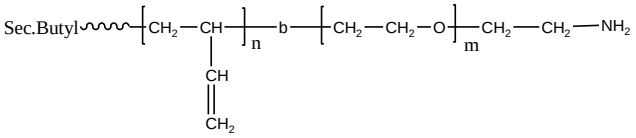
Sample Name: **Amino end functionalized Poly(butadiene-b-ethylene oxide)**

Sample #: **P10950A-BdEONH2**
(poly butadiene block rich in 1,2 microstructure)

Structure of 1,2-rich microstructure:



Composition:

Mn x 10^3 Bd-b-EO-NH2	Mw/Mn (PDI)	% 1,2 addition Butadiene
2.2-b-1.5	1.09	89
NH2 Functionality: >99%		

Synthesis Procedure:

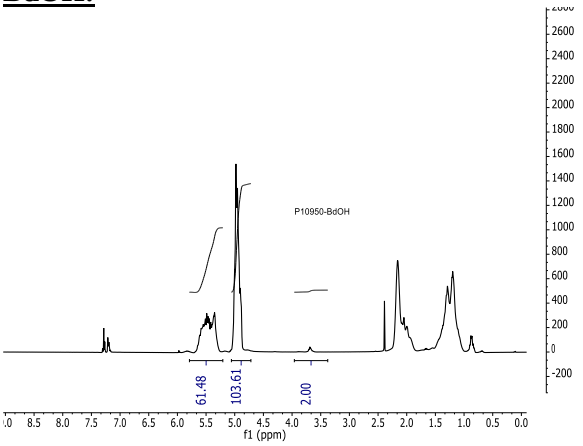
Poly(butadiene(1,4 addtion or 1,2 addition)-b-ethylene oxide) can be prepared by the different routes as reported in the literature (ref: Macromolecules 1996, 29, 6994). The direct synthesis of diblock copolymer using lithium counter ion in the presence of **Phosphazene Base *t*-**BuP_4 is interesting 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.

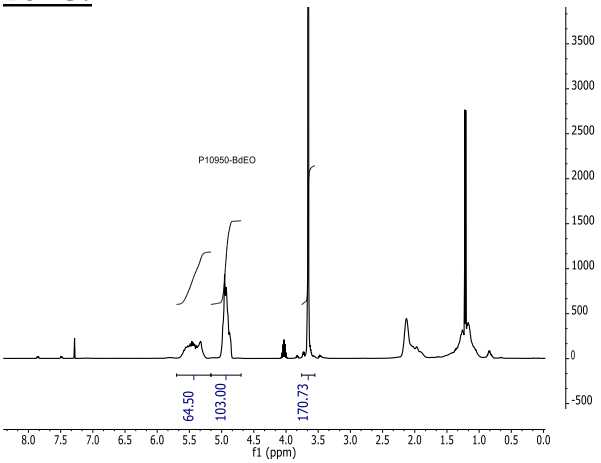
Titration: the degree of functionality was confirmed by titration with $HClO_4$ using crystal violet as the indicator.

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

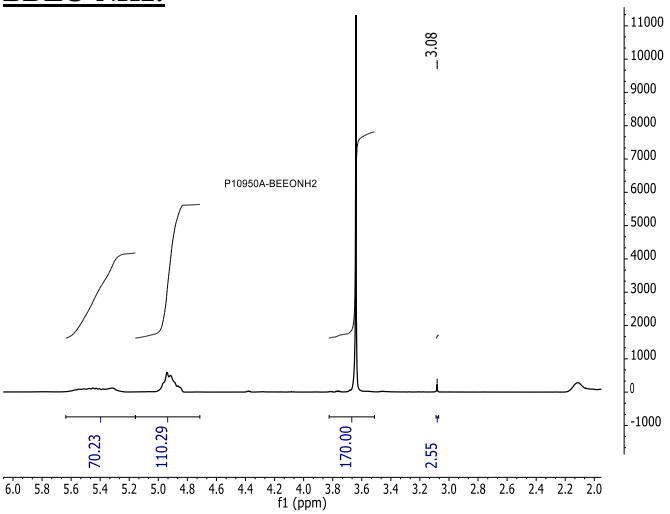
BdOH:



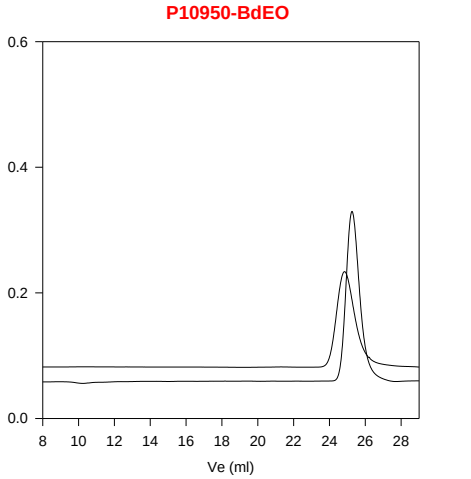
BdEO:



BDEO-NH2:



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



Size exclusion chromatography of poly(butadiene-b-ethylene oxide):

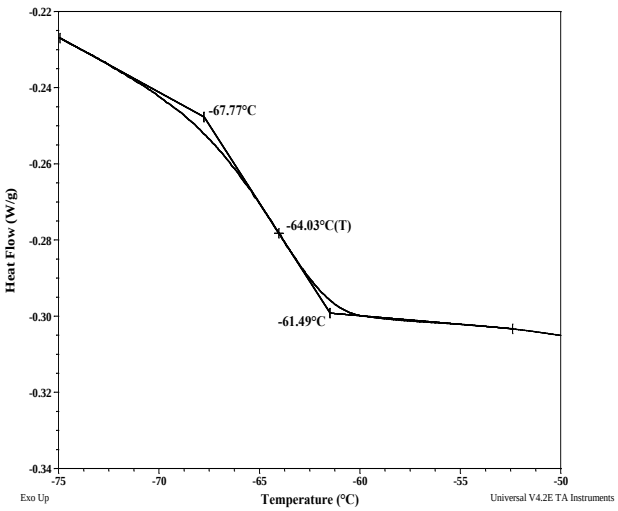
—— 1,4 polybutadiene M_n=2200, M_w=2300, PI=1.05

—— Block Copolymer PBd(2200)-b-PEO(1500), PI=1.09
Composition from H NMR

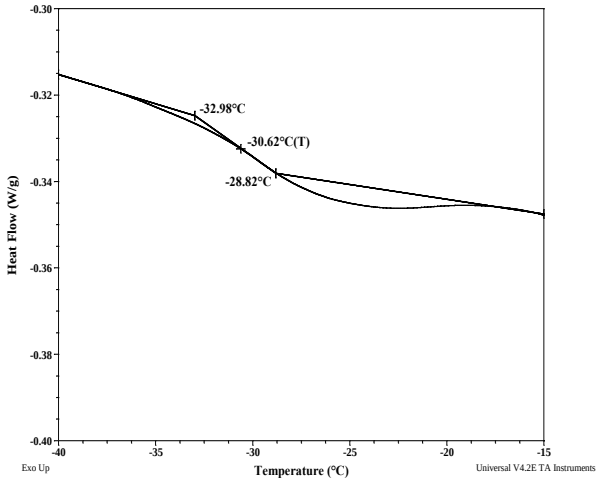
Thermal analysis of the sample P10950-BdEO – precursor for P10950A BdEONH2

Thermal analysis of the samples was carried out on a TA Q100 differential scanning calorimeter at a heating rate of 10ºC/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).

Thermogram for PEO block:



Thermogram for PBd block:



Thermal analysis results at a glance

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

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: