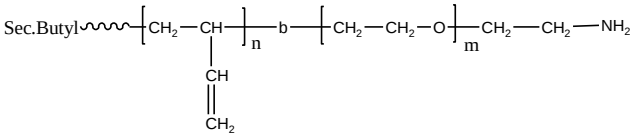
Sample Name: **Amino end functionalized Poly(butadiene-b-ethylene oxide)**

Sample #: **P10192-BdEONH2**
(poly butadiene block rich in 1,2 microstructure)

Structure of 1,2-rich microstructure:



Composition:

Mn x 10^3 Bd-b-EO	Mw/Mn (PDI)	% 1,2 addition Butadiene
1.9-b-0.9	1.09	95

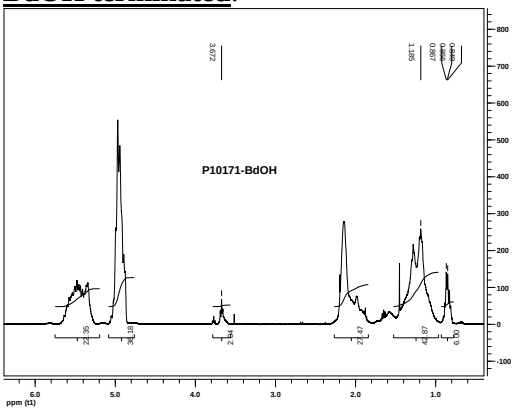
Synthesis Procedure:
Poly(butadiene(1,4 addtion or 1,2 addition)-b-ethylene oxide) can be prepared by the different routes as reported in the literature (ref: Macromolecules 1996, 29, 6994). The direct synthesis of diblock copolymer using lithium counter ion in the presence of Phosphazene Base *t*-BuP_4 is interesting as reported in *Macromolecules,* **32** (8), 2783 -2785, 1999. These polymers can also be successfully synthesized using the different end functionalized polymers as investigated in our lab. These methodologies are proprietary.

Characterization:
Polybutadiene polymer was analyzed by size exclusion chromatography (SEC) to obtain the molecular weight and polydispersity index (PDI). The final block copolymer composition was calculated from ^{1}H-NMR spectroscopy by comparing the peak area of the vinylic butadiene protons between about 5.0-5.4 ppm with the ethylene oxide protons at 3.6 ppm. Block copolymer PDI is determined by SEC. Note: The ^{1}H-NMR of 1,2-polybutadiene is composed of 1 proton signal at 5.4 ppm and 2 proton signals at 5.0 ppm. Signals due to vinylic 1,4-polybutadiene are also present at 5.4 ppm.

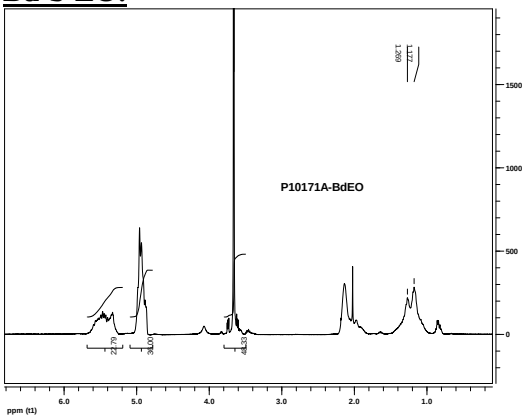
Solubility:
Amino end functionalized Poly(butadiene-b-ethylene oxide) is soluble in THF, $CHCl_3$, and toluene. The polymer has variable solubility in hexane, methanol, ethanol and water depending on its composition.

Titration: the degree of functionality was confirmed by titration with $HClO_4$ using crystal violet as the indicator.

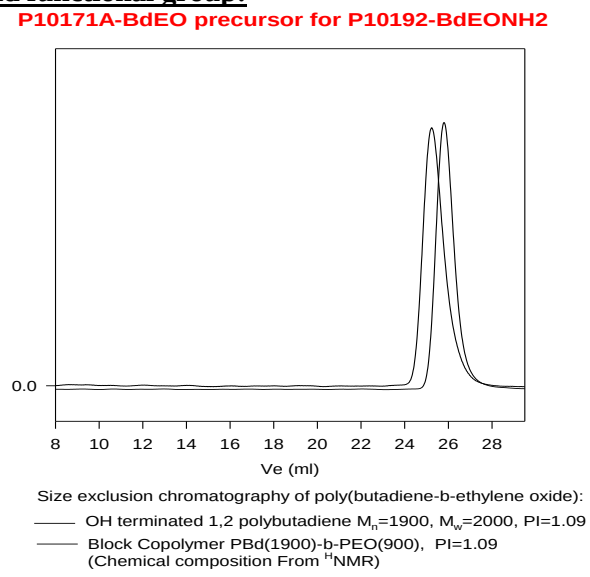
^{1}H NMR spectrum of the sample at different steps:
BdOH terminated:



Bd-b-EO:



SEC profile of the BDEO before converting to NH2 end functional group:



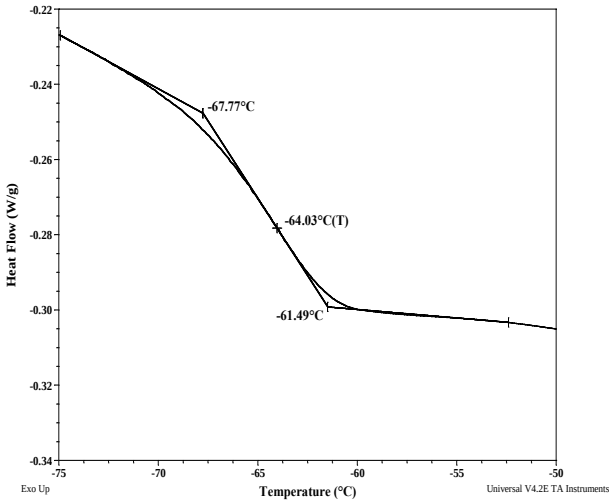
Thermal analysis of the sample P10171A-BdEO precursor for P10192 BdEONH2

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).

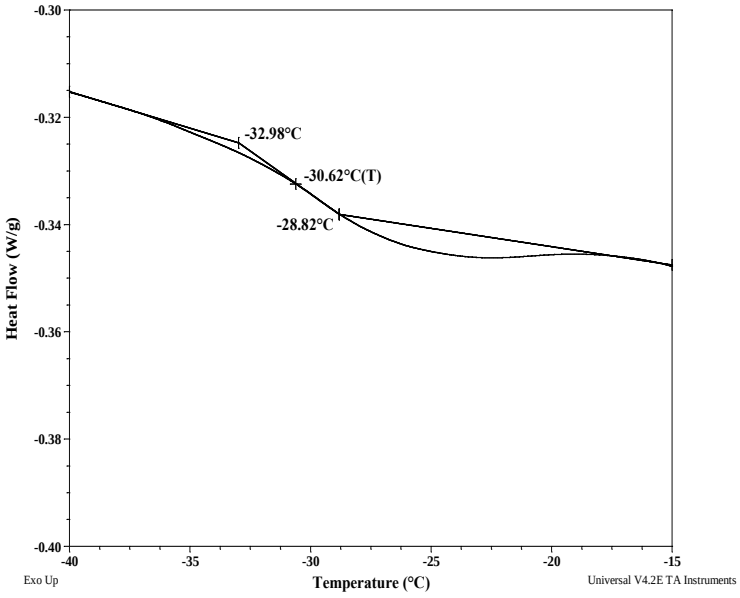
Thermal analysis results at a glance

For Bd block		
T_g: -31°C	T_m: -	T_c: -
For PEO block		
T_g: -64°C	T_m: 48°C	T_c: Not found

Thermogram for PEO block:



Thermogram for PBd block:



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.

Melting curve for PEO block: