrer under a COS atmosphere. After COS (1.2 MPa) was introduced, the reaction mixture was stirred at 80 °C for 1 h. The autoclave was cooled and the pressure was slowly vented. A small amount of the polymerization mixture was picked out and characterized by GC-MS (Figure S8B). The crude polymer was purified and analyzed by ESI-MS.

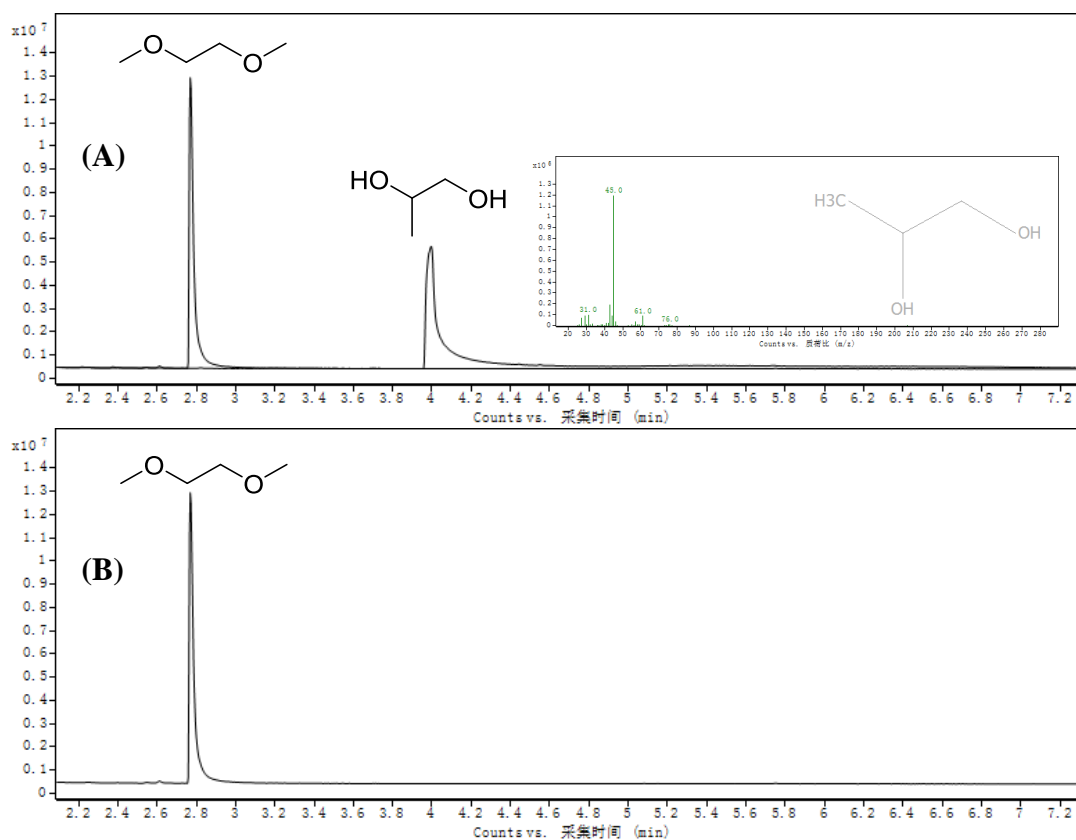


Figure S8. GC mass spectra of (A) the mixture of PO, catalyst **1** and 1,2-propanediol in 1,2-dimethoxyethane and (B) the poly(propylene monothiocarbonate) oligomer in 1,2-dimethoxyethane. (β -Cyclodex-B, 120 °C, isothermal)

7. Synthesis of PEMC-*b*-PPMC-*b*-PEMC copolymer

To a stirred mixture of complex **1** (0.015 mmol, 1 equiv.) was dissolved in propylene oxide (150 mmol, 10000 equiv.) to form a red-brown solution in a nitrogen atmosphere. The mixture solution was added 1,2-propanediol (1.88 mmol) and 1,2-dimethoxyethane (53 mL), then charged into a pre-dried 150 ml autoclave equipped with a magnetic stirrer under a COS atmosphere. After COS (1.2 MPa) was introduced, the reaction mixture was stirred at 80 °C for 1 h. Then a small amount of the polymerization mixture was picked out to determine the conversion of propylene oxide (>99%), the polymer selectivity (>99%), molecular weight ($M_n = 8990 \text{ g}\cdot\text{mol}^{-1}$), and molecular weight distribution ($M_w/M_n = 1.19$). The rest of the polymerization mixture was added ethylene oxide (75 mmol, 5000 equiv.). The reaction mixture was stirred at 80 °C for 5 h. The COS pressure was released, and then a small amount of the polymerization mixture was picked out to determine the polymer selectivity (>99%), molecular weight ($M_n = 13300 \text{ g}\cdot\text{mol}^{-1}$), and molecular weight distribution ($M_w/M_n = 1.18$). The crude polymer was suspended in a 50 mL DMSO and stirred for 10 min at 80 °C. When the mixture was cooled to room temperature, 200 mL methanol was added and filtered. This process was repeated 3-5 times to completely remove the catalyst. The white precipitate was collected and dried in vacuum at 50 °C to constant weight. The obtained copolymer was analyzed by ^1H NMR and ^{13}C NMR spectroscopy, as well as TGA.

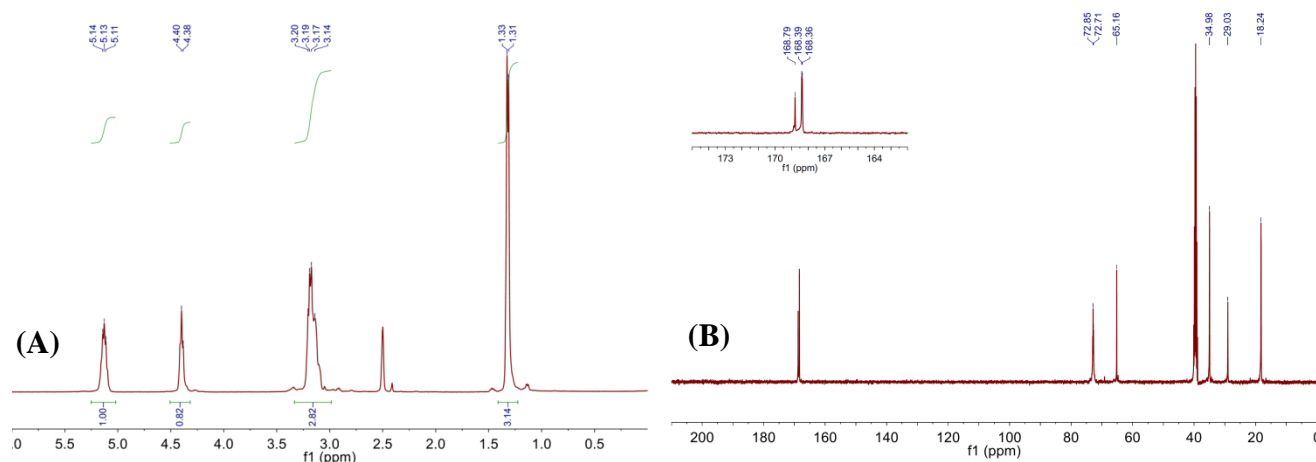


Figure S9. (A) ^1H NMR spectrum of the PEMC-*b*-PPMC-*b*-PEMC copolymer (400 MHz, DMSO- d_6) and (B) ^{13}C NMR spectrum of the PEMC-*b*-PPMC-*b*-PEMC copolymer (100 MHz, DMSO- d_6 , 80 °C).

