

## PolyDODT: A Macrocyclic Elastomer with Unusual Properties

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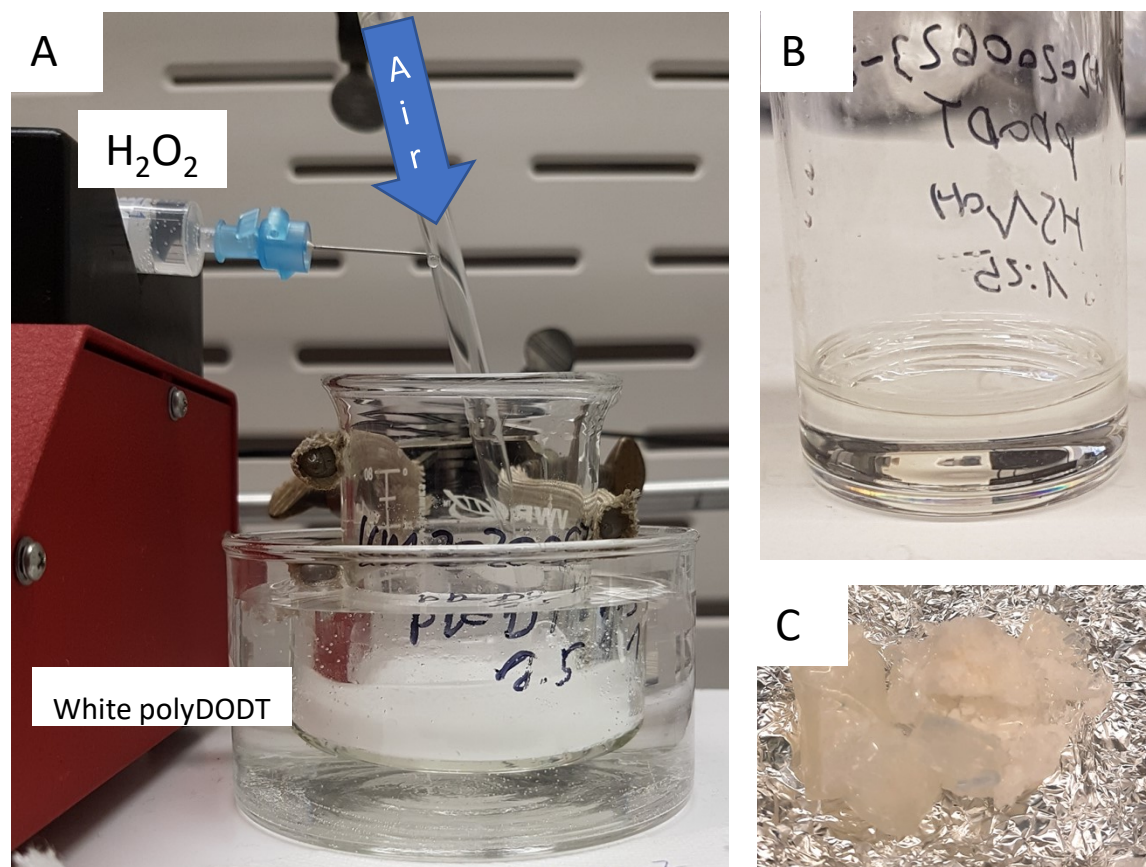


Figure S1. Setup for the synthesis of polyDODTs, where the precipitated white rubber is visible at the bottom of the beaker (A) and pictures of the final, water-clear low molecular weight (B) and high molecular weight (C) products after purification.

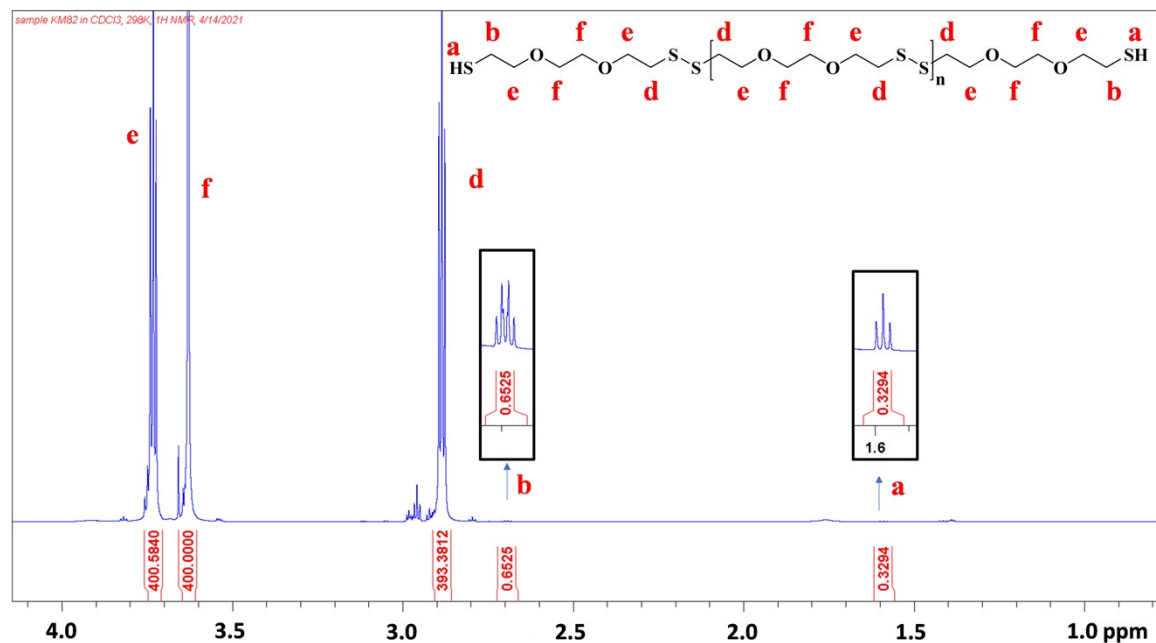


Figure S2. 800 MHz <sup>1</sup>H NMR of L2.2 M<sub>n</sub> (NMR) = 82,900 g/mol, Table 4). Scaling factor is 1 and for the insets it is 64. Resonances of the main chain are δH(800 MHz; CDCl<sub>3</sub>; CDCl<sub>3</sub>) 2.98 (4 H<sub>d</sub>, t, CH<sub>2</sub>SSCH<sub>2</sub>); 3.65 (4 H<sub>f</sub>, s, OCH<sub>2</sub>CH<sub>2</sub>O); 3.75 (4 H<sub>e</sub>, t, OCH<sub>2</sub>CH<sub>2</sub>SSCH<sub>2</sub>CH<sub>2</sub>O) ppm, while resonances related to the end group appear at 1.6 (2 H<sub>a</sub>, t, SH) and 2.75 (4 H<sub>b</sub>, q, CH<sub>2</sub>SH) ppm.

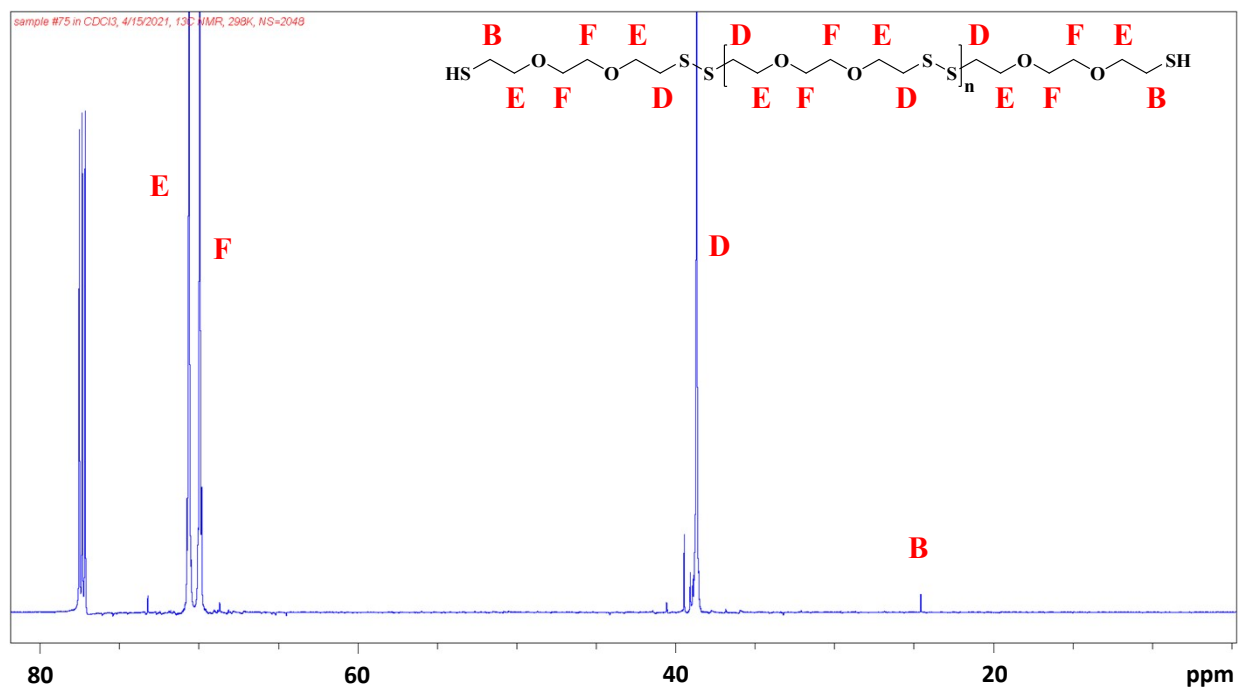


Figure S3. <sup>13</sup>C NMR (700 MHz) of sample L1.1. (M<sub>n</sub> (NMR) = 33,800 g/mol, Table 4) in CDCl<sub>3</sub>. Scaling factor is 8. The main chain carbon signals are δC (700 MHz; CDCl<sub>3</sub>; CDCl<sub>3</sub>) 38.6 (2 C<sub>D</sub>, s, CH<sub>2</sub>SSCH<sub>2</sub>); 69.9 (2 C<sub>F</sub>, s, OCH<sub>2</sub>CH<sub>2</sub>O); 70.6 (C<sub>E</sub>, s, OCH<sub>2</sub>CH<sub>2</sub>S) ppm, while a signal related to the methylene carbon next to the thiol end group can be seen at 24.6 ppm.

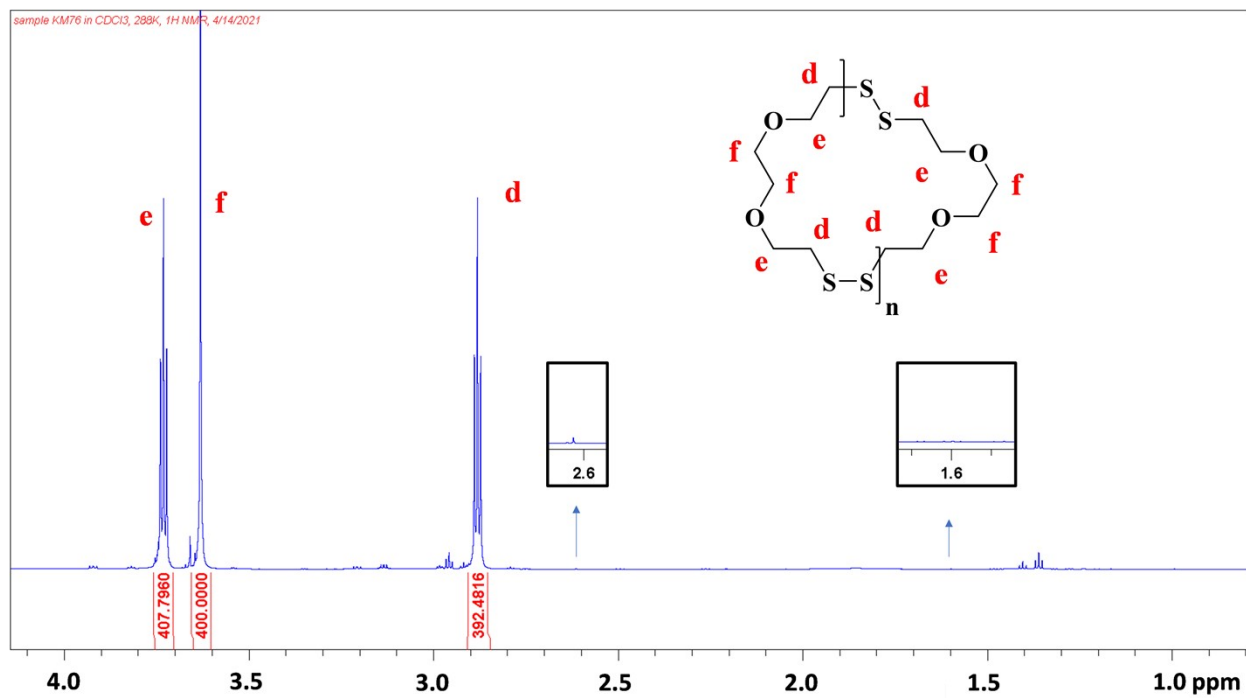


Figure S4. 800 MHz <sup>1</sup>H NMR spectrum of C3.1 M<sub>n</sub> (SEC) = 35,800 g/mol. Insets: enlarged regions to show the absence of -CH<sub>2</sub>-SH at 2.71 ppm and -CH<sub>2</sub>-SH at 1.6 ppm 1.5 – 1.8 ppm. Scaling factor is 1 and for the insets it is 64.