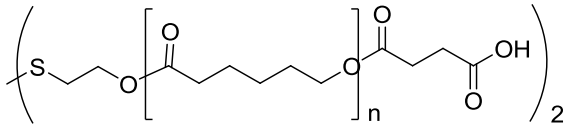
**Sample Name: α,ω–diCarboxy–terminated Poly(ε–caprolactone), bearing dithiodiethanol core**

**Sample #: P20022Bre_CL2COOHdisulf**

**Structure:**

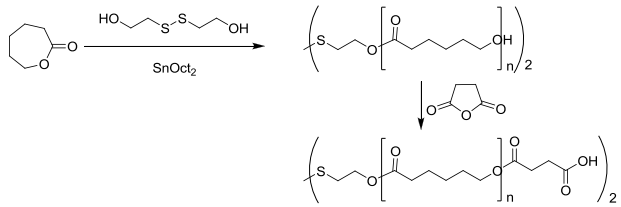


**Composition:**

| $M_n \times 10^3$ HOOC–PCL–SS–PCL–COOH | PDI |
|---|---|
| 7.0 (SEC–LS) | 1.1 |
| SS / COOH functionality ≥95% | |

**Synthetic Procedure:**

$(\text{-S–PCL–COOH})_2$ is prepared by ring–opening polymerization of ε–caprolactone using disulfide–based initiator, followed by reaction with succinic anhydride. The scheme of the reaction is illustrated below:



**Characterization:**

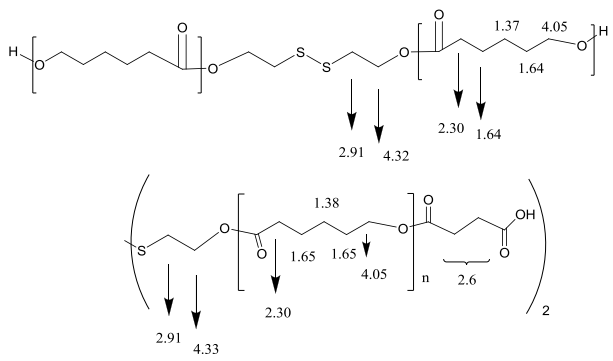
PCLs bearing the above functionalities were analyzed by size exclusion chromatography with light–scattering detector (SEC–LS) to obtain the $M_n$ and polydispersities (PDI). Due to the strong adsorption of COOH moieties to the column packing material, SEC profiles for carboxy–functionalized PCL are n/a.

Completeness of carboxylic functionalization was judged from disappearance of the peak at 3.64 ppm.

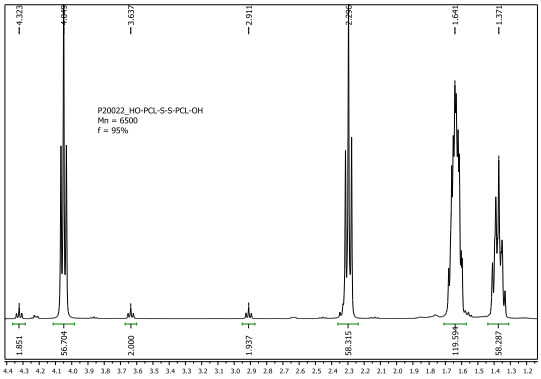
**Solubility:**

Poly(ε–caprolactone) is soluble in $CHCl_3$, Acetone, THF, insoluble in methanol, ethanol. Precipitated from Acetone or $CHCl_3$ into hexane/EtOH or ether/EtOH.

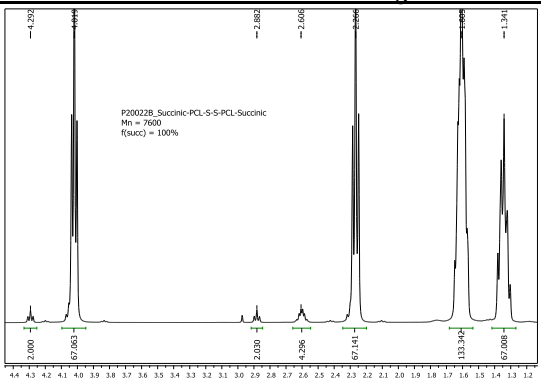
**Chemical shifts assignments**




**$^1$H–NMR of the PCL bearing disulfide linkage:**




**$^1$HNMR of the HOOC–PCL–COOH bearing disulfide linkage:**




**SEC of precursor HOPCL–SS–PCLOH:**

**P20022**