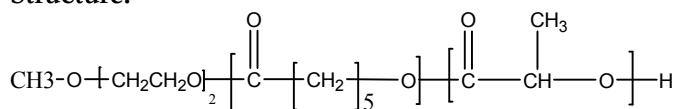


Sample Name: Poly( $\epsilon$ -caprolactone-b- Lactide)

Sample #: P7634-CLLA

Lactide is DL form

**Structure:**

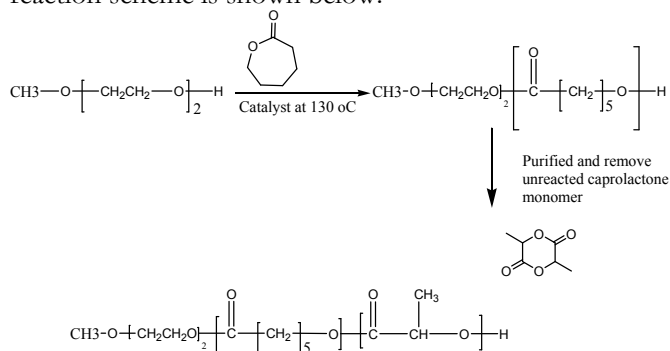


**Composition:**

$M_n \times 10^3$ CL-b-LA	Mw/Mn (PDI)
20.0-b-20.0	1.15

**Synthesis Procedure:**

Poly( $\epsilon$ -caprolactone-b-Lactide) is prepared by ring opening polymerization using tin catalyst and mono functional methoxy diethylene glycol as initiator. The reaction scheme is shown below:



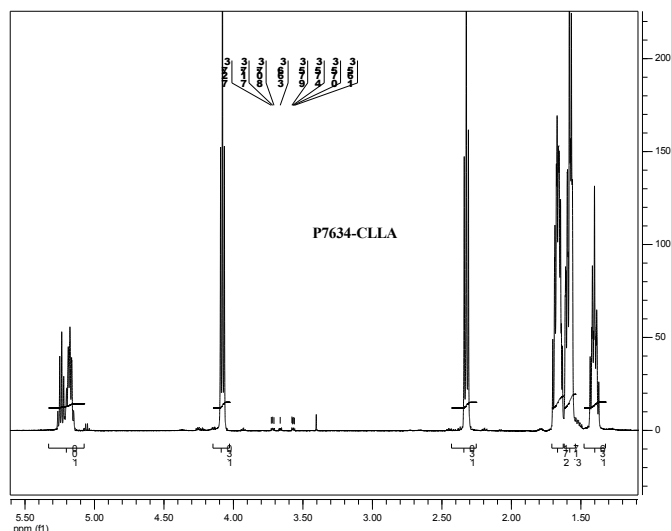
**Characterization:**

An aliquot of the polystyrene block was terminated before addition of  $\epsilon$ -caprolactone and analyzed by size exclusion chromatography (SEC) to obtain the molecular weight and polydispersity index (PDI). The final block copolymer composition was calculated from  $^1\text{H-NMR}$  spectroscopy by comparing the peak area of the styrene protons at 6.3-7.2 ppm with the peak area of  $\epsilon$ -caprolactone protons at 4.1 ppm. Block copolymer PDI is determined by SEC.

**Solubility:**

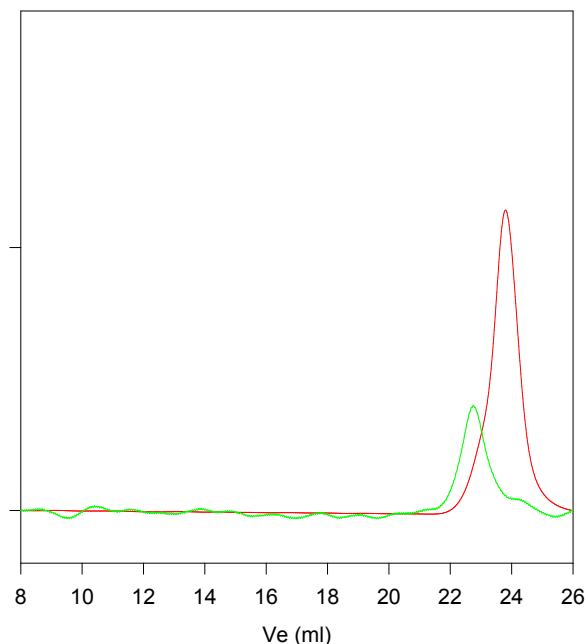
Poly(styrene-b- $\epsilon$ -caprolactone) is soluble in THF, Chloroform, DMF, and precipitated in methanol and hexanes.

$^1\text{H NMR}$  spectrum of the sample:



SEC profile of the block copolymer:

**P7634-CLLA (DL form LA)**



Size exclusion chromatography of poly(styrene-b-2-vinyl pyridine)

- Poly caprolactone,  $M_n=20,000$  Mw:22,000 PI=1.10
- Poly caprolactone (20,000)-b-Poly(lactide)(20,000),PI=1.15

## Thermal analysis of the sample# P7634-CLLA

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 ( $T_g$ ).

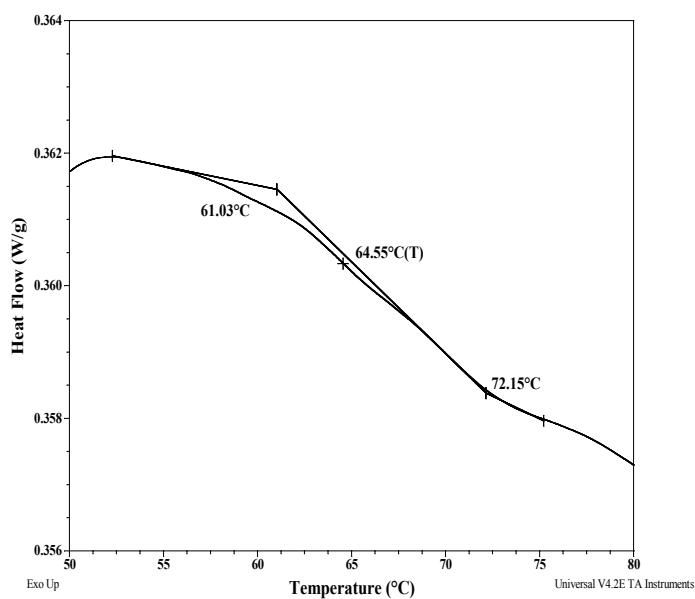
### Melting and crystallization curve for the sample

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.

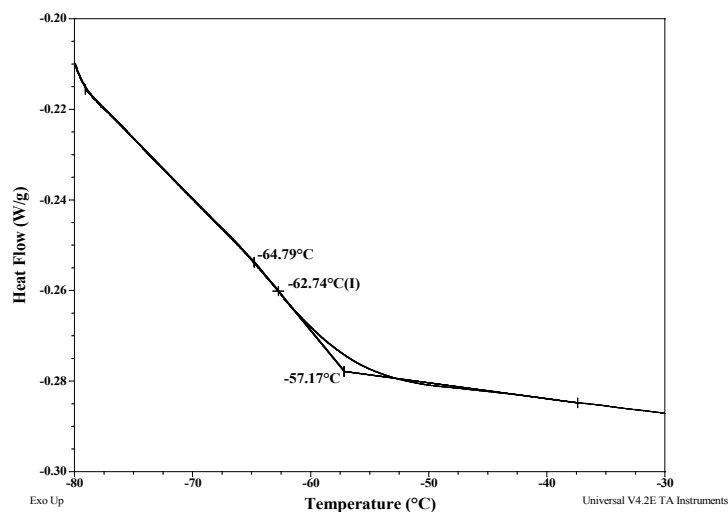
### Thermal analysis results at a glance

Sample	$T_m$ (°C)	$T_c$ (°C)	$T_g$ (°C)
ε-CL	55	25	-63
LA	-	-	65

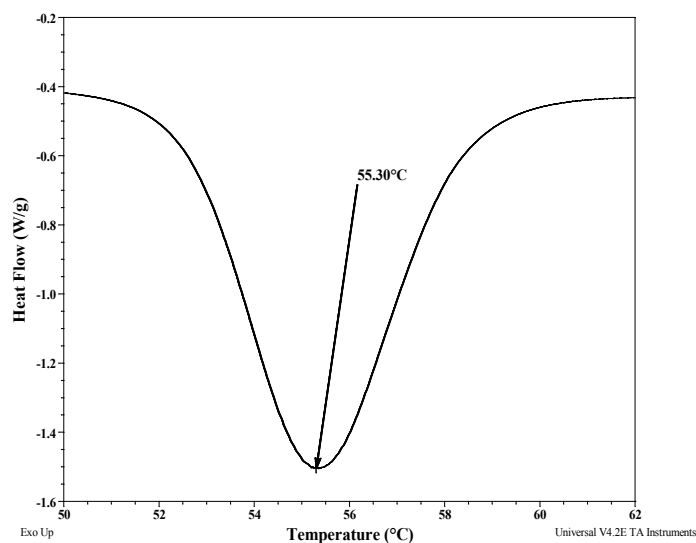
### Thermogram for LA block:



### Thermogram for ε-caprolactone block:



### Melting curve for ε-caprolactone block:



### Crystallization curve for ε-caprolactone block:

