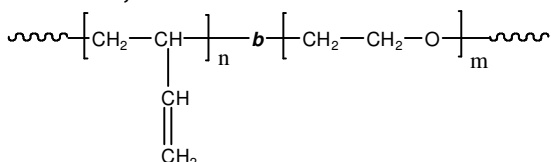


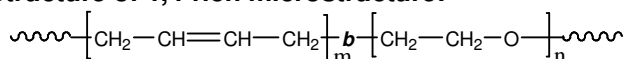
Sample Name: **Poly(butadiene-b-ethylene oxide)**

Sample #: **P19504-BdEO**  
(poly butadiene block rich in 1,2-addition)

Structure of 1,2-rich microstructure:



Structure of 1,4-rich microstructure:



Composition:

| $M_n \times 10^3$<br>Bd- <i>b</i> -EO | $M_w/M_n$ | Polybutadiene:<br>1,2-addition |
|---------------------------------------|-----------|--------------------------------|
| 144.0- <i>b</i> -24.0                 | 1.10      | 92 %                           |

### Synthesis Procedure:

Poly(butadiene[1,4- 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<sub>4</sub> is reported in *Macromolecules* 1999, 32 (8), 2783–785. The polymers can also be successfully synthesized using the different end-functionalized polymers as investigated in our lab. These methodologies are proprietary.

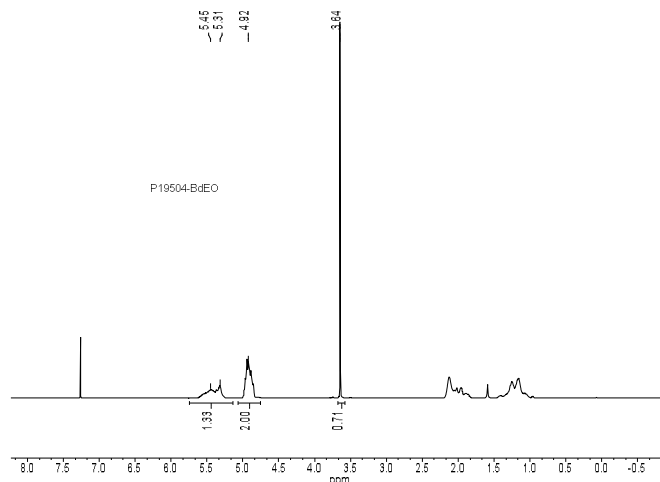
### Characterization:

OH-terminated 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 <sup>1</sup>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 <sup>1</sup>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:

Poly(butadiene-*b*-ethylene oxide) is soluble in THF, CHCl<sub>3</sub>, and toluene. The polymer has variable solubility in hexane, methanol, ethanol and water depending on its composition.

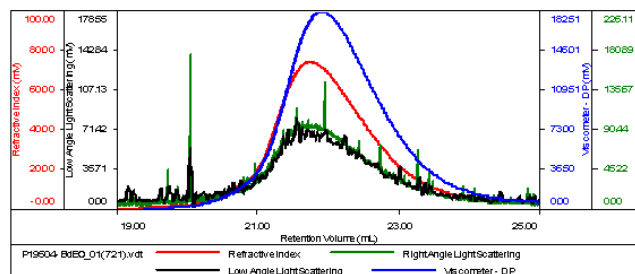
### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum:



### SEC elugram of the block copolymer:

Sample IDP19504-BdEC

|                       |                            |
|-----------------------|----------------------------|
| Concentration (mg/mL) | 0.0019                     |
| Sample dn/dc (mL/g)   | 0.1200                     |
| Method File           | P980K-June30-2015-0000.vcm |
| Column Set            | 3x PL 1113600              |
| Solvent               | THF                        |

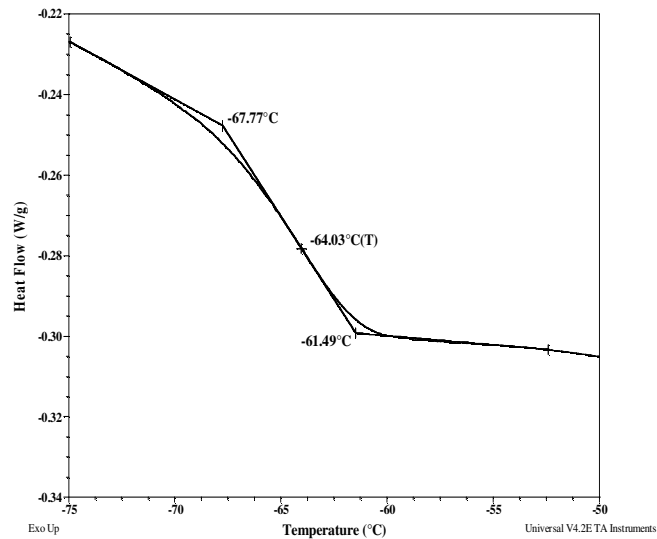


| Sample                 | MW Number Average (Da) | MW Weight Average (Da) | MW at Peak (Da) | Polydispersity | Intrinsic Viscosity (dL/g) |
|------------------------|------------------------|------------------------|-----------------|----------------|----------------------------|
| P19504-BdEO_01(721).vd | 109,895                | 135,837                | 101,681         | 1.09           | 8.4738                     |

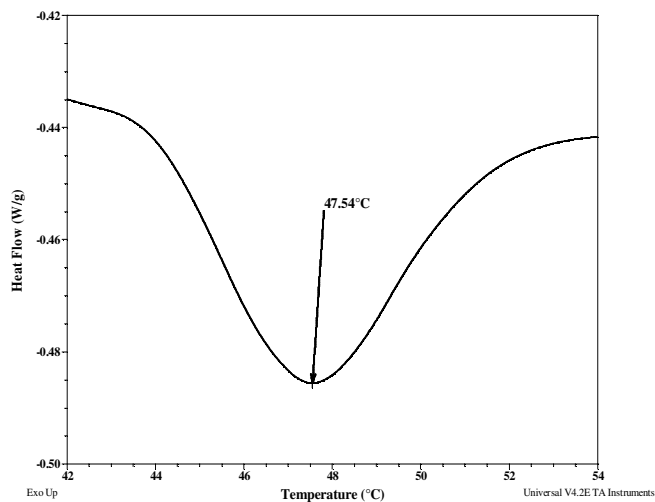
### DSC thermal analysis:

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*<sub>g</sub>). The melting temperature (*T*<sub>m</sub>) was taken as the maximum of the endothermic peak where as the crystallization temperature (*T*<sub>c</sub>) was considered as the minimum of the exothermic peak.

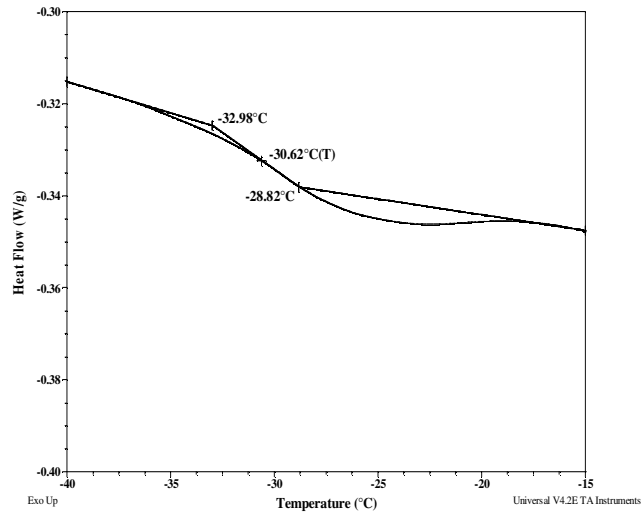
DSC thermogram for PEO block:



DSC melting curve for PEO block:



DSC thermogram for PBd block:



Summary of thermal analysis results for P19504:

| For Bd block           |                       |                            |
|------------------------|-----------------------|----------------------------|
| T <sub>g</sub> : -31°C | T <sub>m</sub> : -    | T <sub>c</sub> : -         |
| For PEO block          |                       |                            |
| T <sub>g</sub> : -64°C | T <sub>m</sub> : 48°C | T <sub>c</sub> : not found |