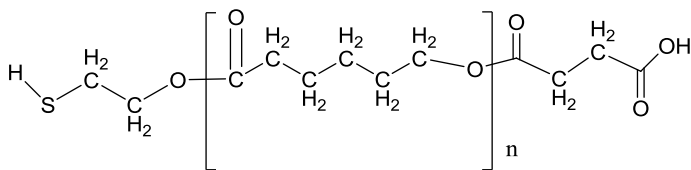


Sample Name: α -Thiol- ω -Carboxy-terminated Poly(ϵ -caprolactone)

Sample #: P20022BSH_CL-COOHSH

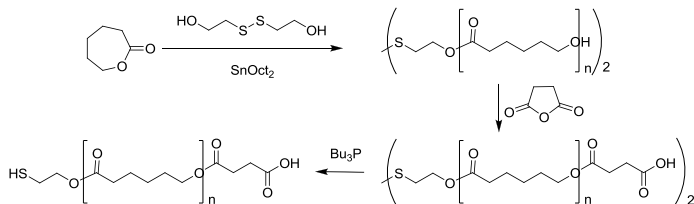
Structure:



Composition (NMR):

$M_n \times 10^3$ HS-PCL-COOH	PDI
4.0 (average)	1.3
SH functionality $\geq 95\%$	
Contains DTT as a stabilizer	

Synthetic Procedure: HS-PCL-COOH is prepared by ring-opening polymerization of ϵ -caprolactone using disulfide-based initiator, followed by reaction with succinic anhydride and subsequent disulfide bond cleavage. The scheme of the reaction is illustrated below:

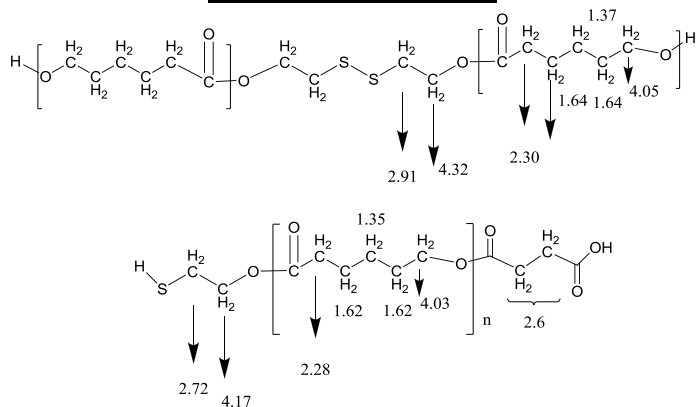


Characterization: PCL bearing disulfide, disulfide and carboxyl, and free thiol end were analyzed by size exclusion chromatography (SEC) to obtain the polydispersity index (PDI). SEC analysis carried out in THF, and COOH and SH end functionalized PCLs show broadening in their distribution. This might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

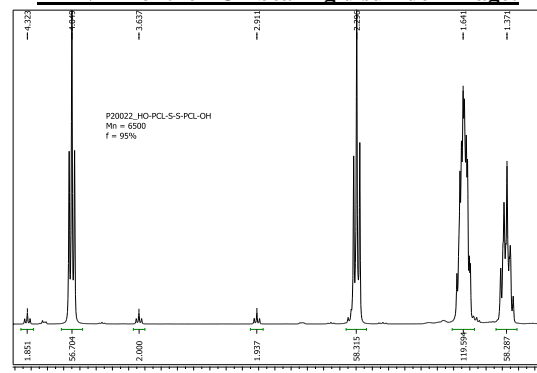
M_n was calculated from $^1\text{H-NMR}$ spectrum by comparing the peak area of $\text{CH}_2\text{CH}_2\text{OCO}$ protons of the main chain at 4.05 ppm with $\text{CH}_2\text{CH}_2\text{OH}$ protons of the terminal unit at 3.64 ppm. Completeness of carboxylic functionalization and disulfide reduction was judged from disappearance of the peaks at 3.64 and 2.88 ppm, respectively.

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.

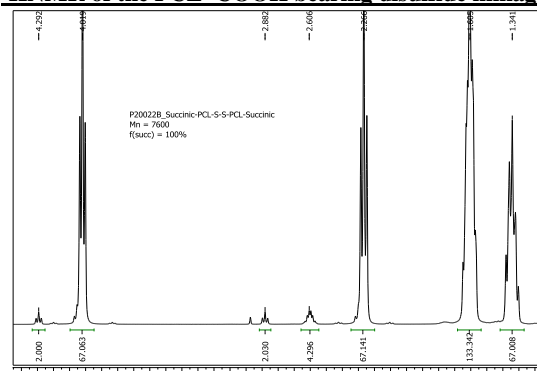
Chemical shifts assignments



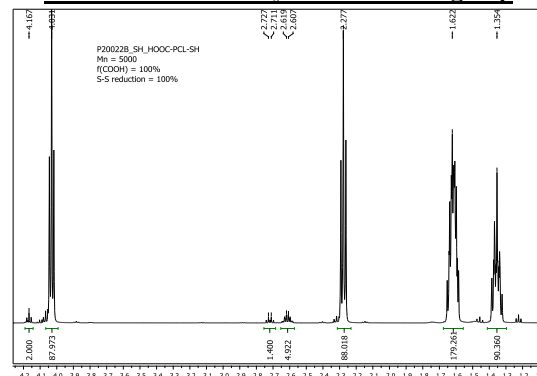
$^1\text{H-NMR}$ of the PCL bearing disulfide linkage:



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

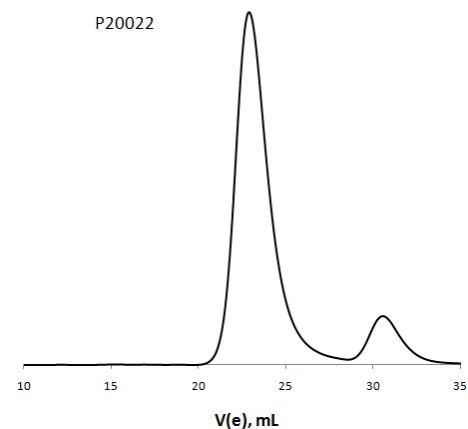


PCL with free Carboxyl and Thiol End group



SEC of the polymer:

P20022



Size-exclusion chromatography of the product:
Before functionalization/cleavage: $M_w / M_n = 1.3$
After: $M_w / M_n = n/a$