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

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Table of Contents

Experimental	S3
Figure S1. ¹ H NMR (DMSO-d6) spectrum of the crude product of entry 1 in Table 1	S5
Figure S2. ¹ H NMR (DMSO-d6) spectrum of the crude product of entry 2 in Table 1	S6
Figure S3. ¹ H NMR (DMSO-d6) spectrum of the crude product of entry 3 in Table 1	S6
Figure S4. ¹ H NMR (DMSO-d6) spectrum of the crude product of entry 4 in Table 1	S7
Figure S5. ¹ H NMR (DMSO-d6) spectrum of the crude product of entry 5 in Table 1	S7
Figure S6. ¹ H NMR (DMSO-d6) spectrum of the crude product of entry 6 in Table 1	S8
Figure S7. ¹ H NMR (DMSO-d6) spectrum of the crude product of entry 7 in Table 1	S 8
Figure S8. ¹ H NMR (DMSO-d6) spectrum of the crude product of entry 8 in Table 1	S9
Figure S9. ¹ H NMR (DMSO-d6) spectrum of the crude product of entry 9 in Table 1	S9
Figure S10. ¹ H NMR (DMSO-d6) spectrum of the crude product of entry 10 in Table 1	S10
Figure S11. ¹ H NMR (DMSO-d6) spectrum of the crude product of entry 11 in Table 1	S10
Figure S12. ¹ H NMR (DMSO-d6) spectrum of the crude product of entry 12 in Table 1	S11
Figure S13. ¹ H NMR (DMSO-d6) spectrum of the crude product of entry 13 in Table 1	S11
Figure S14. ¹ H NMR (DMSO-d6) spectrum of the crude product of entry 14 in Table 1	S12
Figure S15. ¹ H NMR (DMSO-d6) spectrum of the crude product of entry 15 in Table 1	S12
Figure S17. ¹ H NMR (DMSO-d6) spectrum of the crude product of entry 17 in Table 1	S13
Figure S18. Comparison of ¹ H NMR (DMSO-d6) spectra of thermal degradation	
product of the COS-MeAz copolymer of different heating time	S14
Figure S19. ¹ H NMR (CDCl ₃) spectrum of the distilled product from the thermal	

decomposition product of the lead absorption	S14
Figure S20. Video screenshots of the atmospheric copolymerization progress	S15
Figure S21. Original full-range MALDI-TOF-MS spectrum of entry 2 in Table 1	S17
Figure S22. Original full-range MALDI-TOF-MS spectrum of entry 5 in Table 2	S17
Figure S23. The DSC curve with the complete three run of the copolymer of	
entry 2 in Table 1	S18
Figure S24. The powder X-ray diffraction (XRD) curve of the copolymer	S18
Figure S25. The LC-MS spectrum of the cyclic product	S19
Figure S26. The GPC curve of entry 1 in Table 1	S20
Figure S27. The GPC curve of entry 2 in Table 1	S20
Figure S28. The GPC curve of entry 3 in Table 1	S21
Figure S29. The GPC curve of entry 4 in Table 1	S21
Figure S30. The GPC curve of entry 5 in Table 1	S22
Figure S31. The GPC curve of entry 6 in Table 1	S22
Figure S32. The GPC curve of entry 7 in Table 1	S23
Figure S33. The GPC curve of entry 8 in Table 1	S23
Figure S34. The GPC curve of entry 9 in Table 1	S24
Figure S35. The GPC curve of entry 10 in Table 1	S24
Figure S36. The GPC curve of entry 11 in Table 1	S25
Figure S37. The GPC curve of entry 12 in Table 1	S25
Figure S38. The GPC curve of entry 13 in Table 1	S26
Figure S39. The GPC curve of entry 14 in Table 1	S26
Figure S40. The GPC curve of entry 15 in Table 1	S27
Figure S41. The GPC curve of entry 16 in Table 1	S27
Figure S42. The GPC curve of entry 17 in Table 1	S28
Figure S43. The GPC curve of entry 2 in Table 2.	S28
Figure S44. The GPC curve of entry 3 in Table 2.	S29
Figure S45. The GPC curve of entry 4 in Table 2.	S29
Figure S46. The GPC curve of entry 5 in Table 2.	S30
Figure S47. The GPC curve of entry 6 in Table 2.	S30
Figure S48. The XPS spectrum of the black solid in lead recovery	S31
Figure S49. XPS spectra of the Pb 4f and depicted elemental quantification.	S31
Figure S50. XPS spectra of the Cl 2p and depicted elemental quantification.	S32
References	S32

EXPERIMENTAL

Materials. Carbonyl sulfide (COS) (99.9%) was purchased from the APK (Shanghai) Gas Company LTD and used directly. 2-methyl aziridine (MeAz) was synthesized according to literature¹. Anhydrous solvents and all the other reagents were purchased from Energy Chemical and used without further purification.

Characterizations.

Nuclear Magnetic Resonance (NMR). ¹H and ¹³C NMR spectra were measured on a Bruker Avance 500 MHz NMR spectrometer using deuterated dimethyl sulfoxide as solvent and tetramethylsilane (TMS, $\delta = 0$) as internal reference.

Gel Permeation Chromatography (GPC). The number- (M_n) and weight- (M_w) average molecular weights and dispersity ($D = M_w/M_n$) of the polymers were estimated by a Waters 1515 gel permeation chromatography system. DMF/LiBr solution (0.05 M LiBr) was used as eluent at a flow rate of 1 mL/min.

Thermogravimetry (TG). Thermogravimetric analysis was carried out on a Netzsch TG 209 F3 and the sample was heated from room temperature to 800 °C at a rate of 10 °C/min under nitrogen atmosphere.

Differential Scanning Calorimetry (DSC). The glass transition temperature (T_g) of the resultant polymers were determined by using a Mettler Toledo differential scanning calorimetry. The sample was heated from room temperature to 195 °C at a rate of 10 °C/min and kept isothermal for 3 min, then cooled to -80 °C at a rate of -10 °C/min and kept isothermal for 3 min, finally heated from -80 °C to 195 °C at a rate of 10 °C/min. T_g was determined from the third run.

Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry (MALDI-TOF-MS). MALDI-TOF spectra were obtained on a Bruker Microflex (nitrogen laser of 337 nm) operating in linear mode. The polymer sample (entry 2, Table 1) solutions (10 mg/mL DMF) and a DCTB solution (matrix, 10 mg/mL THF) were mixed in a 10:1 volume ratio, 1 μL of which was then spotted onto the MALDI-TOF sample plate before being air-dried.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES). The concentration of metal ion was determined on a ICP-AES PE Optimia8000.

Liquid Chromatography-Mass Spectrum (LC-MS). The Mass spectrum of the cyclic product was obtained on a Agilent 1260/6120 liquid chromatography-sass instrument. Methanol was used as solvent.

Polymerization. A typical synthetic procedure for the preparation of **COS-MeAz copolymer** is given below as an example (entry 2 in Table 1). MeAz (0.3 mL, 4.20 mmol) and THF (1 mL) were sealed in Schlenk tubes and used through a Schlenk Line under N₂. They were added into a 10 ml autoclave equipped with a magnetic stirrer under air atmosphere, after seal of the autoclave, 2 MPa COS was added, then the reaction mixture was stirred at 20 °C for 2 hours. The autoclave was cooled with ice water after the reaction, then the COS was released slowly. A portion of the crude product was sent for NMR measurement to determine the selectivity of the copolymer. The remaining crude product was precipitated in methanol three times (3 × 50 mL), and the precipitate was dried in a vacuum oven at 60 °C for 12 h to obtain pure product.

Characterization data of monomer, copolymer and cyclic product.

Characterization data for **2-methyl aziridine** (*MeAz*) *monomer.* ¹H NMR (500 MHz, DMSO-d6), δ (TMS, ppm): 1.78 (s, 1H, CH), 1.51 (s, 1H, CH₂), 1.04 (d, 1H, CH₂; 3H, CH₃), 0.86 (s, 1H, NH). There are overlaps between the three peaks of one proton of methene group, three protons of methyl group and one proton of NH group. The result is corresponding with literature.²

Characterization data for **COS-MeAz copolymer.** As for entry 2 in Table 1, a white solid was obtained in 95% yield. $M_w = 15.2 \text{ kg/mol}, M_w/M_n = 1.68$. ¹H NMR (500 MHz, DMSO-d6), δ (TMS, ppm): 8.15 (s, 1H, NH), 3.81 (m, 1H, CH), 2.87 (m, 2H, CH₂), 1.09 (d, 3H, CH₃). ¹³C NMR (125 MHz, CDCl₃), δ (TMS, ppm): 164.69 (C=O), 47.71, 34.32, 19.54.

Characterization data for Cyclic Product. A clear light yellow liquid. ¹H NMR (500 MHz, DMSOd6), δ (TMS, ppm): 8.07 (s, 1H, N*H*), 3.86 (m, 1H, C*H*), 3.46 (m, 1H, C*H*₂), 2.98 (m, 1H, C*H*₂), 1.19 (d, 3H, C*H*₃). ¹³C NMR (125 MHz, CDCl₃), δ (TMS, ppm): 175.66 (C=O), 51.40, 36.77, 20.74.

¹H and ¹³C NMR spectra



Figure S1. ¹H NMR (DMSO-d6) spectrum of the crude product of entry 1 in Table 1.

The resonance of methine proton in copolymer and the cyclic product appeared at 3.80 ppm and 3.82 ppm, respectively, and they were assigned to peak **b** and **b**' which have an overlap with each other. The resonance of the two methylene protons of the cyclic product were found at 3.46 ppm and 2.99 ppm, and they were assigned to peaks **c**'. As the peak **c**' at 3.46 ppm was isolated and could be well-defined integrated (set Area to 1), we assumed that the integral of peak **b**' and peak **c**' (3.46 ppm) were the same, then the integral Area of **b**' is 1. The integral of peak **b** could be achieved by the Subtract 1 with the total integral of **b** and **b**' (Area = 3.45 in Figure S1). Copolymer selectivity (%) = (A_{3.28-3.80} - A_{3.46})/A_{3.28-3.80} = 71%.



Figure S2. ¹H NMR (DMSO-d6) spectrum of the crude product of entry 2 in Table 1.



Figure S3. ¹H NMR (DMSO-d6) spectrum of the crude product of entry 3 in Table 1.



Figure S4. ¹H NMR (DMSO-d6) spectrum of the crude product of entry 4 in Table 1.



Figure S5. ¹H NMR (DMSO-d6) spectrum of the crude product of entry 5 in Table 1.



Figure S6. ¹H NMR (DMSO-d6) spectrum of the crude product of entry 6 in Table 1.



Figure S7. ¹H NMR (DMSO-d6) spectrum of the crude product of entry 7 in Table 1.



Figure S8. ¹H NMR (DMSO-d6) spectrum of the crude product of entry 8 in Table 1.



Figure S9. ¹H NMR (DMSO-d6) spectrum of the crude product of entry 9 in Table 1.



Figure S10. ¹H NMR (DMSO-d6) spectrum of the crude product of entry 10 in Table 1.



Figure S11. ¹H NMR (DMSO-d6) spectrum of the crude product of entry 11 in Table 1.



Figure S12. ¹H NMR (DMSO-d6) spectrum of the crude product of entry 12 in Table 1.



Figure S13. ¹H NMR (DMSO-d6) spectrum of the crude product of entry 13 in Table 1.