8. Thermo-gravimetric analysis

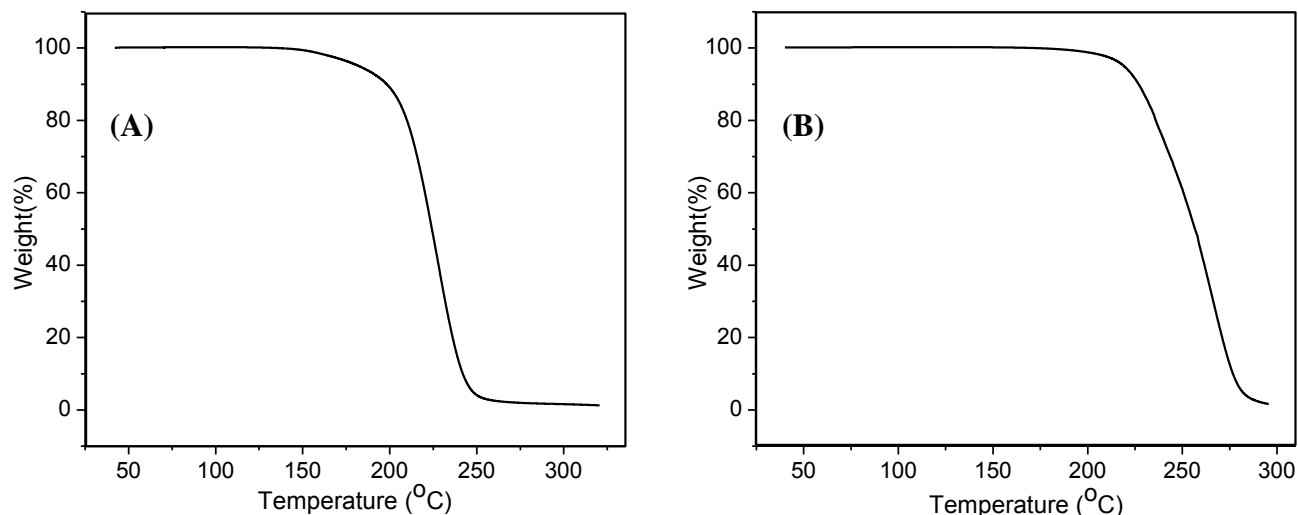


Figure S10 Thermolysis curves of (A) the poly(ethylene monothiocarbonate) with a M_n of 193.3 kg/mol and (B) the PEMC-*b*-PPMC-*b*-PEMC copolymer.

9. The elastic recovery

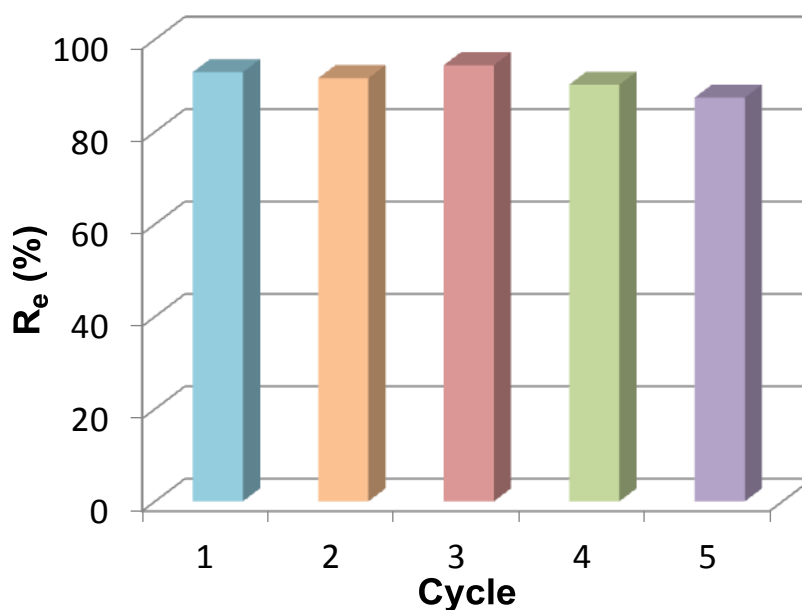


Figure S11. The recovery of the 300% strain after each prestretch. Elasticity was determined from the equation

$$R_e (\%) = (\varepsilon_f - \varepsilon_r) / (\varepsilon_f - \varepsilon_i) \times 100$$

Where ε_i is a small initial strain (where stress equals zero), ε_f is the strain that the polymer is stretched to, and ε_r is the strain recovered (where stress equals zero upon unloading).



Figure S12. A picture of an elastomer being stretched.