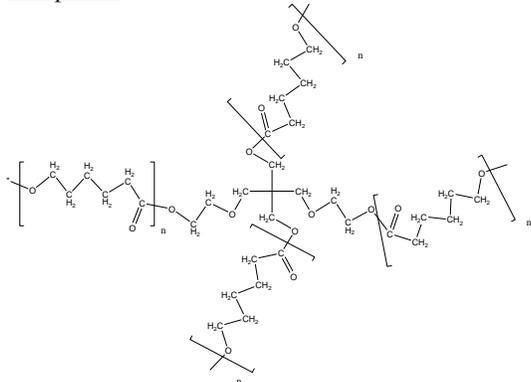


Sample Name: **Four arm Poly( $\epsilon$ -caprolactone)**

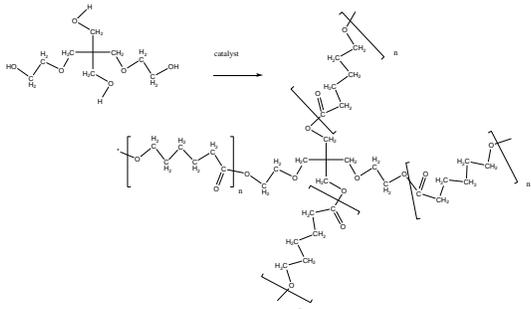
Sample #: **P10005A-4CL**



$M_n \times 10^3$ (branch)	PDI
0.150 ( $M_n$ total 680)	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  $M_n$  average of 224. The scheme of the reaction is illustrated below:



### Characterization:

The  $M_n$  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  $\epsilon$ -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.

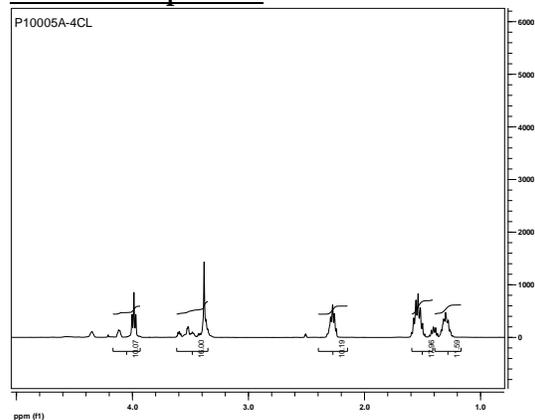
### Purification of the obtained polymer:

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.

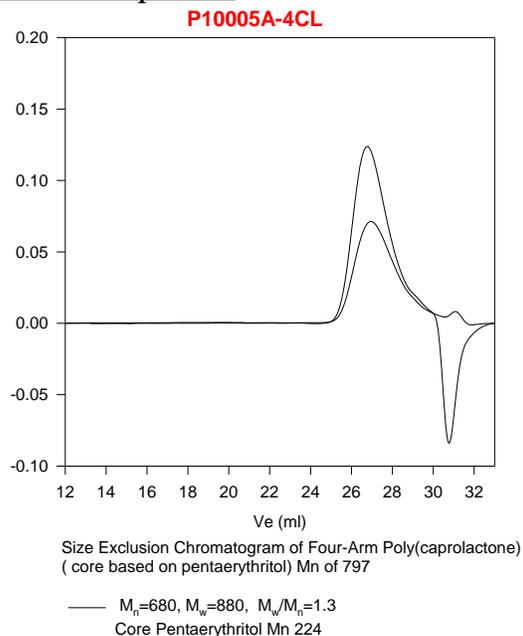
1. Dissolved the polymer dichloromethane, solution was filtered and then passed through a column packed with basic  $Al_2O_3$ .

2. Solution was concentrated on rota-evaporator
3. Solution was precipitated in cold diethyl ether.
4. Dried under vacuum for 48h at 150 °C to remove any low molecular weights oligomeric species.

### NMR of the product



### SEC of the product



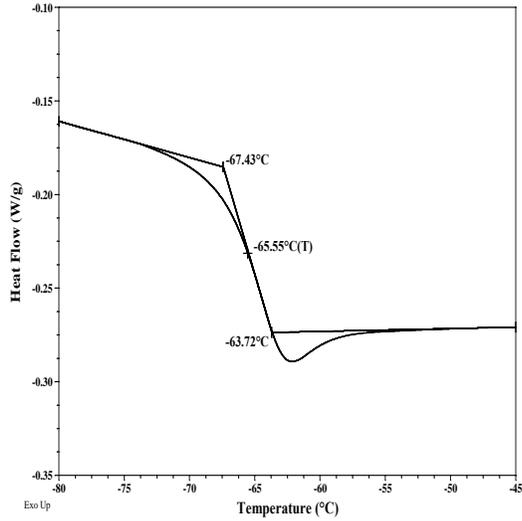
### Thermal analysis of the sample

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 ( $T_g$ ).

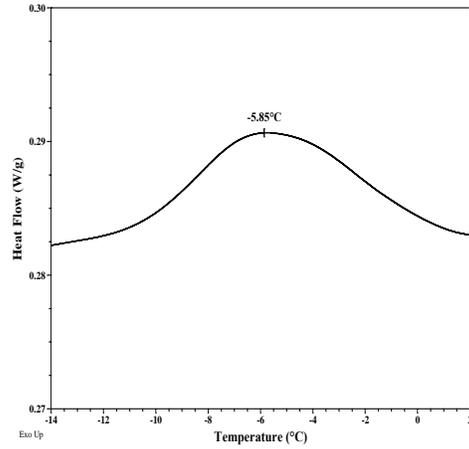
### Melting and crystallization curve for the sample

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



### Crystallization curve for the CL sample:



### Thermal analysis results at a glance

$T_m$ (°C)	$T_c$ (°C)	$T_g$ (°C)
30	-06	-66

### Melting curve for the CL sample:

