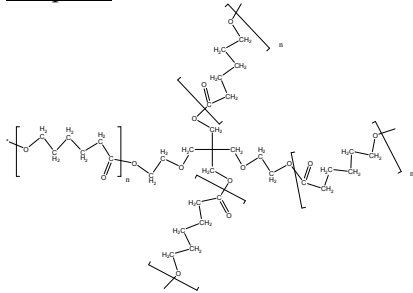


Sample Name:

Four arm Poly( $\epsilon$ -caprolactone)

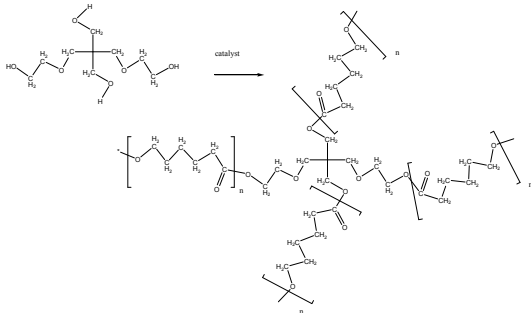
Sample #: P10004-4EOCL



Mn x 10 <sup>3</sup> (branch)	PDI
0.27-b-1.9 (0.475)	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 <sup>1</sup>H-NMR spectroscopy by comparing the peak area of the core protons at about 3.6 ppm with the  $\epsilon$ -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)<sub>3</sub>N as the eluent.

### Purification of the obtained polymer:

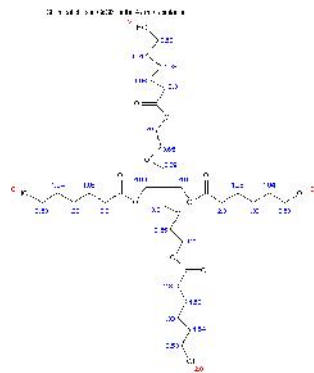
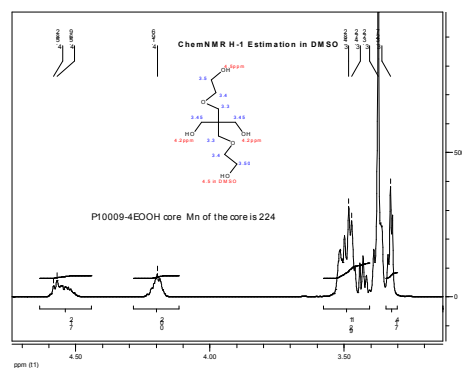
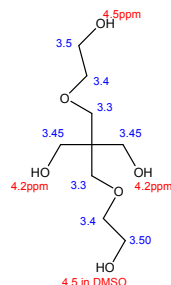
Purification of the obtained polymer was carried out rigorously as discussed below to ensure the removal of the catalyst and traces amount of unreacted 4 -Hydroxy core based on pentaerythritol.

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

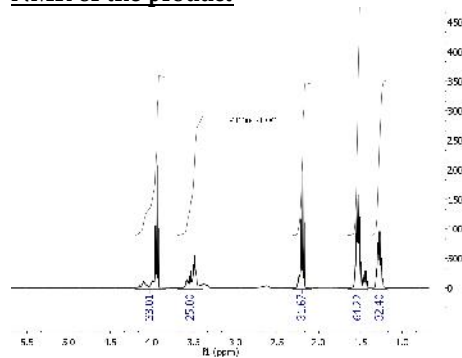
4. Dried under vacuum for 48h at 150 °C to remove any low molecular weights oligomeric species

Analysis by H NMR: Core

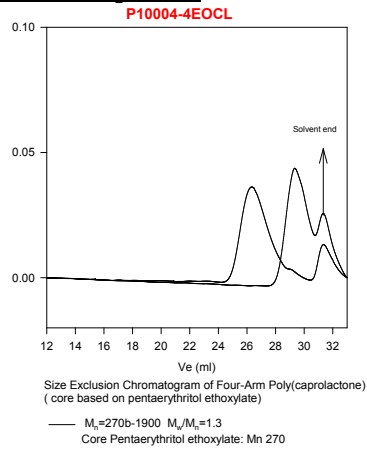
Chemical shifts of Core: Estimation in DMSO



### NMR of the product



## SEC of the product



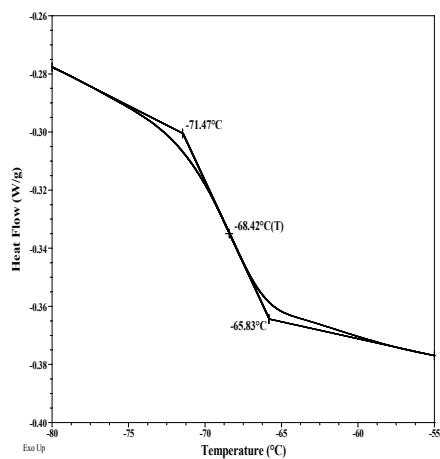
## Thermal analysis of the sample P10004-4CL

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.

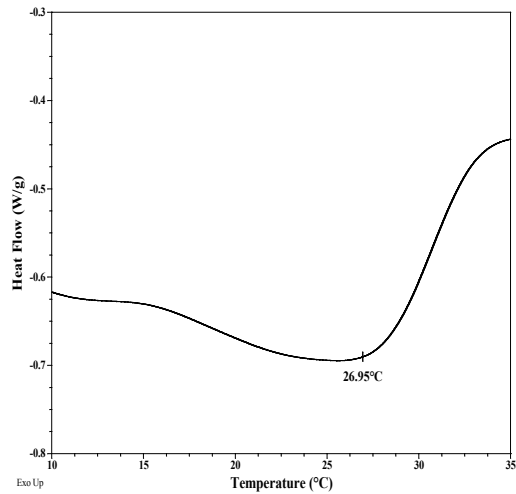
## Glass transition temperature for 4CL



## 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:

