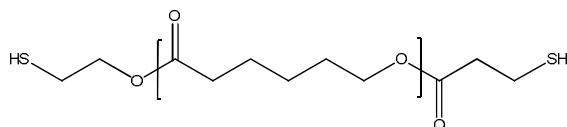


Sample Name: α , ω -diThiol-terminated Poly(ϵ -caprolactone)

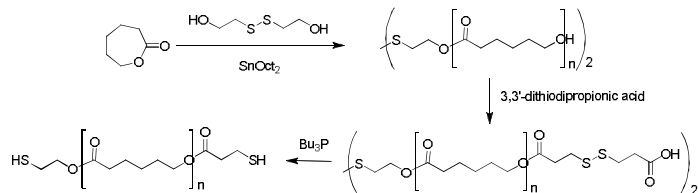
Sample #: P20022E1_CL-2SH



Composition (NMR):

$M_n \times 10^3$ HS-PCL-SH	PDI
3.5	1.4
Dual SH functionality $\geq 80\%$	
Contains DTT as a stabilizer	

Synthetic Procedure: HS-PCL-SH is prepared by ring-opening polymerization of ϵ -caprolactone using disulfide-based initiator, followed by reaction with 3,3'-dithiodipropionic acid and subsequent disulfide bond cleavage. The scheme of the reaction is illustrated below:

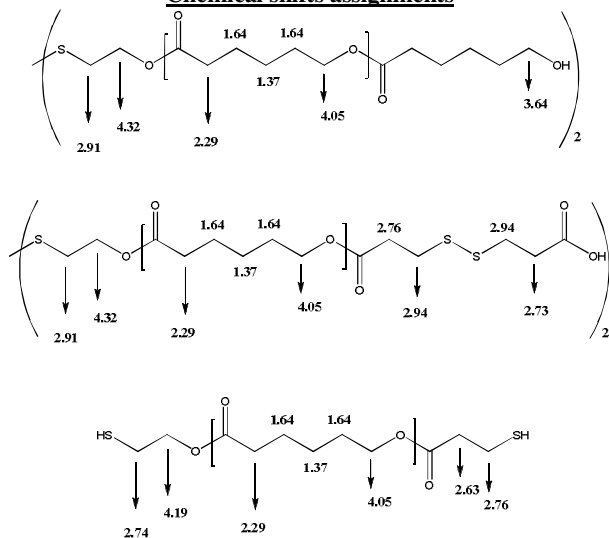


Characterization: PCLs bearing disulfide and free thiol ends were analyzed by size exclusion chromatography (SEC) to obtain the polydispersity indices (PDI). SEC analysis carried out in THF-TEA, and COOH end functionalized PCL was not analyzed due to a very strong adsorption to column packing material. The SEC profiles indicate a quantitative cleavage of disulfide linkages.

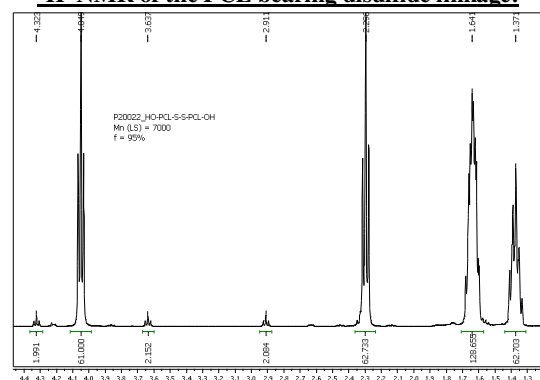
Initial M_n was determined by SEC-LS. Percentage of thiol functionality was estimated from the integrals of the peaks at 2.63, 2.74, 2.76 and 4.19 ppm presuming the maximum integral value for each is 2.0 and NMR shows 1.6 in average (80%). Completeness of disulfide reduction was judged based on disappearance of the peaks at 2.91 and 2.94 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.

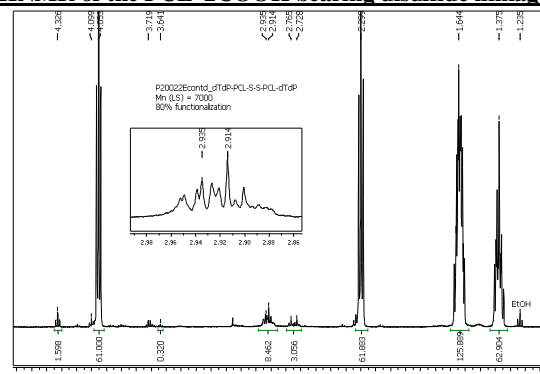
Chemical shifts assignments



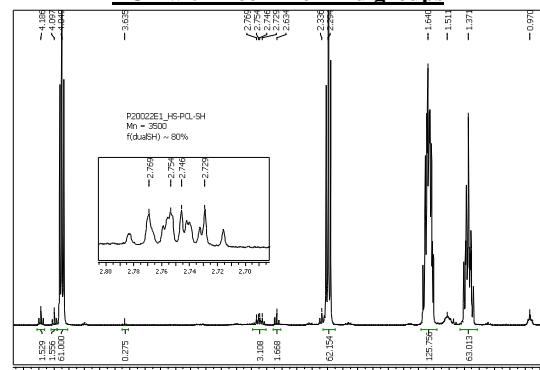
^1H -NMR of the PCL bearing disulfide linkage:



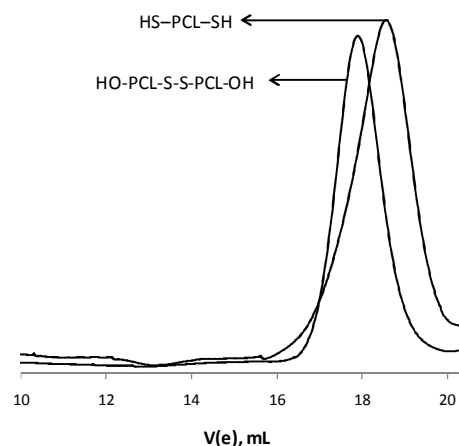
^1H NMR of the PCL-2COOH bearing disulfide linkages:



PCL with free Thiol End groups



SEC of the polymer:



N.B.: Certain broadening of the elugram might be due to the strong interaction of SH-groups with the column packing material