Figure S14. ¹H NMR (DMSO-d6) spectrum of the crude product of entry 14 in Table 1.



Figure S15. ¹H NMR (DMSO-d6) spectrum of the crude product of entry 15 in Table 1.



Figure S16. ¹H NMR (DMSO-d6) spectrum of the crude product of entry 16 in Table 1.



Figure S17. ¹H NMR (DMSO-d6) spectrum of the crude product of entry 17 in Table 1.



Figure S18. Comparison of ¹H NMR (DMSO-d6) spectra (in full region) of thermal degradation product of the COS-MeAz copolymer of different heating time.



Figure S19. ¹H NMR (CDCl₃) spectrum of the distilled product from the thermal decomposition product of the lead absorption.

Video screenshots of the atmospheric copolymerization progress.

The reaction was carried out in a round bottom flask and COS was bubbled into the flask from an air bag through a long needle to the bottom. The flask was sealed with a rubber plug. We recorded video of the five-minutes polymerization progress, and we took the screenshots at 1 second, 0.5 min, 1 min, 1.5 min, 2 min, 2.5 min, 3 min, 3.5 min, 4 min, 4.5 min and 5 min. Shown as follows:





Figure S20. Video screenshots of the atmospheric copolymerization progress.





Figure S21. Original full-range MALDI-TOF-MS spectrum of entry 2 in Table 1.



Figure S22. Original full-range MALDI-TOF-MS spectrum of entry 5 in Table 2.



Figure S23. The DSC curve with the complete three run of the copolymer of entry 2 in Table 1.



Figure S24. The powder X-ray diffraction (XRD) curve of the copolymer.



Figure S25. The LC-MS spectrum of the cyclic product.



Figure S26. The GPC curve of entry 1 in Table 1.



Figure S27. The GPC curve of entry 2 in Table 1.



Figure S28. The GPC curve of entry 3 in Table 1.



Figure S29. The GPC curve of entry 4 in Table 1.



Figure S30. The GPC curve of entry 5 in Table 1.



Figure S31. The GPC curve of entry 6 in Table 1.



Figure S32. The GPC curve of entry 7 in Table 1.



Figure S33. The GPC curve of entry 8 in Table 1.



Figure S34. The GPC curve of entry 9 in Table 1.



Figure S35. The GPC curve of entry 10 in Table 1.



Figure S36. The GPC curve of entry 11 in Table 1.



Figure S37. The GPC curve of entry 12 in Table 1.



Figure S38. The GPC curve of entry 13 in Table 1.



Figure S39. The GPC curve of entry 14 in Table 1.



Figure S40. The GPC curve of entry 15 in Table 1.



Figure S41. The GPC curve of entry 16 in Table 1.



Figure S42. The GPC curve of entry 17 in Table 1.



Figure S43. The GPC curve of entry 2 in Table 2.



Figure S44. The GPC curve of entry 3 in Table 2.



Figure S45. The GPC curve of entry 4 in Table 2.



Figure S46. The GPC curve of entry 5 in Table 2.



Figure S47. The GPC curve of entry 6 in Table 2.

XPS spectrum



Figure S48. The XPS spectrum of the black solid in lead recovery.



Figure S49. XPS spectra of the Pb 4f and depicted elemental quantification.



Figure S50. XPS spectra of the Cl 2p and depicted elemental quantification.

References:

1. Li, G.; Liu, Y.; Zhang, K.; Shi, J.; Wan, X.; Cao, S. Effect of salen-metal complexes on thermosensitive reversibility of stimuli-responsive water-soluble poly(urethane amine)s. *J. Appl. Polym. Sci.* **2013**, *129*, 3696–3703.

2. Osamu, I.; Yoshihito, K.; Takao, I. Synthesis of thermoresponsive polyurethane from 2methylaziridine and supercritical carbon dioxide. *Angew. Chem. Int. Ed.* **2004**, *43*, 717–719.