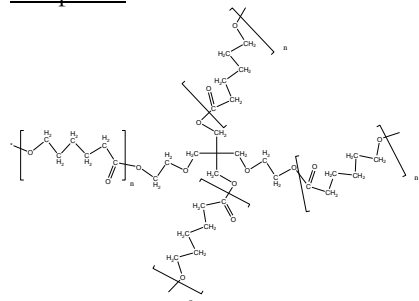


Sample Name:

Four arm Poly(ϵ -caprolactone)

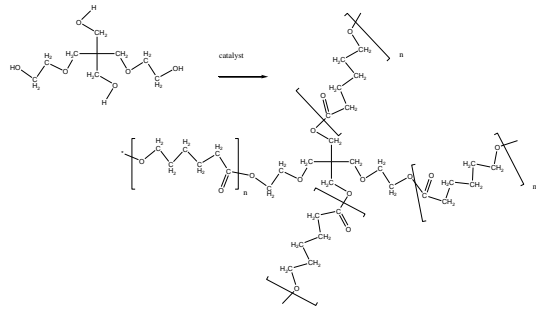
Sample #: **P10013-4CL**



Mn x 10 ³ (branch)	PDI
0.275 (Mn total 1100)	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:

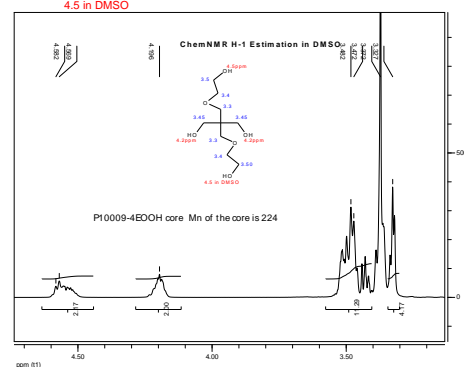
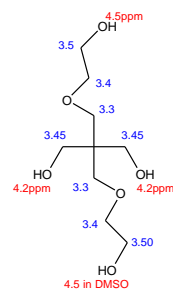
Purification of the obtained polymer was carried out rigorously as discussed below to ensure the removal of the catalyst and traces amount of unreacted 4 – Hydroxy core based on pentaerythritol.

1. Dissolve the polymer dichloromethane, solution was filtered and then passed through a column packed with basic Al₂O₃.
2. Solution was concentrated on rota-evaporator
3. Solution was precipitated in cold diethyl ether.

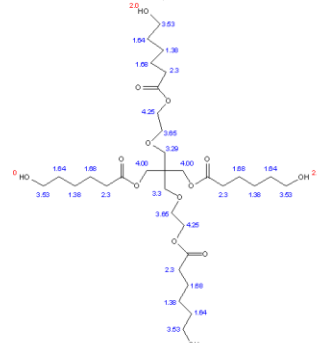
4. Dried under vacuum for 48h at 150 °C to remove any low molecular weights oligomeric species.

Analysis by HNMR: Core

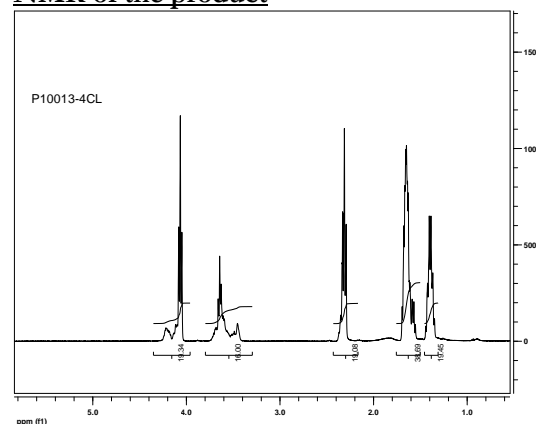
Chemical shifts of Core: Estimation in DMSO



Chemical shifts in CDCl₃ for the 4 arm Caprolactone



NMR of the product



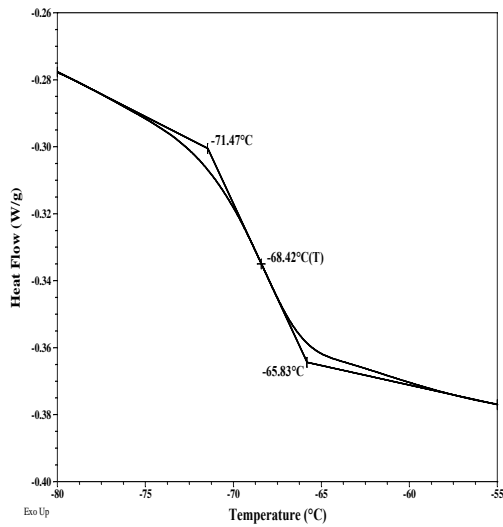
Thermal analysis of the sample

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.

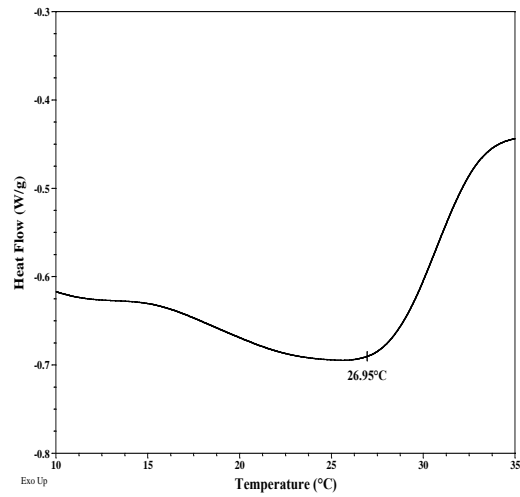
Glass transition temperature for 4CL



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:

