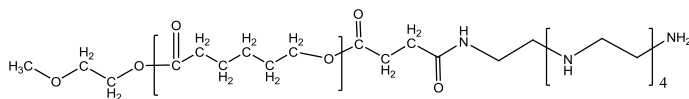**Sample Name:** ω–PentaethyleneHexamine–terminated Poly(ε–caprolactone)

Sample #: P20026–2_CL-PEHA

Structure:

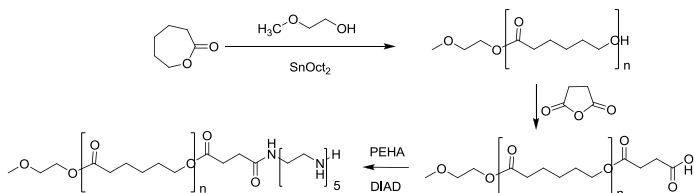**Composition (NMR):**

$M_n \times 10^3$ PCL–PEHAmine	PDI
2.0 (average)	1.5
PEHA functionality ≥95%	

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's from each step were analyzed by size exclusion chromatography (SEC) to obtain the polydispersity index (PDI) and to ensure no dimmers are formed. SEC analysis carried out in THF.

M_n was calculated from ^{1}H–NMR spectrum by comparing the peak area of CH$_2$CH$_2$OCO protons of the main chain at 4.05 ppm with CH$_2$CH$_2$OH protons of the terminal unit at 3.64 ppm in initial PCL. Completeness of carboxylic functionalization and amine functionalization was judged from disappearance of the peaks: 1) at 3.64 and 2) 2.63 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.

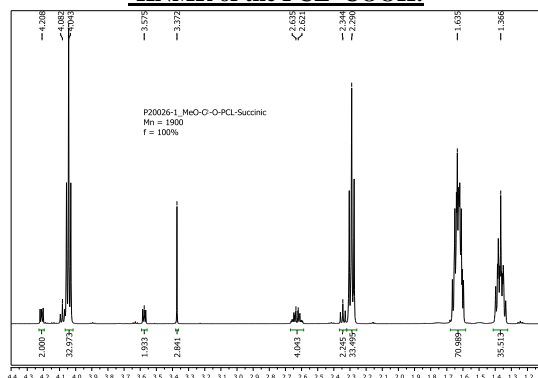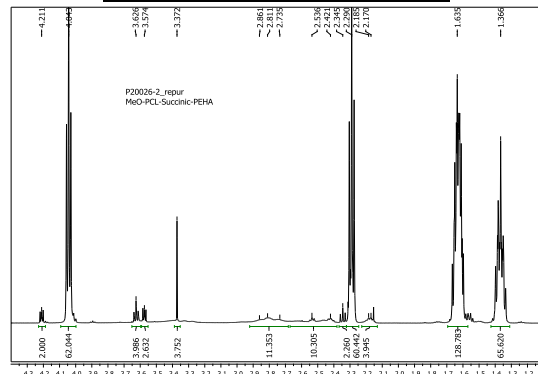**Chemical shifts assignments**
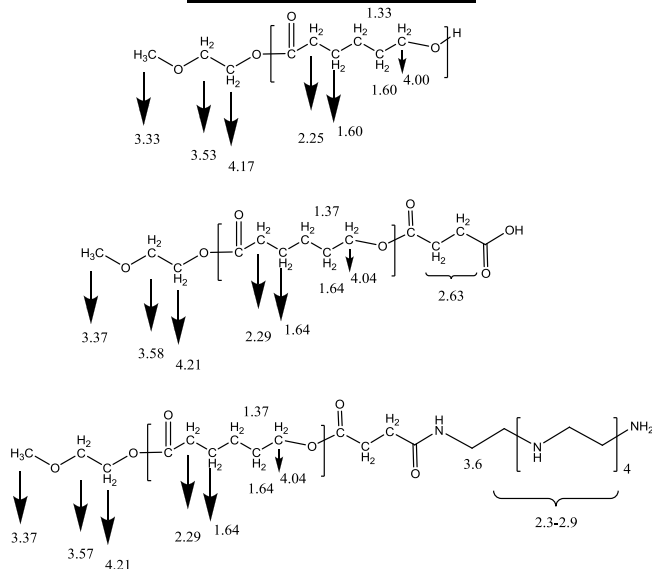
^{1}H–NMR of the initial PCL:
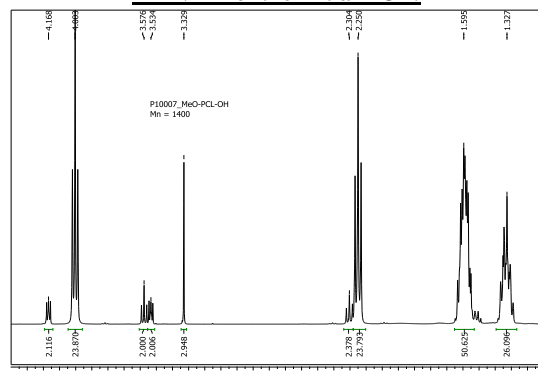
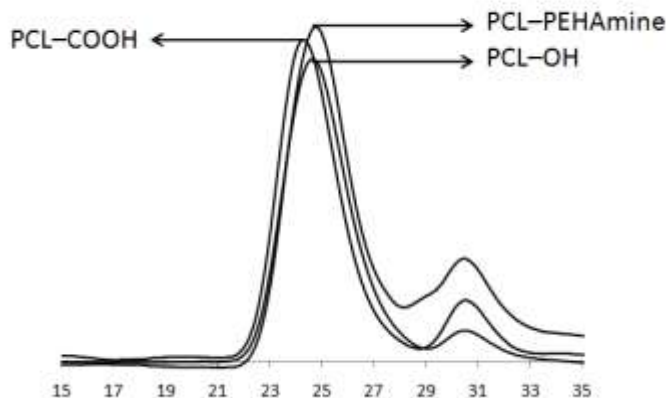**^{1}HNMR of the PCL–COOH:**

PCL with PEH-Amine End group

SEC of the polymer:

P20026-2

Size–exclusion chromatography of the product:
Before functionalization: $M_w / M_n = 1.5$
After: $M_w / M_n = 1.5$