Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Straightforward synthesis of aliphatic polydithiocarbonates from commercially available starting materials

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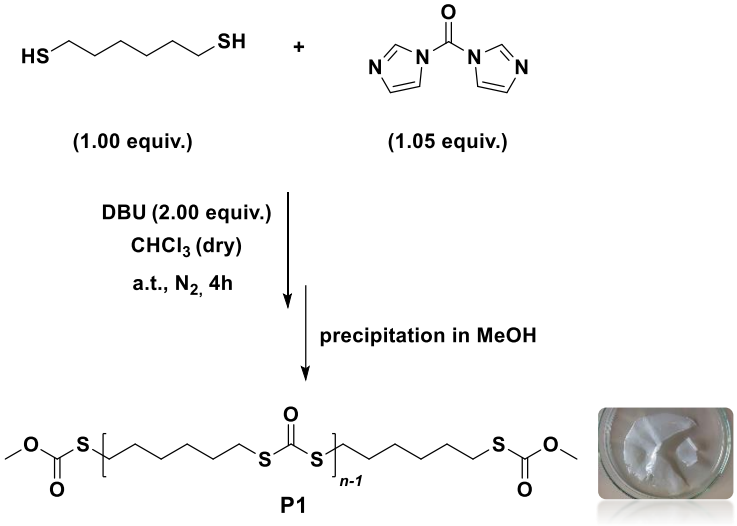
Section A. Materials

The compounds were synthesized using the following starting materials from the stated manufacturers with given purities and without further purification: 1,1´-carbonyldiimidazole (ACROS ORGANICS, 97%), 1,6-hexamethylenedithiol (ALFA AESAR, 97%), 1,8-diazabicyclo[5.4.0]undec-7-ene (MERCK. >98%), 3,6-dioxa-1,8-octanedithiol (SIGMA ALDRICH, 95%), methanol (FISCHER CHEMICAL, >99.9%), chloroform (SIGMA ALDRICH, >99%), dichloromethane (DCM, Acros Organics, >99.9%).

Section B. Synthetic Procedures

B.1. Synthetic procedure and characterization of P1

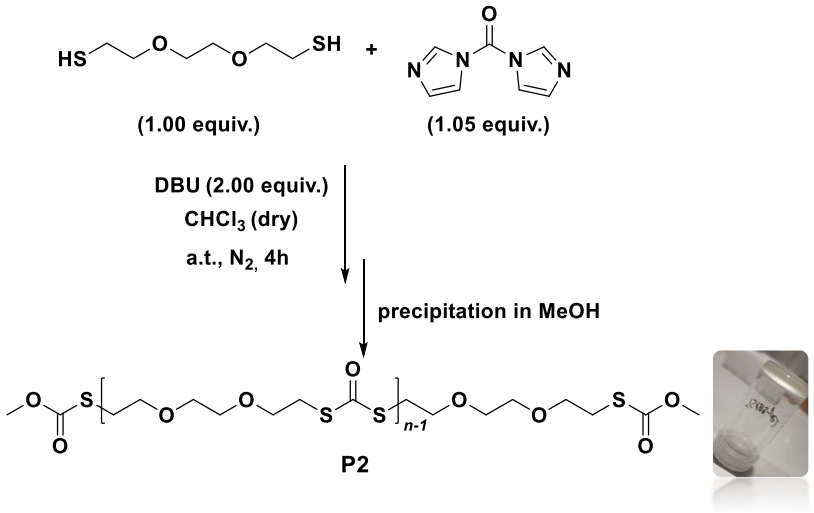


First, a 5.00 mL crimp vial was charged with 1,1´-carbonyldiimidazole (566 mg, 3.49 mmol, 1.05 equiv.) and a stirring bar. After purging the reaction vessel with nitrogen for 5 minutes, dry chloroform (0.83 M), 1,6-hexamethylenedithiol (500 mg, 3.33 mmol, 0.51 mL, 1.00 equiv.) and 1,8-Diazabicyclo[5.4.0]undec-7-ene (1.02 g, 1.00 mL, 6.70 mmol, 2.00 equiv.) were sequentially added under a continuous nitrogen flow. The reaction mixture was stirred under inert atmosphere for 4 hours at ambient temperature. Subsequently, **P1** was precipitated twice in ice cold methanol (150 mL), filtrated, and redissolved in DCM (10 mL). After evaporation of the solvent under reduced pressure, the obtained polymer **P1** was additionally dried under reduced pressure at 40°C for 12 hours. The desired product was obtained as a white polymer film (Yield = 81 %).

^{1}H NMR (400 MHz, $CDCl_3$): depicted in the main text in Figure 1D

^{13}C NMR (100 MHz, $CDCl_3$): shown in Section D. Additional Data, Figure S4

B.2. Synthetic procedure and characterization of P2

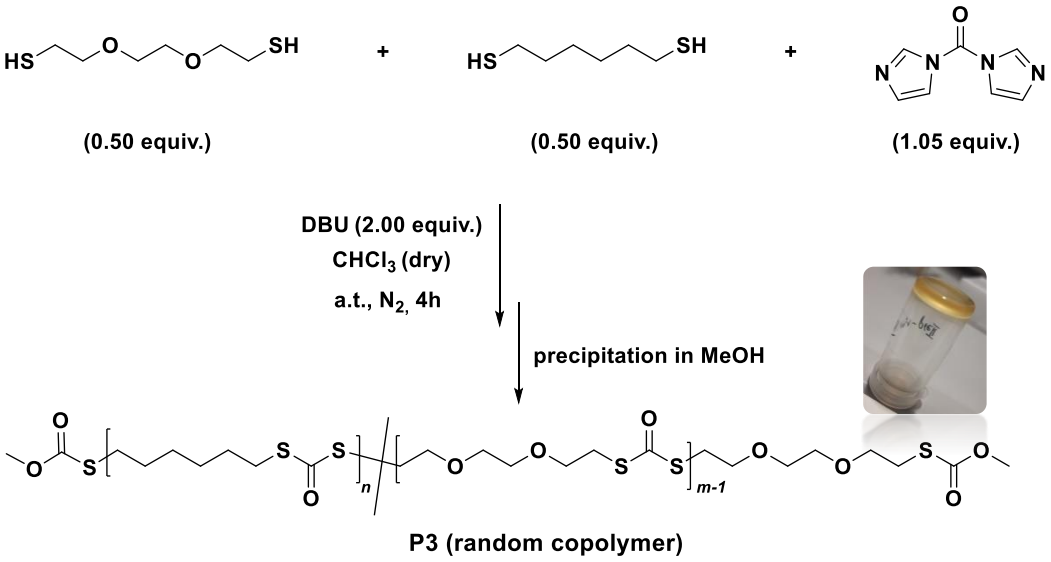


First, a 5.00 mL crimp vial was charged with 1,1´-carbonyldiimidazole (566 mg, 3.49 mmol, 1.05 equiv.) and a stirring bar. After purging the reaction vessel with nitrogen for 5 minutes, dry chloroform (0.83 M), 3,6-dioxa-1,8-octanedithiol (607 mg, 3.33 mmol, 0.55 mL, 1.00 equiv.) and 1,8-Diazabicyclo[5.4.0]undec-7-ene (1.02 g, 1.00 mL, 6.70 mmol, 2.00 equiv.) were sequentially added under a continuous nitrogen flow. The reaction mixture was stirred under inert atmosphere for 4 hours at ambient temperature. Subsequently, **P2** was precipitated twice in ice cold methanol (150 mL), filtrated, and redissolved in DCM (10 mL). After evaporation of the solvent under reduced pressure, the obtained polymer **P2** was additionally dried under reduced pressure at 40°C for 12 hours. The desired product was obtained as a white highly viscous liquid (Yield = 92 %).

^{1}H NMR (400 MHz, $CDCl_3$): shown in the main text in Figure 2A

^{13}C NMR (100 MHz, $CDCl_3$): shown in Section D. Additional Data, Figure S7

B.3. Synthetic procedure and characterization of P3



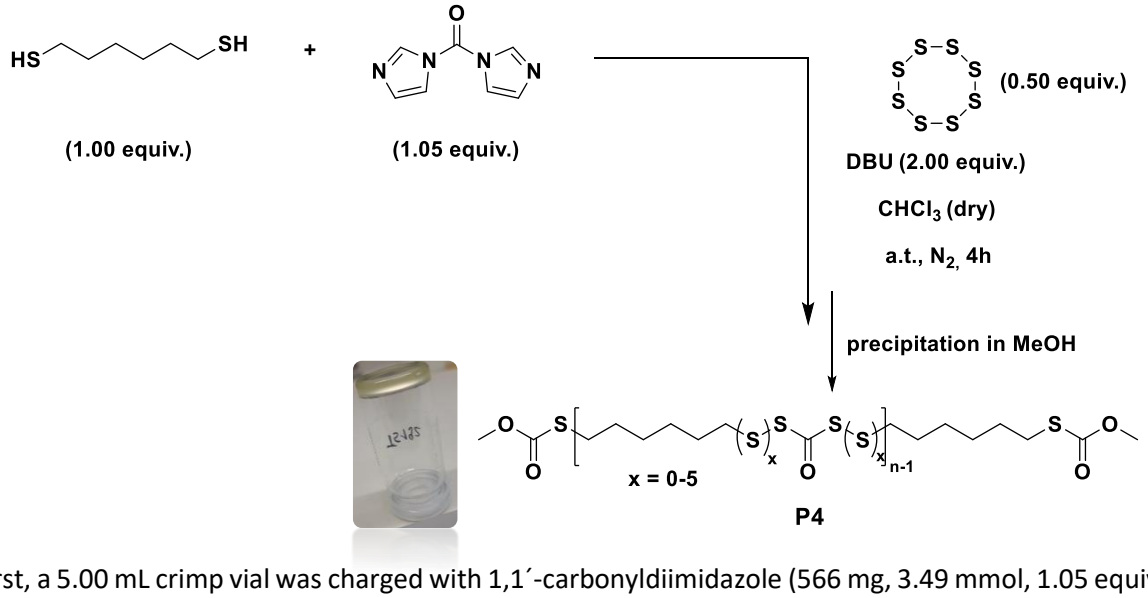
First, a 5.00 mL crimp vial was charged with 1,1´-carbonyldiimidazole (566 mg, 3.49 mmol, 1.05 equiv.) and a stirring bar. After purging the reaction vessel with nitrogen for 5 minutes, dry chloroform (0.83

M), 1,6-hexamethylenedithiol (309 mg, 1.70 mmol, 0.26 mL, 0.50 equiv.) and 1,8-Diazabicyclo[5.4.0]undec-7-ene (0.51 g, 0.50 mL, 3.35 mmol, 1.00 equiv.) were sequentially added under a continuous nitrogen flow. Simultaneously, a second vial was charged with 3,6-dioxa-1,8-octanedithiol (302 mg, 0.27 mL, 1.66 mmol, 0.50 equiv.), dry chloroform (0.8 M) and Diazabicyclo[5.4.0]undec-7-ene (0.51 g, 0.50 mL, 3.35 mmol, 1.00 equiv.) under inert atmosphere. After stirring for 5 minutes at ambient temperature, the reaction mixture of vial 2 was transferred into vial 1. Subsequently, the resulting reaction solution was additionally stirred under inert atmosphere for 4 hours at ambient temperature. Finally, copolymer **P3** was precipitated twice in ice cold methanol (150 mL), filtrated, and redissolved in DCM (10 mL). After evaporation of the solvent under reduced pressure, the obtained copolymer **P3** was additionally dried for 12 hours under reduced pressure at 40°C. The desired product was obtained as a yellow solid (Yield = 82%).

^{1}H ^{1}H NMR (400 MHz, $CDCl_3$): shown in the main text in Figure 2A

^{13}C NMR (100 MHz, $CDCl_3$): shown in Section D. Additional Data, Figure S10

B.4. Synthetic procedure and characterization of P4



First, a 5.00 mL crimp vial was charged with 1,1´-carbonyldiimidazole (566 mg, 3.49 mmol, 1.05 equiv.) and a stirring bar. After purging the reaction vessel with nitrogen for 5 minutes, dry chloroform (0.83 M), 1,6-hexamethylenedithiol (500 mg, 3.33 mmol, 0.51 mL, 1.00 equiv.), elemental sulfur (53.4 mg, 1.67 mmol, 0.50 equiv.) and 1,8-Diazabicyclo[5.4.0]undec-7-ene (1.02 g, 1.00 mL, 6.70 mmol, 2.00 equiv.) were sequentially added under a continuous nitrogen flow. The reaction mixture was stirred under inert atmosphere for 4 hours at ambient temperature. Subsequently, **P4** was precipitated twice in ice cold methanol (150 mL), filtrated and redissolved in DCM (10 mL). After evaporation of the solvent under reduced pressure, the obtained polymer **P4** was additionally dried under reduced pressure at 40°C for 12 hours. The desired product was obtained as a yellowish solid (Yield = 65 %).

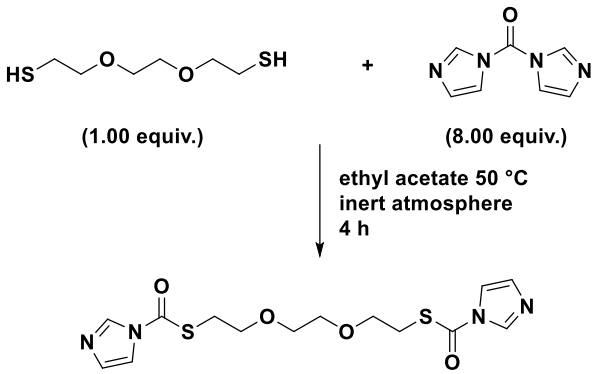
^{1}H NMR (400 MHz, $CDCl_3$): shown in Section D. Additional Data, Figure S13

^{13}C NMR (100 MHz, $CDCl_3$): shown in Section D. Additional Data, Figure S14

B.5. Synthesis of DBU-Imidazole ionic liquid

First, a 5.00 mL crimp vial was charged with Imidazole (453 mg, 0.368 mL, 6.66 mmol, 1.00 equiv.) and a stirring bar. After purging the reaction vessel with nitrogen for 5 minutes, dry chloroform (4 mL) and 1,8-Diazabicyclo[5.4.0]-7-undecene (1.01 g, 0.994 mL, 6.66 mmol, 1.01 equiv) were sequentially added under a continuous nitrogen flow. The mixture was stirred for a 5 min and an aliquot was withdrawn. The aliquot was dissolved in sufficient amount of deuterated Chloroform and was further subjected to NMR analysis.

B.6. Synthetic procedure of 3,6-Dioxa-1,8-octanedithio-*bis*-carbonylimidazole



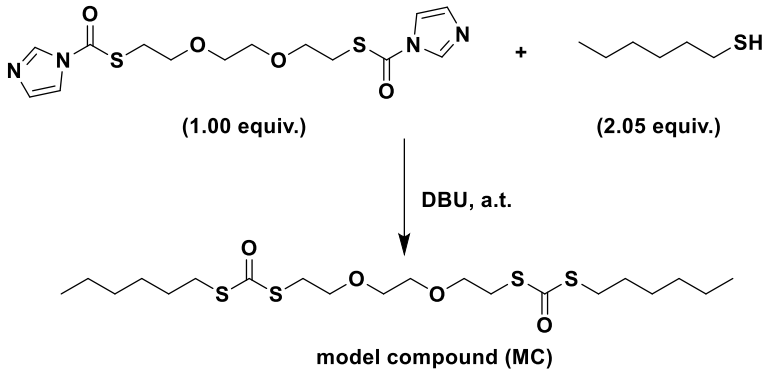
3,6-Dioxa-1,8-octanedithio-*bis*-carbonylimidazole

1,1'-carbonyldiimidazole (8.00 g, 49.2 mmol, 8.00 equiv.) was suspended in ethyl acetate (50.00 mL) under continuous nitrogen flow by stirring for 5 minutes before it was heated up to 65 °C. After the reaction mixture became a clear solution 3,6-Dioxa-1,8-octanedithiol (1.12 g, 1.00 mL, 6.14 mmol, 1.00 equiv.) was added dropwise under a constant N_2-flow. The mixture was stirred for 2 h at 65 °C. Subsequently, the mixture was cooled down to ambient temperature before the solvent evaporated. The residue was dissolved in deionized water (100 mL) and the aqueous phase was extracted with DCM (6 x 50 mL). The combined organic phases were washed with deionized water (3 x 50 mL) and brine (1 x 50mL) and dried over Na_2SO_4. After evaporation of the solvent, the resulting product was dried under reduced pressure at 50°C for 12 hours. **3,6-Dioxa-1,8-octanedithio-*bis*-carbonylimidazole** was obtained as an orange highly viscous liquid in a quantitative yield.

^{1}H NMR (400 MHz, $CDCl_3$): shown in Section D. Additional Data, Figure S25

^{13}C NMR (100 MHz, $CDCl_3$): shown in Section D. Additional Data, Figure S26

B.7. Synthetic procedure of model compound (MC)



First, a 5.00 mL crimp vial was charged with 3,6-Dioxa-1,8-octanedithio-*bis*-carbonylimidazole (300 mg, 0.81 mmol, 1.00 equiv.) and a stirring bar. After purging the vessel with nitrogen for 5 minutes, dry chloroform (0.81 M), hexane-1-thiol (142 mg, 0.23 mL, 1.62 mmol, 2.05 equiv.) and 1,8-Diazabicyclo[5.4.0]undec-7-ene (247 g, 0.242 mL, 1.62 mmol, 2.00 equiv.) were sequentially added under a continuous nitrogen flow. The reaction mixture was stirred under inert atmosphere for 4 hours at ambient temperature. Sequentially, the solvent was evaporated, and the residue was redissolved in DCM (20 mL). The organic phase was washed with water (4 x 50 mL) and brine (1 x 50 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure. No further purification was performed. **MC** was obtained as a yellowish liquid and further utilized for the analysis.

^{1}H NMR (400 MHz, $CDCl_3$): shown in Section D. Additional Data, Figure S27

^{13}C NMR (100 MHz, $CDCl_3$): shown in Section D. Additional Data, Figure S28

Section C. Measurements and Analysis

C.1. Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR spectra were recorded on Bruker Avance 400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer. Spectra were referenced on residual solvent signal according to Nudelman *et al*: 7.26 ppm for $CDCl_3$. Deuterated solvents were purchased from Euriso-TOP and used without further purification.

C.2. Size Exclusion Chromatography (SEC)

The apparent number average molar mass (M_n) and the molar mass distribution [Đ (dispersity) = M_w/M_n] values of the polymers were determined using a 7 Size Exclusion Chromatography (SEC) system equipped with Shimadzu LC20AD pump, Wyatt Optilab rEX refractive index detector and four PLgel 5µ Mixed-C columns. The characterization was performed at 35 °C in THF with a flow rate of 1 mL·min-1 with a sample concentration of 2 $g \cdot L^{-1}$, which was filtered over a 0.2 µL filter prior to the measurement. The molecular weight calibration was based on sixteen narrow molecular weight linear polymethylmethacrylate standards from Polymer Laboratories.

C.3. Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR)

All IR measurements were performed on a Bruker Alpha ATR-IR Spectrometer with a range of 500 to 4000 cm^{-1} at ambient temperature.

C.4. Differential Scanning Calorimetry (DSC)

Thermal properties were measured on a TA DSC 2500 with a heat rate of 10 $K \cdot min^{-1}$ between -80 °C and 200 °C in TA Tzero sample holders. The glass transition temperature (T_g) and melting temperature (T_m) were determined in the second heating run to eliminate possible interference from the polymer's thermal history.

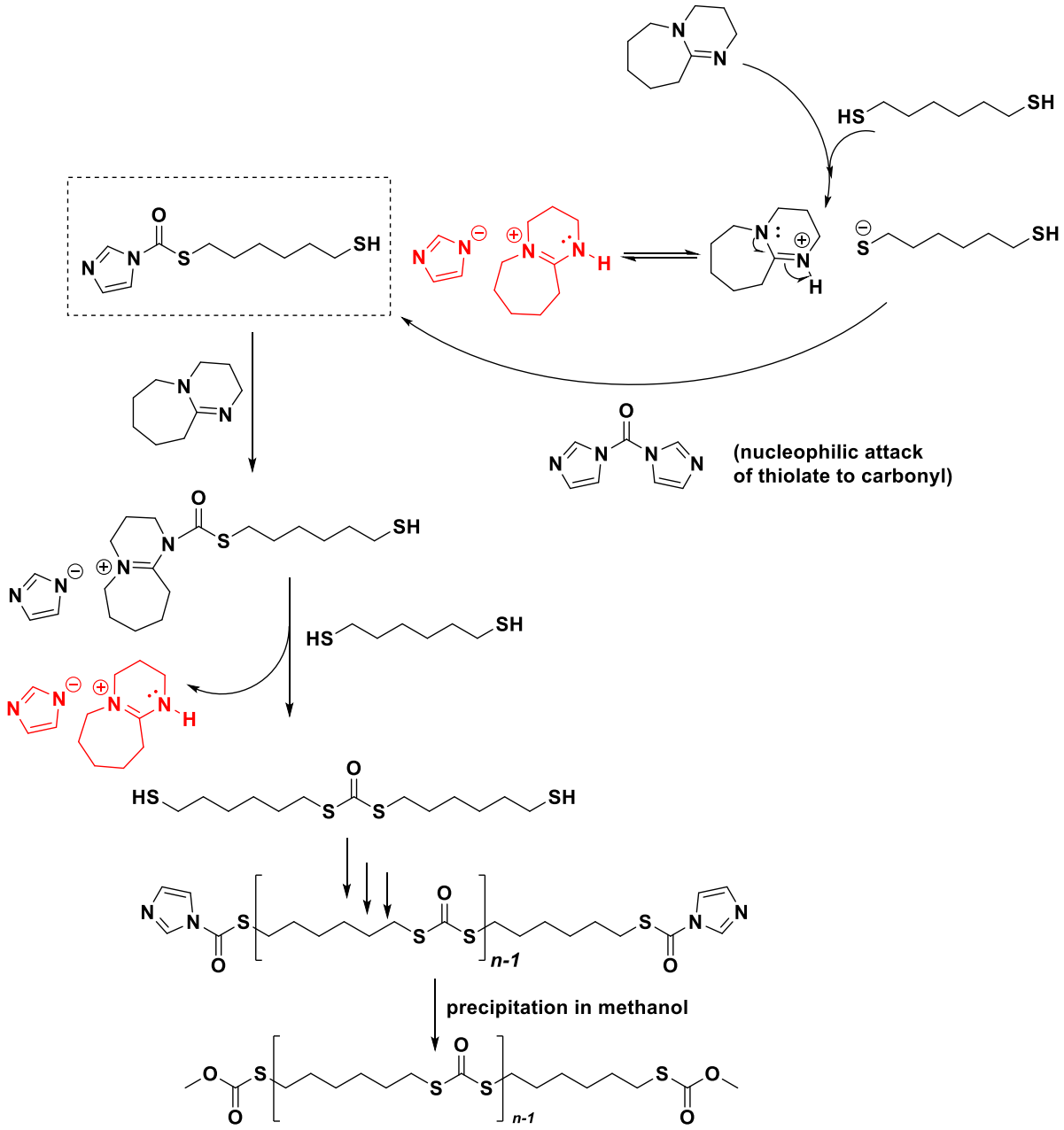
C.5. Thermogravimetric Analysis (TGA)

TGA measurements were carried out on the TA Instruments TGA 5500 under nitrogen atmosphere using platinum TGA sample pans and with a heating rate of 10 K min^{-1} over a temperature range from 25 to 800 °C.

C.6. Ultraviolet-visible (UV-Vis) and Fluorescence spectroscopy

UV-vis spectra in the range of 200−800 nm and fluorescence spectra in the range of 300 to 750 nm were recorded on a fluorescence and absorbance spectrometer, Duetta, Horiba Scientific in DCM at 298 K.

Section D. Additional Data



Scheme S1 Proposed mechanism for the straightforward synthesis of polydithiocarbonates with CDI and dithiols in the presence of DBU in order to provide better understanding for the employed reaction conditions.

Table S1 Polymerization approaches containing different equivalents of diazabicyclo[5.4.0]undec-7-ene (DBU).

	Equiv. M1	Equiv. CDI	Equiv. DBU	Reaction time (h)	Reaction temp. (°C)	Number average of molar mass (M_n)[a]	Dispersity ($Đ$)[a]
P1	**1.00**	**1.05**	**2.00**	**4**	**a.t.**	**26.400 g·mol^{-1}**	**2.5**
P1.1	**1.00**	**1.05**	**0.10**	**4**	**a.t.**	**10.400 g·mol^{-1}**	**1.9**
P1.2	**1.00**	**1.05**	**0.01**	**4**	**a.t.**	**8.500 g·mol^{-1}**	**1.9**
P1.3	**1.00**	**1.05**	**0.00**	**4**	**a.t.**	**4.500 g·mol^{-1}**	**1.9**

[a] M_n and $Đ$ (M_w/M_n) were determined by SEC in tetrahydrofuran (THF) on the basic of polymethylmethacrylate (PMMA) standard.

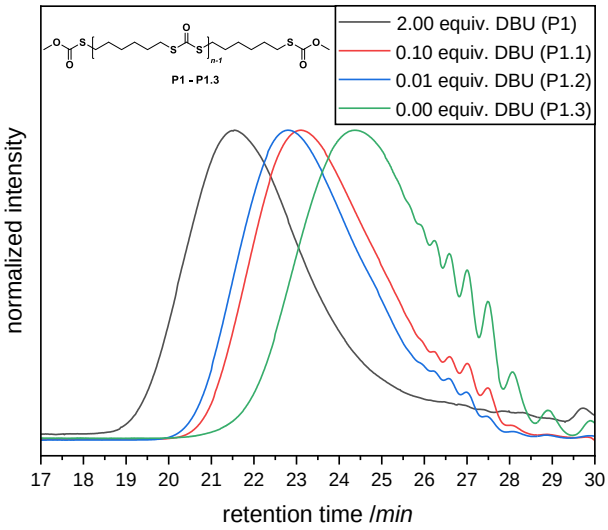


Figure S1 SEC traces of **P1** to **P1.3** in THF + 0.2 % w/v BHT.

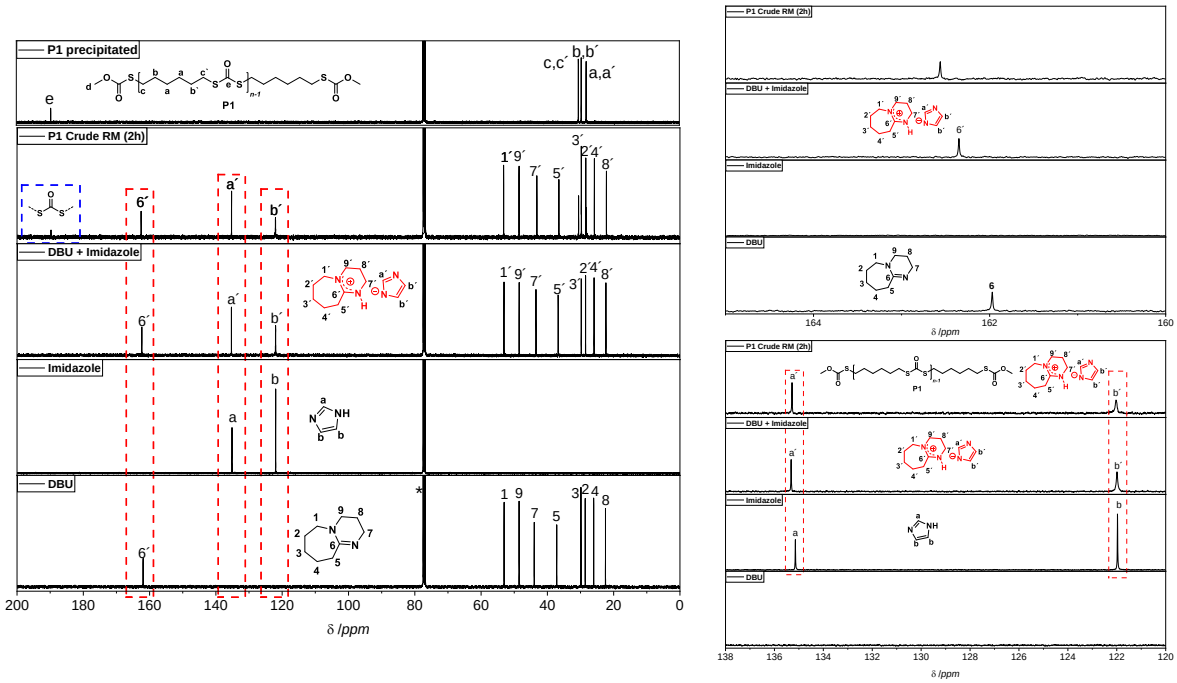


Figure S2 Left: Comparative ^{13}C NMR (100 MHz, $CDCl_3$ (*)) of **P1**-precipitated**, P1** crude reaction mixture (RM, 2h), stochiometric mixture of DBU and imidazole, pure imidazole in additon to DBU at ambient temperature. **Right (up):** Zoom-in in the range of 165-160 ppm. **Right (down):** Zoom-in in the range of 138-120 ppm.

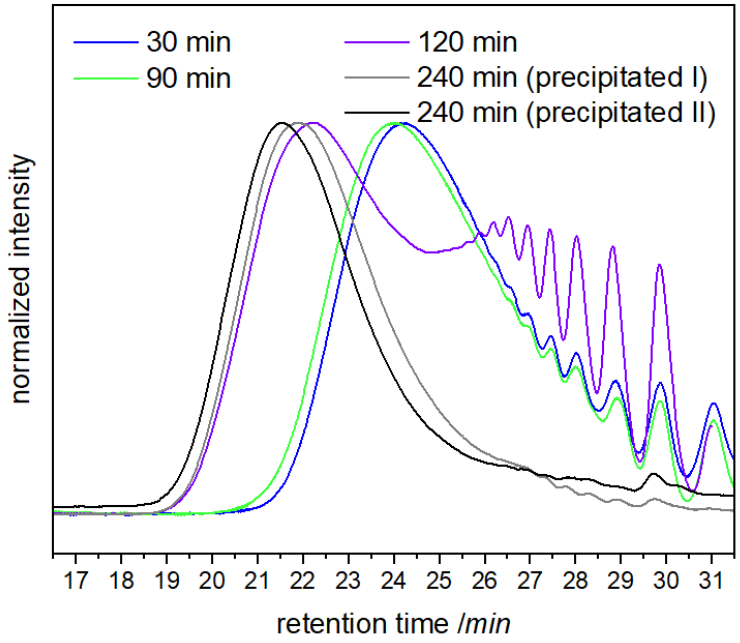


Figure S3 The polymerization reaction of **P1** was monitored by SEC in THF + 0.2 % w/v BHT of reaction aliquots withdrawn at 30, 90, 120 and 240 min, respectively.

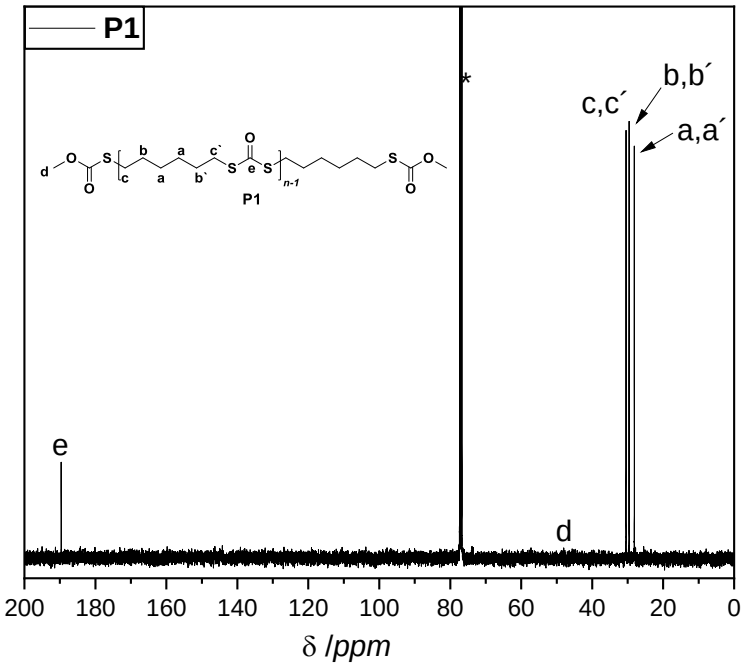


Figure S4 ^{13}C NMR (100 MHz) of **P1** in $CDCl_3$ (*) at ambient temperature.

Table S2 Elemental analysis of **P1**.

Elemental analysis	Polymer	Carbon (%)	Hydrogen (%)	Sulfur (%)
Theoretical	**P1**	**47.7**	**6.86**	**36.4**
Experimental	**P1**	**49.7**	**6.81**	**37.9**

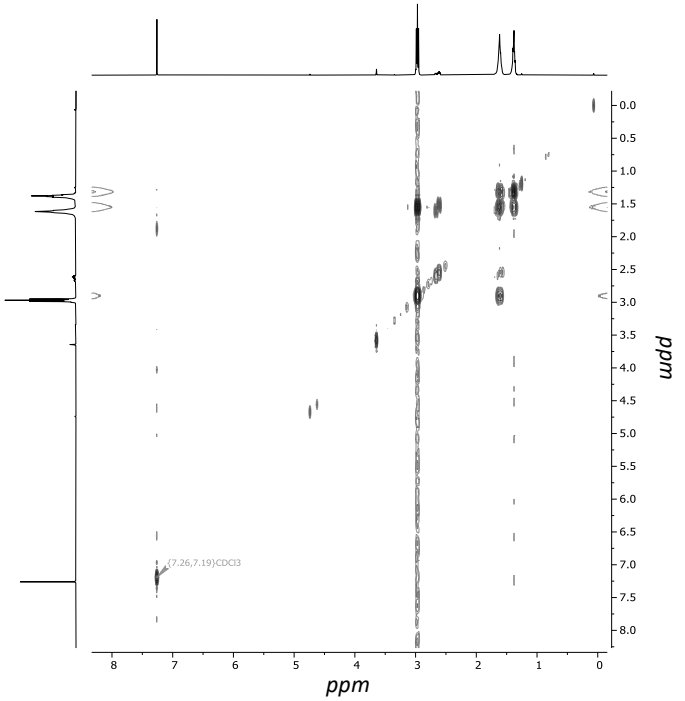


Figure S5 2D ^{1}H-^{1}H COSY spectrum (400 MHz) of **P1** in $CDCl_3$ (*) at ambient temperature.

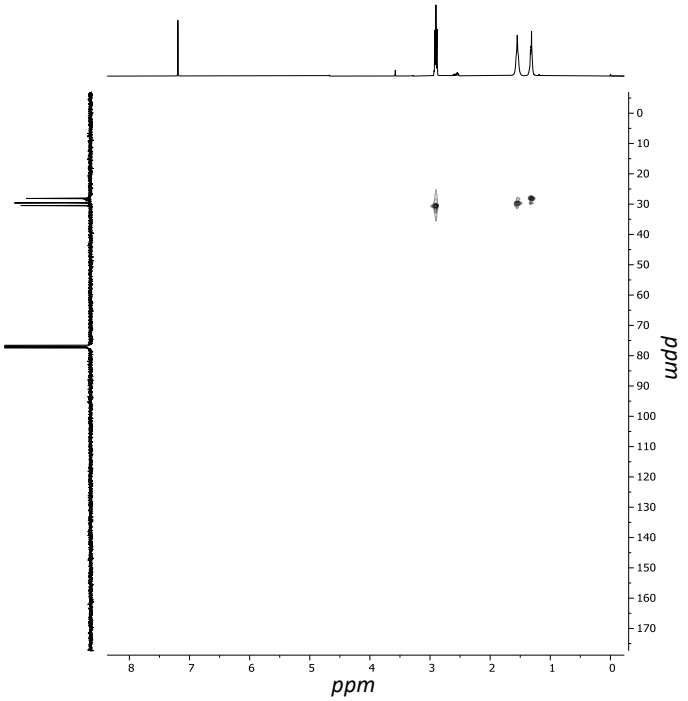


Figure S6 2D ^{1}H-^{13}C HSQC spectrum of **P1** in $CDCl_3$ (*) at ambient temperature.

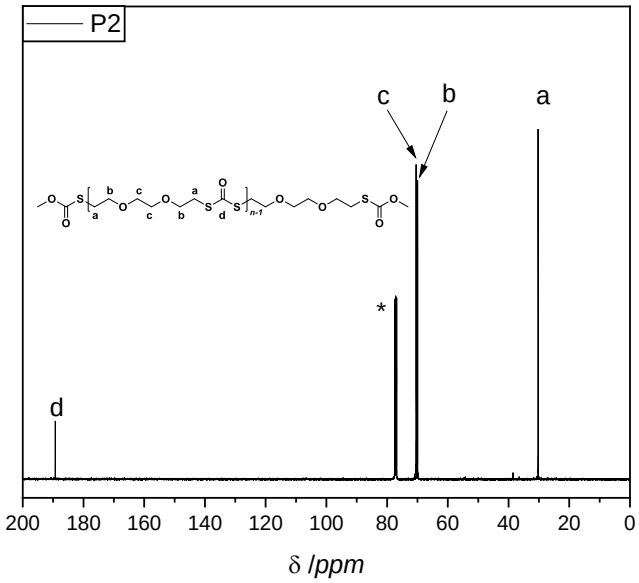


Figure S7 ^{13}C NMR (100 MHz) of **P2** in $CDCl_3$ (*) at ambient temperature.

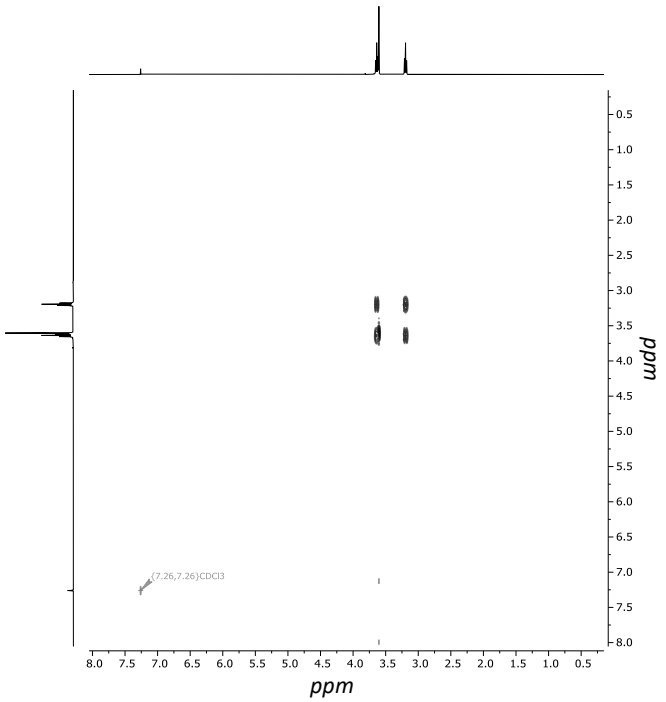


Figure S8 2D ^{1}H-^{1}H COSY spectrum (400 MHz) of **P2** in $CDCl_3$ (*) at ambient temperature.

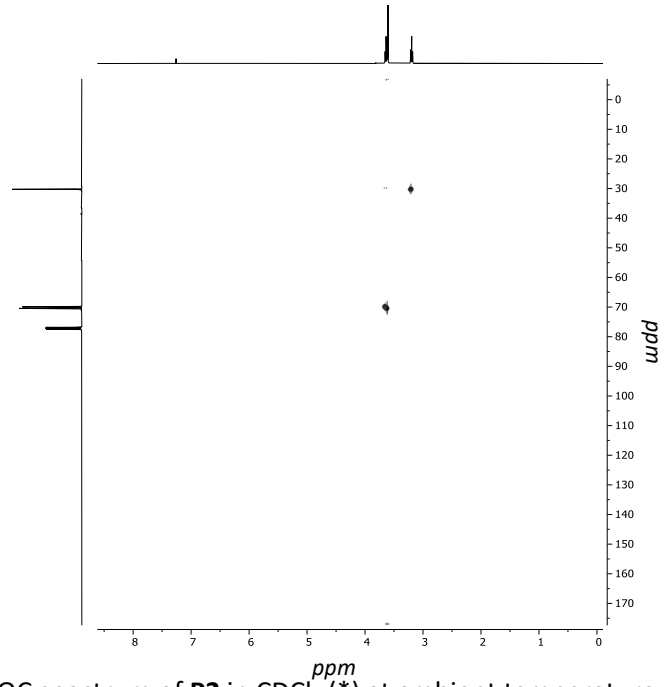


Figure S9 2D ^{1}H-^{13}C HSQC spectrum of **P2** in $CDCl_3$ (*) at ambient temperature.

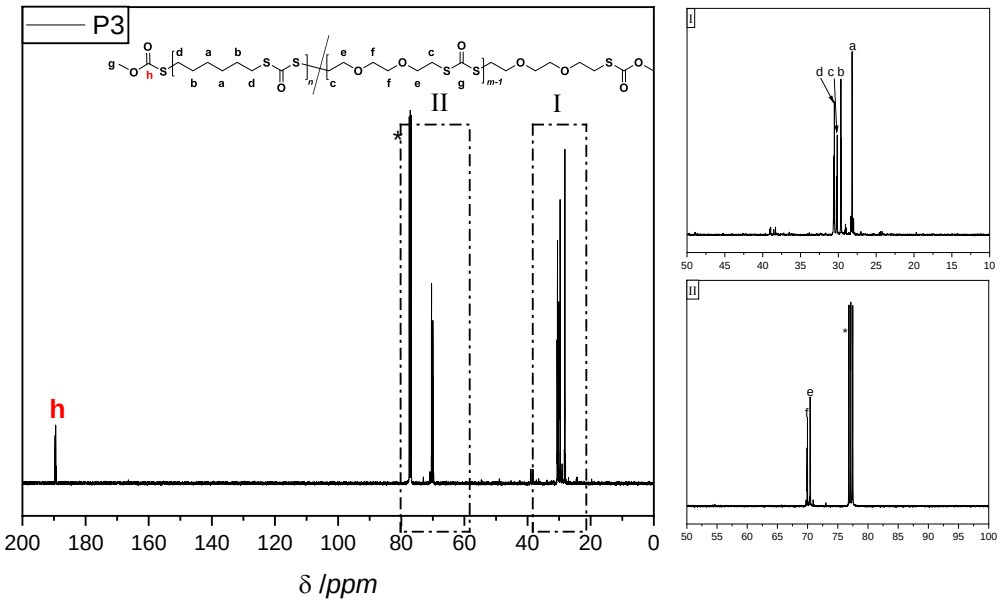


Figure S10 ^{13}C NMR (100 MHz) of **P3** in $CDCl_3$ (*) at ambient temperature.

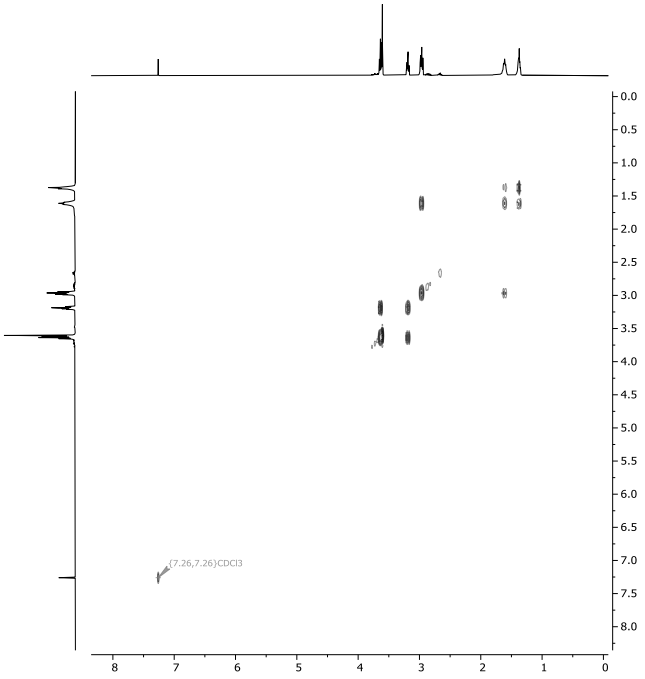


Figure S11 2D ^{1}H-^{1}H COSY spectrum (400 MHz) of **P3** in $CDCl_3$ (*) at ambient temperature.

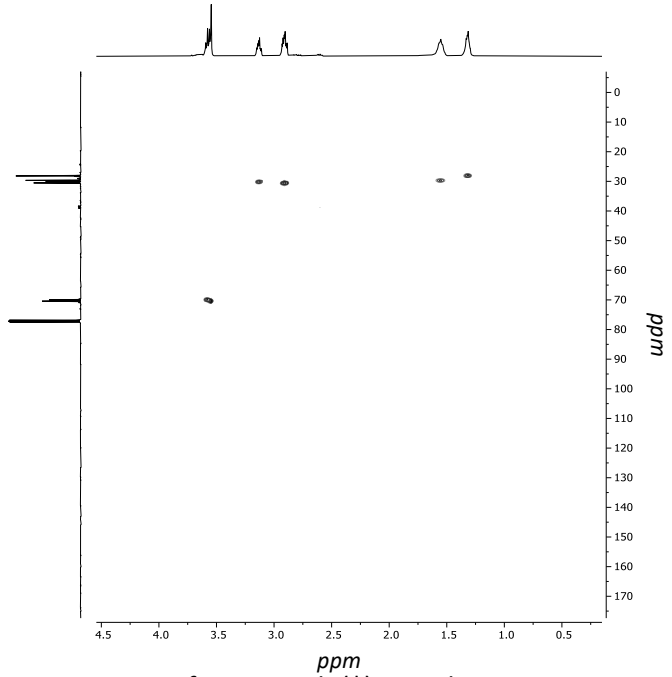
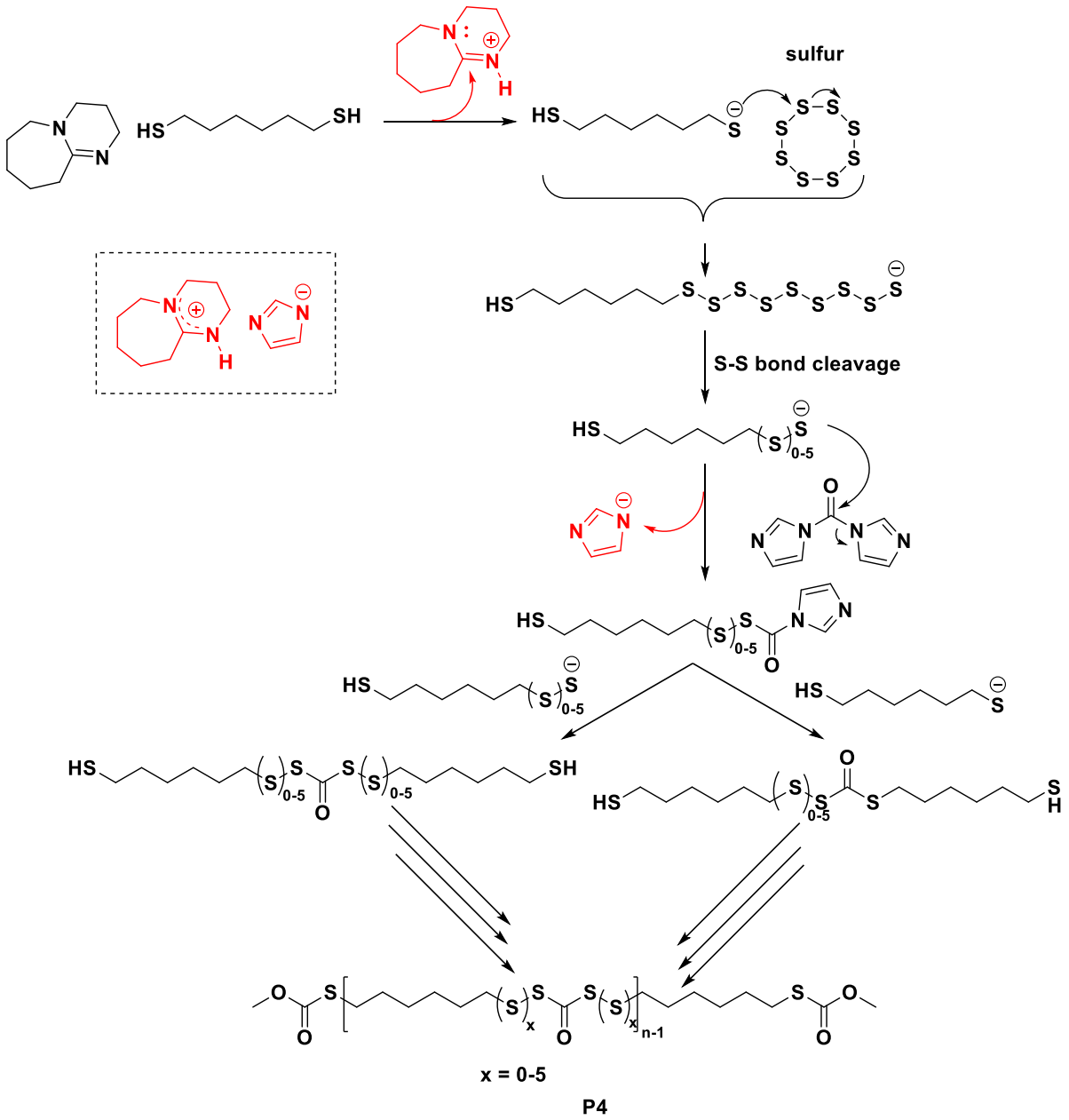


Figure S12 2D ^{1}H-^{13}C HSQC spectrum of **P3** in $CDCl_3$ (*) at ambient temperature.



Scheme S2 Proposed mechanism for the straightforward synthesis of sulfur-rich polydithiocarbonates with CDI and dithiols in the presence of DBU and elemental sulfur.

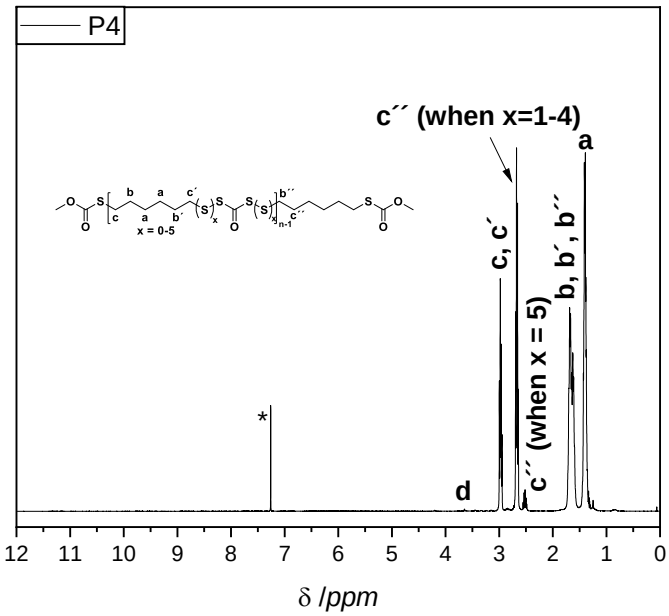


Figure S13 ^{1}H NMR (400 MHz) of **P4** in $CDCl_3$ (*) at ambient temperature.

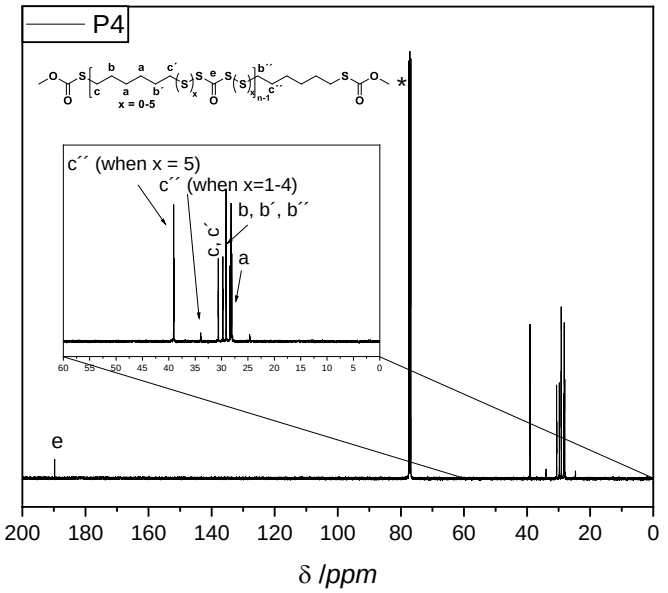


Figure S14 ^{13}C NMR (100 MHz) of **P4** in $CDCl_3$ (*) at ambient temperature.

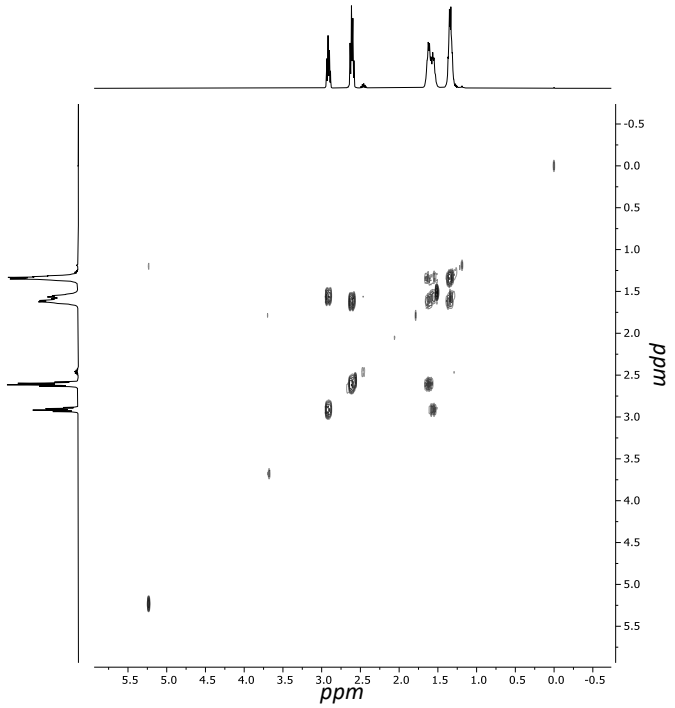


Figure S15 2D ^{1}H-^{1}H COSY spectrum (400 MHz) of **P4** in $CDCl_3$ (*) at ambient temperature.

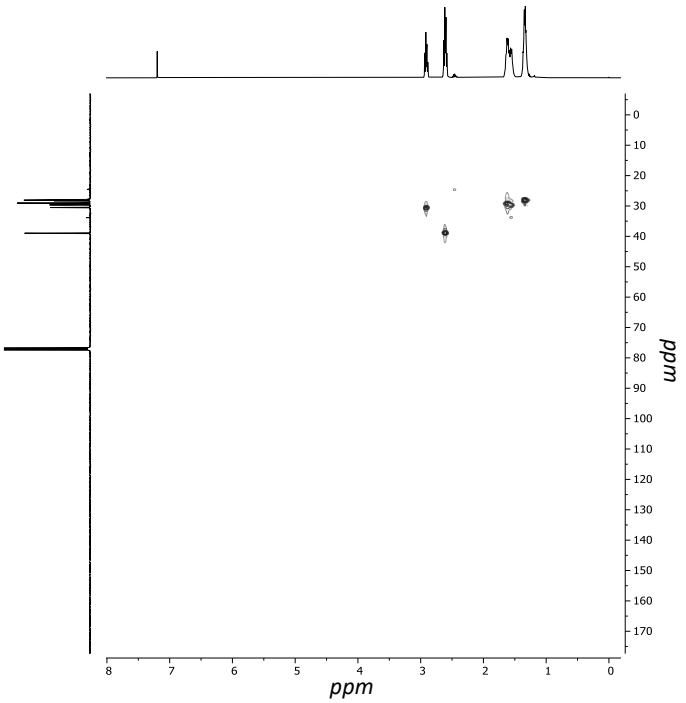


Figure S16 2D ^{1}H-^{13}C HSQC spectrum of **P4** in $CDCl_3$ (*) at ambient temperature.

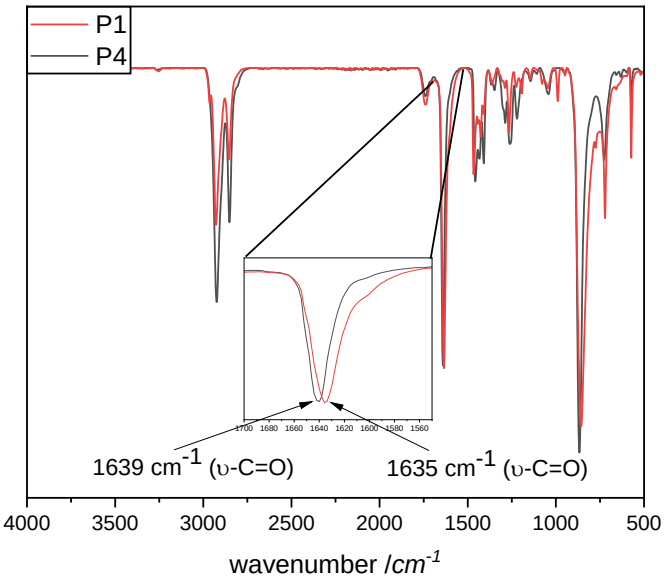


Figure S17 Comparative ATR-IR spectrum (Bruker Alpha ATR-IR) of **P1** and **P4** in the range of 500 to 4000 cm^{-1}.

Table S3 Experimental elemental analysis of **P1** and **P4**.

Elemental analysis	Polymer	Carbon (%)	Hydrogen (%)	Sulfur (%)
Experimental	**P1**	**49.7**	**6.86**	**37.9**
Experimental	**P4**	**49.7**	**8.01**	**42.3**

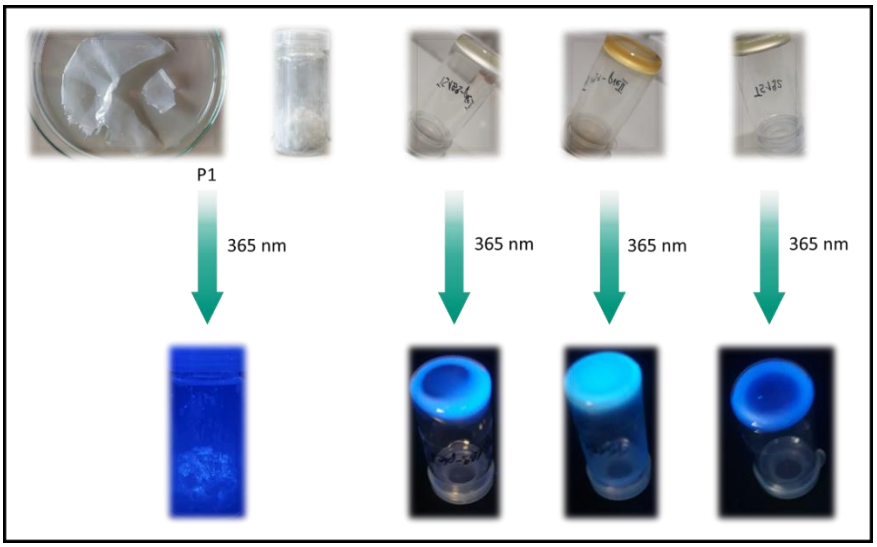


Figure S18 Optical appearance of step growth polymers **P1** (left), **P2** (inside left), **P3** (inside right) and **P4** (right) under natural and UV (365 nm) light.

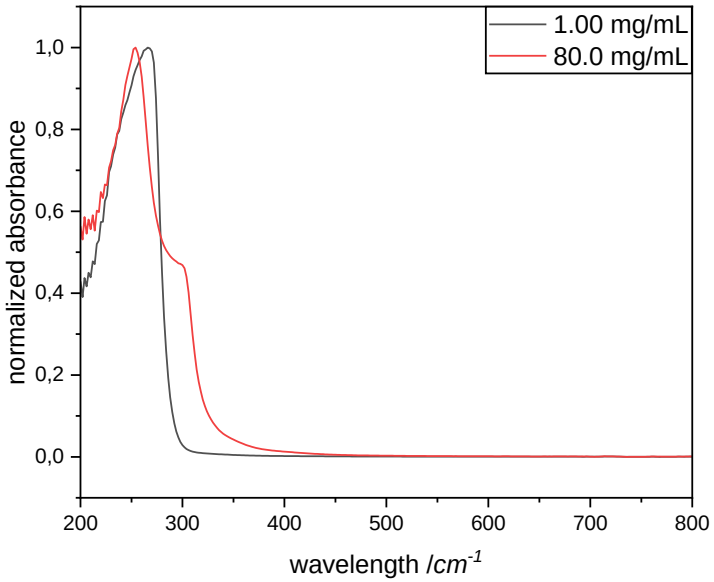


Figure S19 UV-vis absorption traces of **P1** at different concentrations (red: 1.00 mg·mL^{-1}, black: 80.0 mg·mL^{-1}) in DCM (298 K).

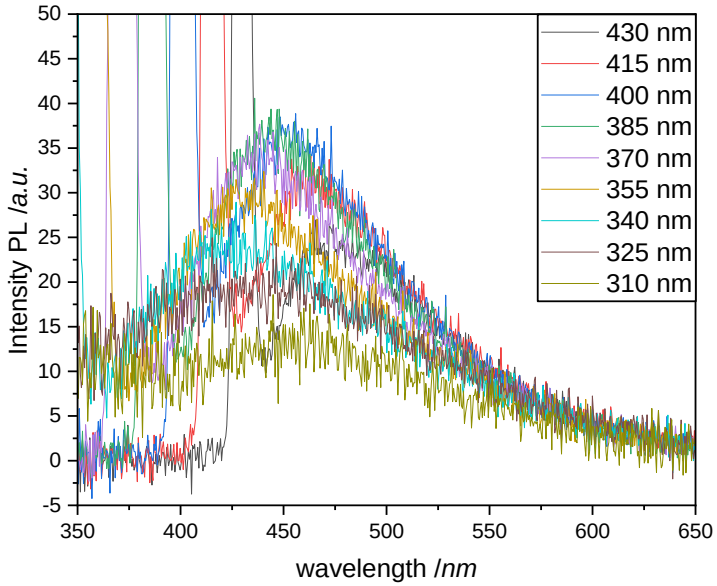


Figure S20 Fluorescence emission spectra of **P1** (80 mg·mL^{-1}) at various excitation wavelengths, i.e., 310 nm to 430 nm.

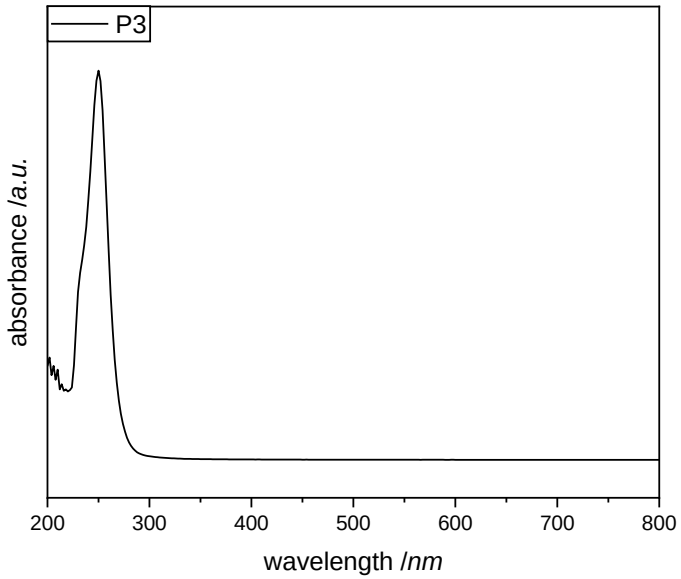


Figure S21 UV-vis absorption trace of **P3** (0.0037 mg·mL^{-1}) in DCM (298 K).

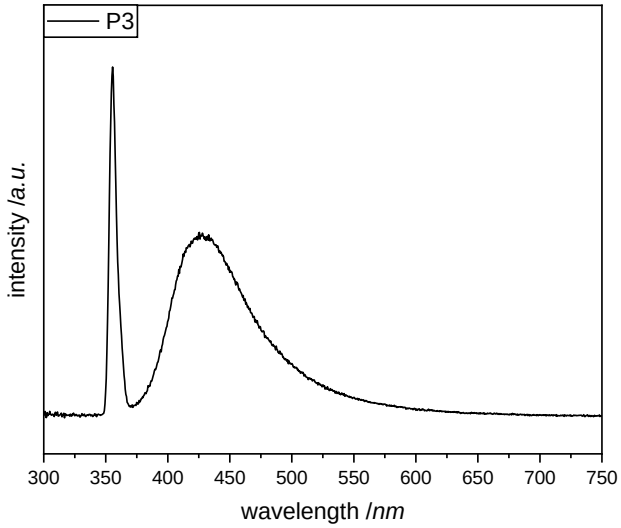


Figure S22 Fluorescence emission spectra of **P3** (39.5 mg·mL^{-1}) at an excitation wavelength of 340 nm.

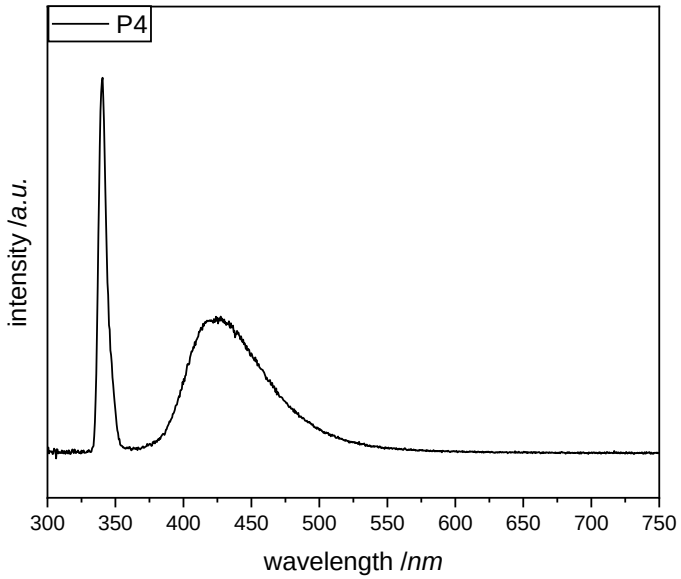


Figure S23 Fluorescence emission spectra of **P4** (39.5 mg·mL^{-1}) at an excitation wavelength of 340 nm.

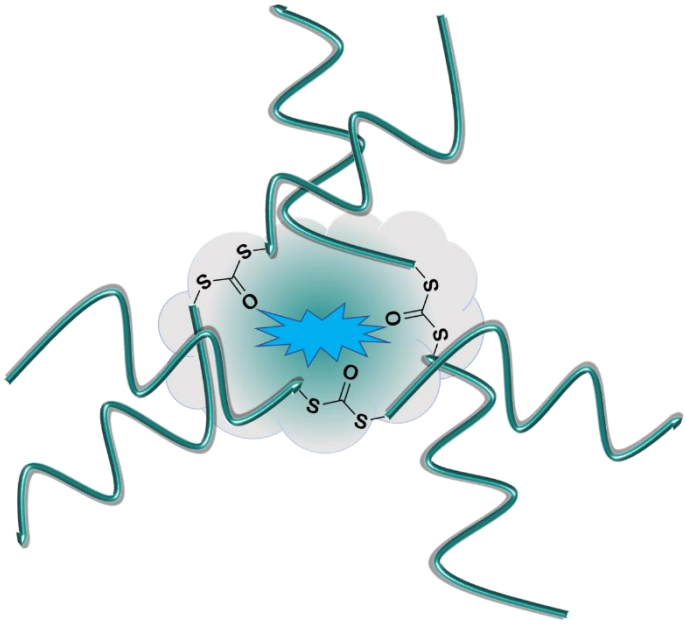


Figure S24 Schematic representation of dithiocarbonate (-S-C(O)-S-) cluster formation.

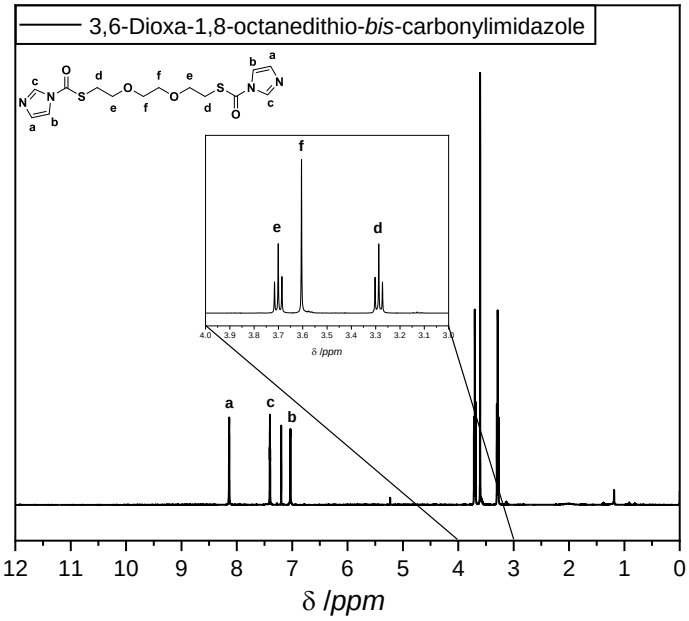


Figure S25 ^{1}H NMR (400 MHz) of **3,6-Dioxa-1,8-octanedithio-*bis*-carbonylimidazole** in $CDCl_3$ (*) at ambient temperature.

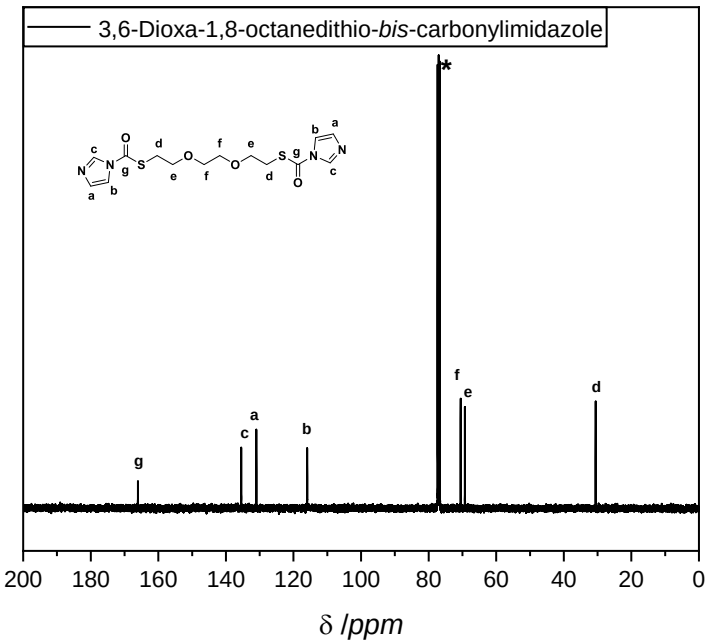


Figure S26 ^{13}C NMR (100 MHz) of **3,6-Dioxa-1,8-octanedithio-*bis*-carbonylimidazole** in $CDCl_3$ (*) at ambient temperature.

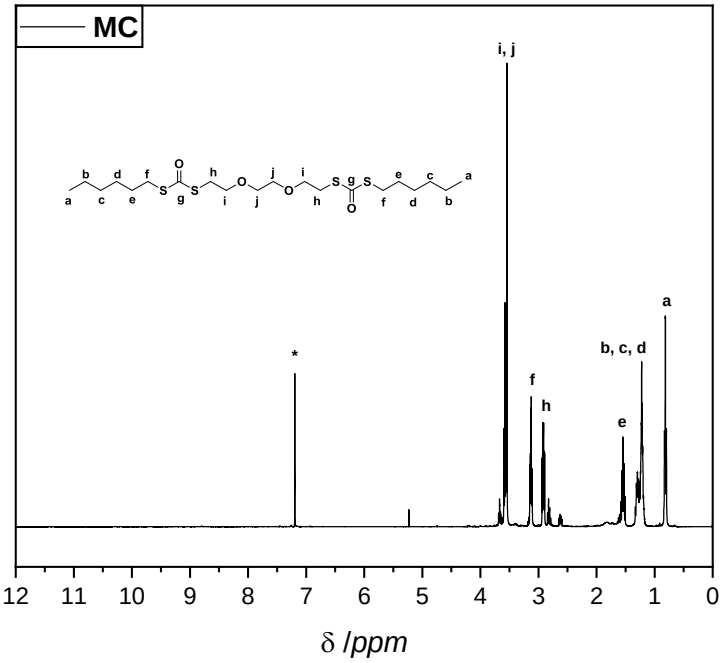


Figure S27 ^{1}H NMR (400 MHz) of **MC** in $CDCl_3$ (*) at ambient temperature.

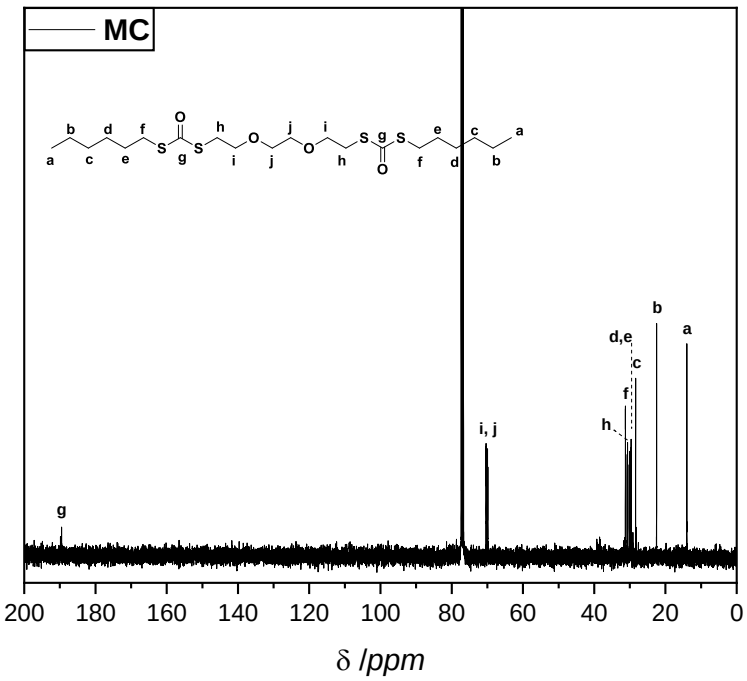


Figure S28 ^{13}C NMR (100 MHz) of **MC** in $CDCl_3$ (*) at ambient temperature.