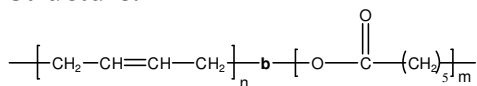


Sample Name: Poly(1,4-butadiene-b-ε-caprolactone)

Sample #: P2097-BdCL

Structure:

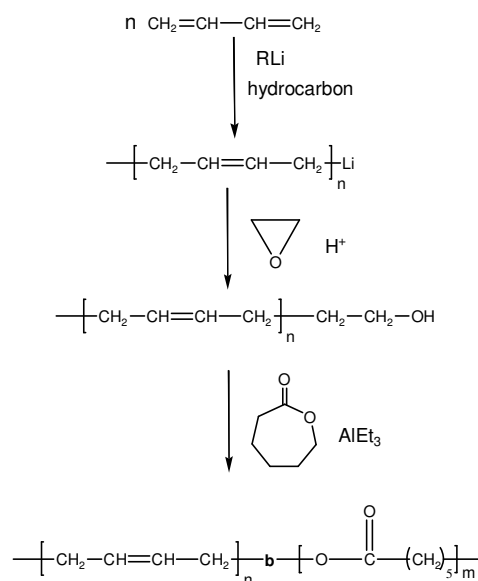


Composition:

| $M_n \times 10^3$ Bd-b-CL | M_w/M_n (PDI) |
|------------------------------|-----------------|
| 11.5-b-12.5 | 1.08 |

Synthesis Procedure:

Poly(1,4-butadiene-b-ε-caprolactone) is prepared by living anionic polymerization addition of butadiene followed coordination polymerization of ε-caprolactone. The reaction scheme is shown below:



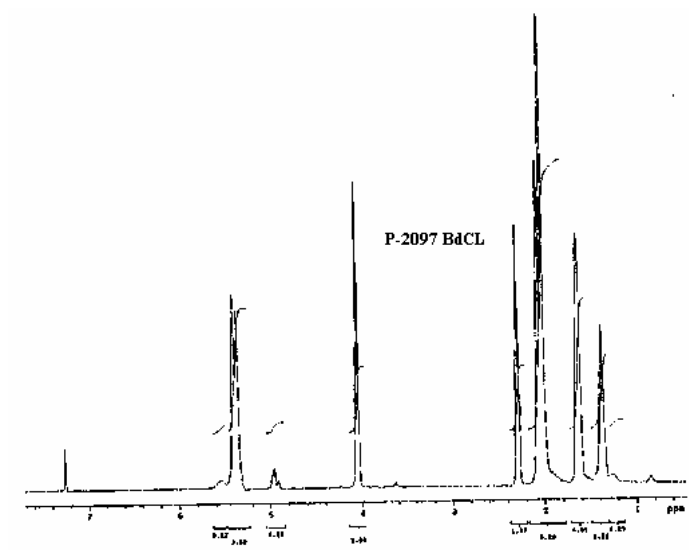
Characterization:

An aliquot of the anionic poly(butadiene) block was terminated before addition of ε-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 ¹H-NMR spectroscopy by comparing the peak area of the vinylic butadiene protons at about 5.4 ppm with the ε-caprolactone protons at about 4.1 ppm. Block copolymer PDI is determined by SEC.

Solubility:

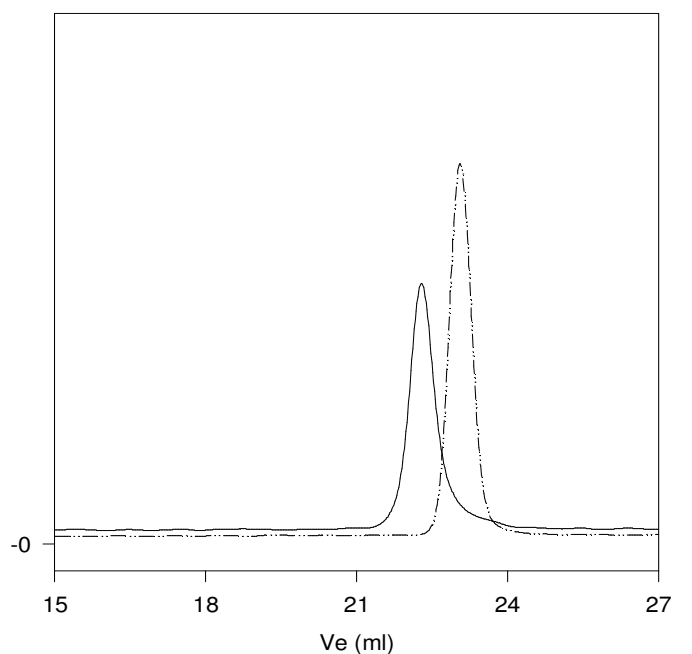
The polymer is soluble in tetrahydrofuran (THF) and chloroform (CHCl₃).

¹H NMR of the block polymer:



SEC of the block copolymer:

P2097-BdCL



- - - - SEC profile of Poly(Butadiene _{1,4 addition} -b-ε-caprolactone):
 - - - - Polybutadiene, $M_n=11500$, $M_w=12000$, $PI=1.03$
 ——— Block Copolymer PBd(11500)-b-PεCL(12500), $PI=1.08$

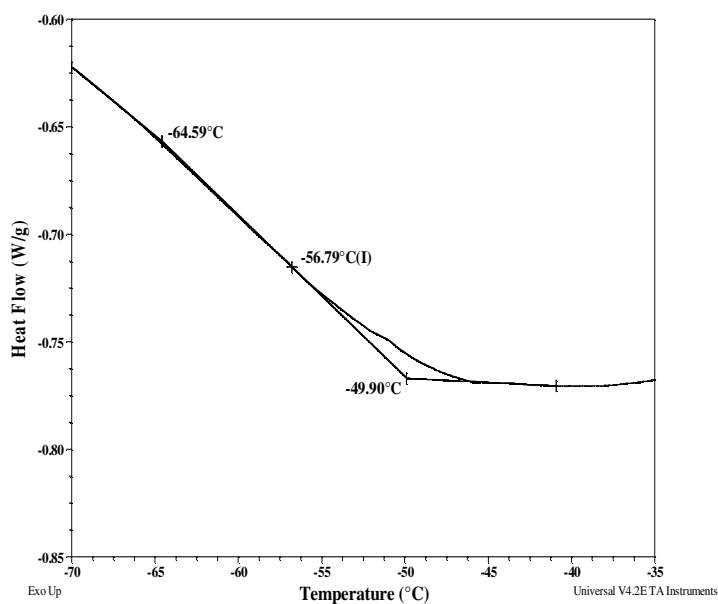
Thermal analysis of the sample# P2097-BdCL

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 whereas the crystallization temperature (T_c) was considered as the minimum of the exothermic peak.

Thermogram for CL block:



Thermal analysis results at a glance

| Sample | T_m (°C) | T_c (°C) | T_g (°C) |
|----------|------------|------------|--------------|
| Bd block | - | - | Not distinct |
| CL block | 59 | 24 | -57 |

Melting & crystallization curves for ϵ -caprolactone block:

