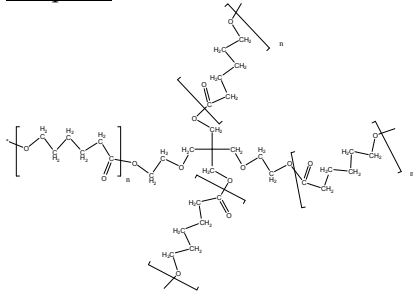


Sample Name:

Four arm Poly(ϵ -caprolactone)

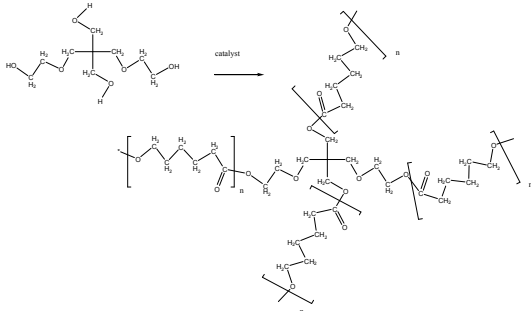
Sample #: P10013-4CL



Mn x 10 ³ (branch)	PDI
0.275 (Mn total 1130)	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:

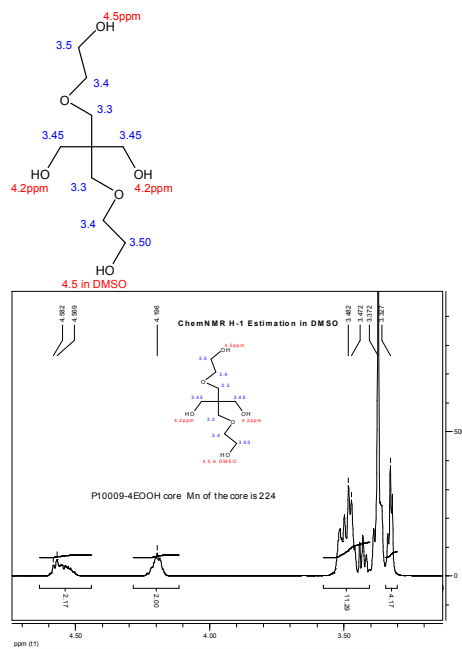
Purification of the obtained polymer was carried out rigorously as discussed below to ensure the removal of the catalyst and traces amount of unreacted 4-Hydroxy core based on pentaerythritol.

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

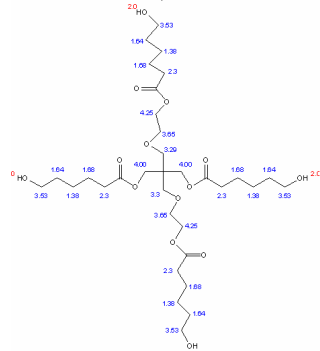
4. Dried under vacuum for 48h at 150 °C to remove any low molecular weights oligomeric species

Analysis by HNMR: Core

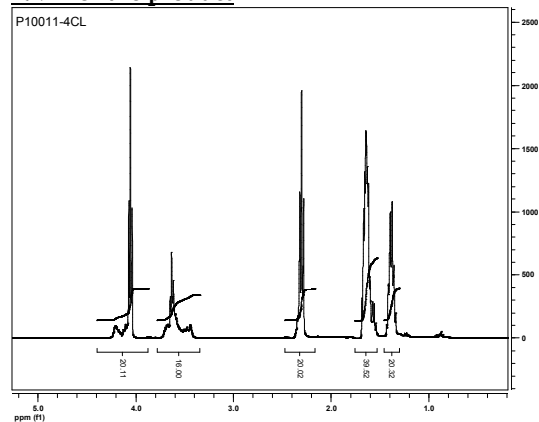
Chemical shifts of Core: Estimation in DMSO



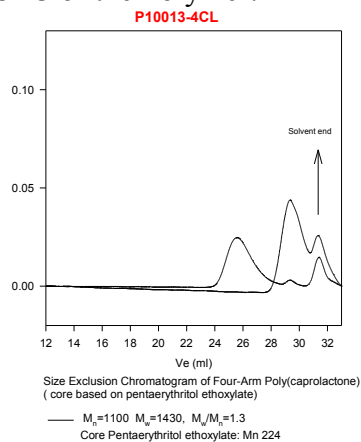
Chemical shifts in CDCl₃ for the 4 arm Caprolactone



NMR of the product



SEC of the Polymer:



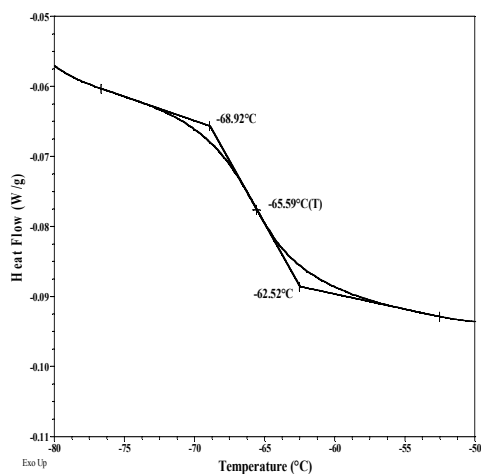
Thermal analysis of the sample P10011-4CL

Thermal analysis of the samples was carried out on a TA Q100 differential scanning calorimeter at a heating rate of $10^\circ\text{C}/\text{min}$. 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.

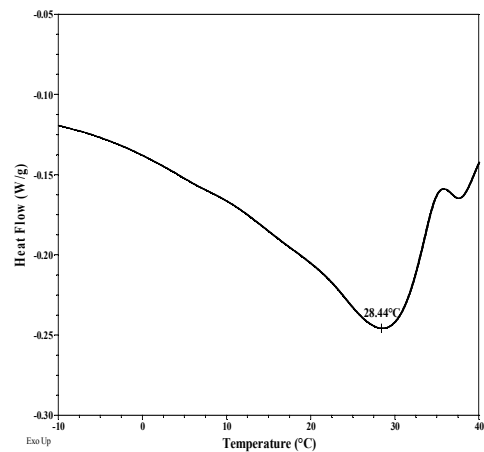
Glass transition temperature for 4CL



Thermal analysis results at a glance

T_m ($^\circ\text{C}$)	T_c ($^\circ\text{C}$)	T_g ($^\circ\text{C}$)
25	-06	-66

Melting curve for the CL sample:



Crystallization curve for the CL sample:

