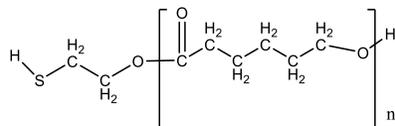


**Sample Name: Poly( $\epsilon$ -caprolactone), ( $\alpha$ -thiol,  $\omega$ -hydroxy)-terminated**

**Sample #: P44073H-CLOHSH**

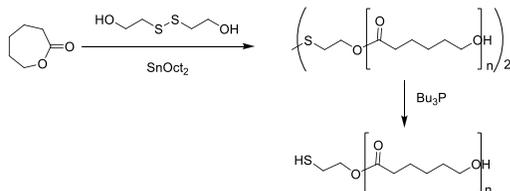
**Structure:**



**Composition (NMR):**

$M_n \times 10^3$	PDI
HS-PCL	1.2
2.0	1.2
SH functionality $\geq 60\%$	
Contains DTT as a stabilizer	

**Synthetic Procedure:** HS-PCL is prepared by ring-opening polymerization of  $\epsilon$ -caprolactone using disulfide-based initiator, followed by disulfide bond cleavage. The scheme of the reaction is illustrated below:

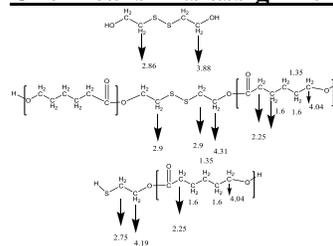


**Characterization:** PCL bearing disulfide and free thiol end PCL were analyzed by size exclusion chromatography (SEC) to obtain the polydispersity index (PDI). SEC analysis carried out in THF after the cleavage, SH end functionalized PCL shows broadening in its distribution. This might be due to the strong adsorption with the column packing material. The SEC profiles indicate a quantitative cleavage of disulfide linkage.

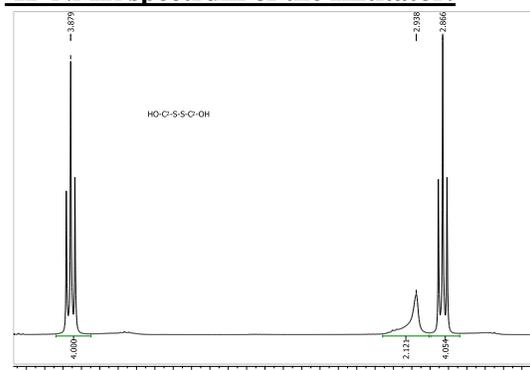
$M_n$  was calculated from  $^1\text{H-NMR}$  spectrum by comparing the peak area of  $\text{CH}_2\text{CH}_2\text{OCO}$  protons of the main chain at 4.05 ppm with  $\text{CH}_2\text{CH}_2\text{OH}$  protons of the terminal unit at 3.64 ppm. Percentage of thiol functionality was determined from the integral's ratio of the peaks at 3.64 and 2.75 ppm.

**Solubility:** Poly( $\epsilon$ -caprolactone) is soluble in  $\text{CHCl}_3$ , Acetone, THF, insoluble in methanol, ethanol. Precipitated from Acetone or  $\text{CHCl}_3$  into hexane/EtOH or ether/EtOH.

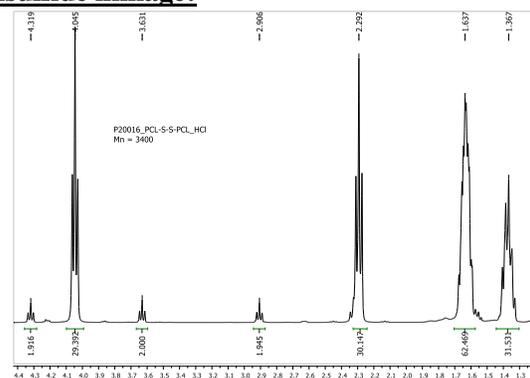
### Chemical shifts assignments



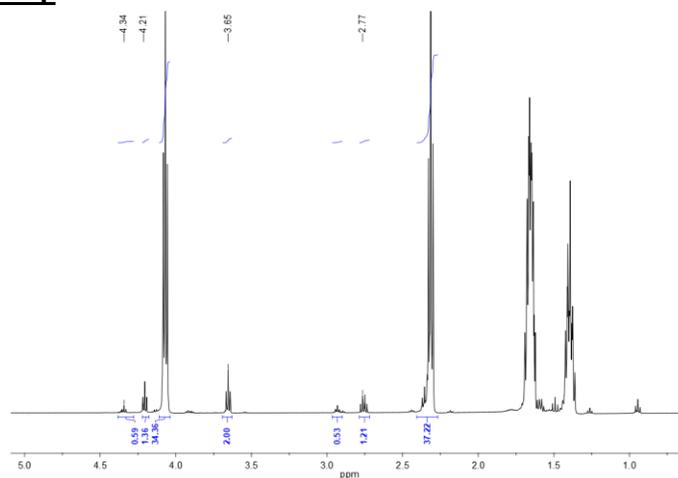
### $^1\text{H-NMR}$ spectrum of the Initiator:



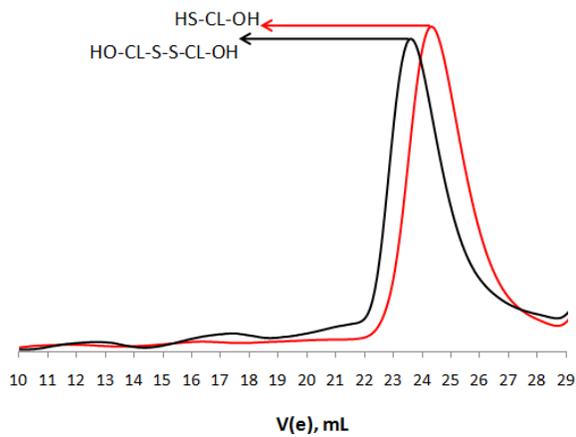
### $^1\text{H-NMR}$ spectrum of the PCL bearing disulfide linkage:



### $^1\text{H-NMR}$ spectrum of PCL with free Thiol End group



**SEC profile of the polymer:**



Size-exclusion chromatography of the product:

Before cleavage:  $M_w / M_n = 1.2$

After cleavage:  $M_w / M_n = n/a$