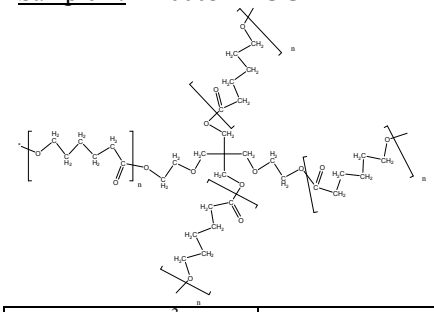
Sample Name:

Four arm Poly(ε-caprolactone)

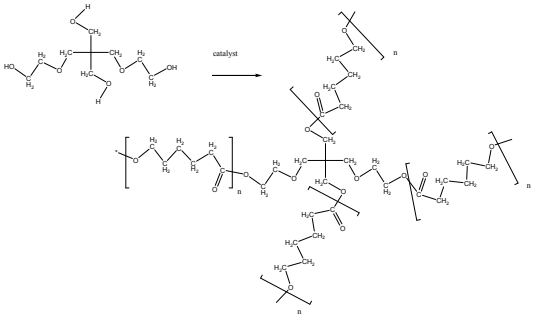
Sample #: **P10003-4EOCL**



Mn x 10^3 (branch)	PDI
0.27-b-1.5 (0.442)	1.3

Synthesis Procedure:

The polymer was prepared by ring opening polymerization of caprolacton 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 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.

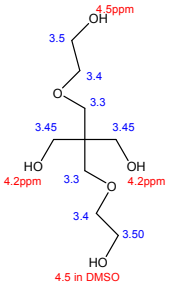
Purification of the obtained polymer:

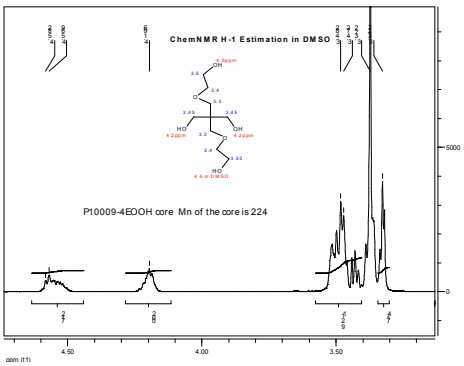
Purification of the obtained polymer was carried out rigorously as discussed below to ensure the removal of the catalyst and traces amount of unreacted 4–hydroxy core based on pentaerythritol.

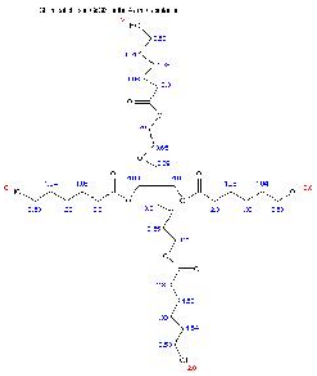
1. Dissolved the polymer dichloromethane, solution filtered and than passed through a column packed with basic Al_2O_3.
2. Solution concentrated on rota-evaporator
3. Solution precipitated in cold diethyl ether.
4. Dried under vacuum for 48h at 150 ^oC to remove any low molecular weights oligomeric species

Analysis by H NMR: Core

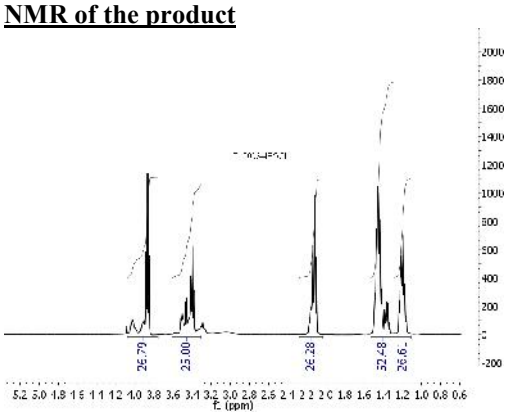
Chemical shifts of Core: Estimation in DMSO



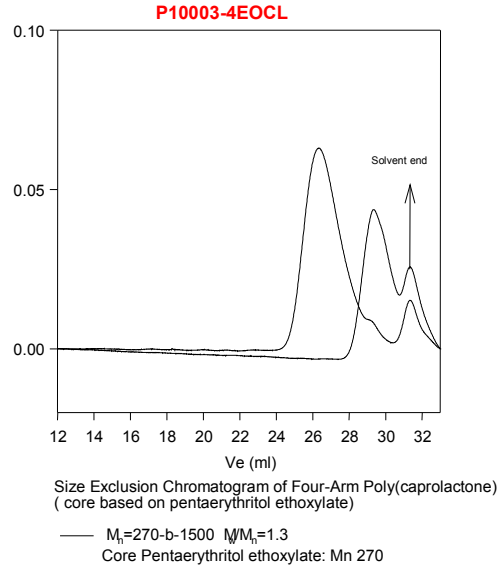




NMR of the product



SEC of the product:



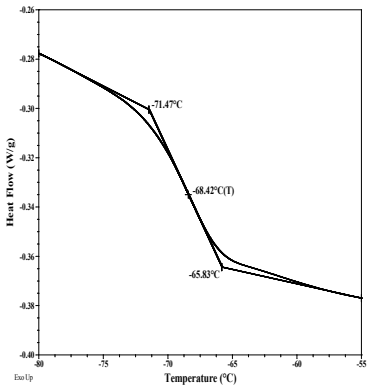
Thermal analysis of the sample

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.

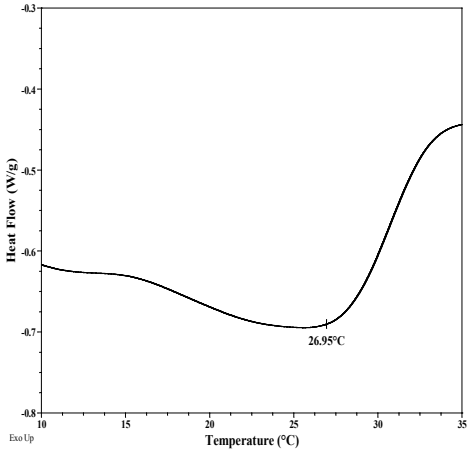
Glass transition temperature for 4CL



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: