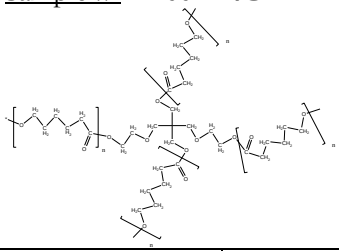
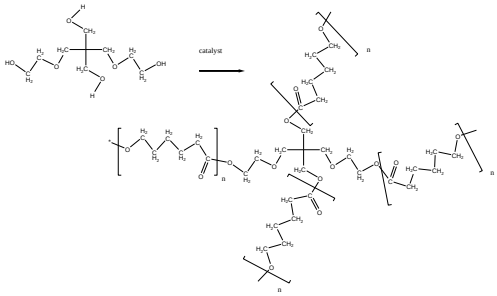
Sample Name:
Four arm Poly(ε-caprolactone)
Sample #: **P10012-4CL**



Mn x 10^3 (branch)	PDI
0.192 (Mn total 770)	1.3

Synthesis Procedure:
The polymer was prepared by ring opening polymerization of caprolactone using Tin octoate as the catalyst and initiator bearing 4 OH groups, bears Mn average of 224. The scheme of the reaction is illustrated below:



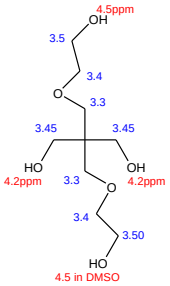
Characterization:
The Mn of the polymer is calculated from 1H-NMR spectroscopy by comparing the peak area of the core protons at about 3.6 ppm with the ε-caprolactone protons at about 4.1 ppm. Polydispersity is determined by size exclusion chromatography (SEC): Varian liquid chromatograph equipped with UV and refractive detector. SEC columns from Supelco were used with THF containing 2 vol% (Et)3N as the eluent.

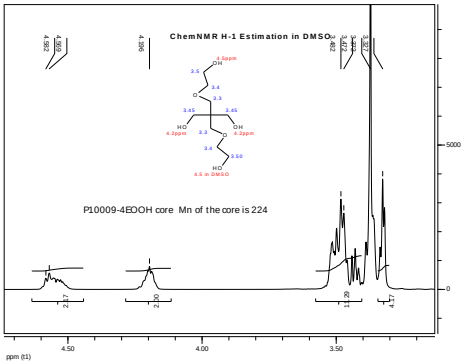
Purification of the obtained polymer:
Purification of the obtained polymer was carried out rigorously as discussed below to ensure the removal of the catalyst and traces amount of unreacted 4 – Hydroxy core based on pentaerythritol.

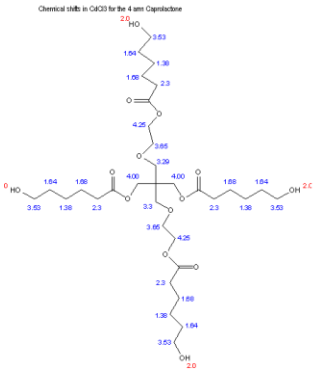
1. Dissolved the polymer dichloromethane, solution was filtered and then passed through a column packed with basic Al_2O_3 .
2. Solution was concentrated on rota-evaporator
3. Solution was precipitated in cold diethyl ether.
4. Dried under vacuum for 48h at 150 ^oC to remove any low molecular weights oligomeric species.

Analysis by HNMR: Core

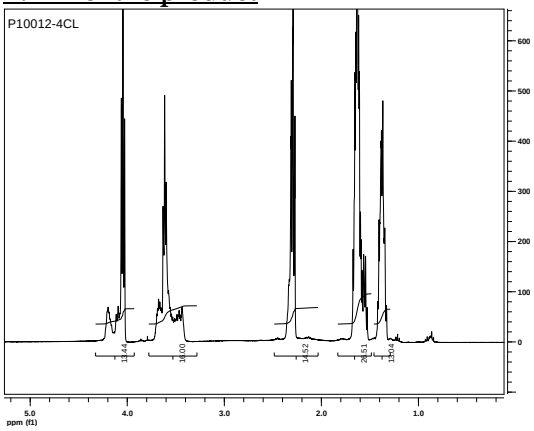
Chemical shifts of Core: Estimation in DMSO



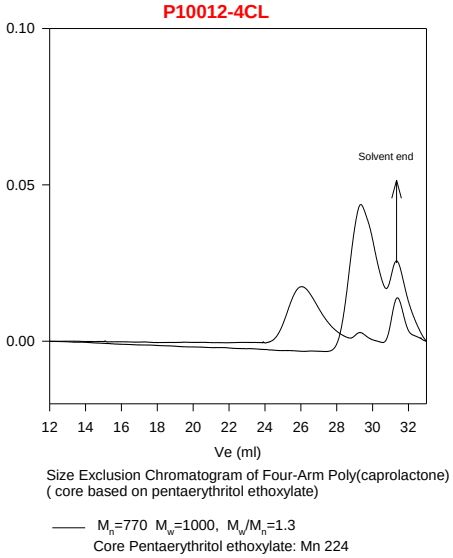




NMR of the product



SEC of the product



Size Exclusion Chromatogram of Four-Arm Poly(caprolactone)
(core based on pentaerythritol ethoxylate)

—— M_n=770 M_w=1000, M_w/M_n=1.3
Core Pentaerythritol ethoxylate: Mn 224

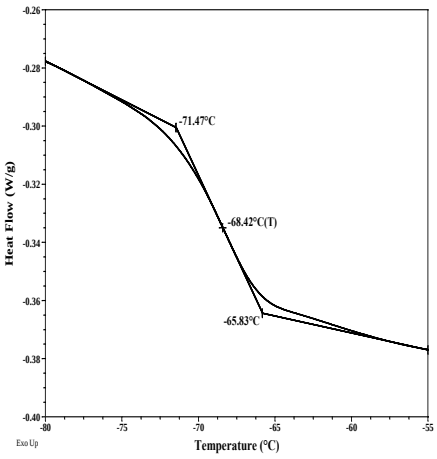
Thermal analysis of the sample P10012-4CL

Thermal analysis of the samples was carried out on a TA Q100 differential scanning calorimeter at a heating rate of 10°C/min.The midpoint of the slope change of the heat flow plot of the second heating scan was considered as the glass transition temperature (T_g).

Melting and crystallization curve for the sample

The melting temperature (T_m) was taken as the maximum of the endothermic peak where as the crystallization temperature (T_c) was considered as the minimum of the exothermic peak.

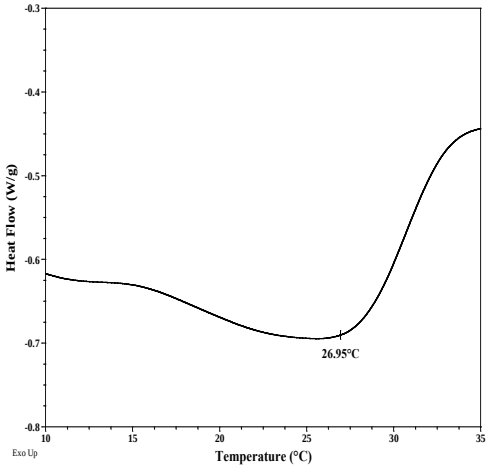
Glass transition temperature for 4CL



Thermal analysis results at a glance

T_m (°C)	T_c (°C)	T_g (°C)
27	-07	-68

Melting curve for the CL sample:



Crystallization curve for the CL sample: