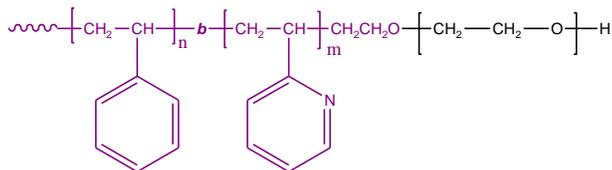


## Sample Name:

Poly(styrene-b-2-vinyl pyridine-ethylene oxide)

## Sample #: P8501-S2VPEO

### Structure:

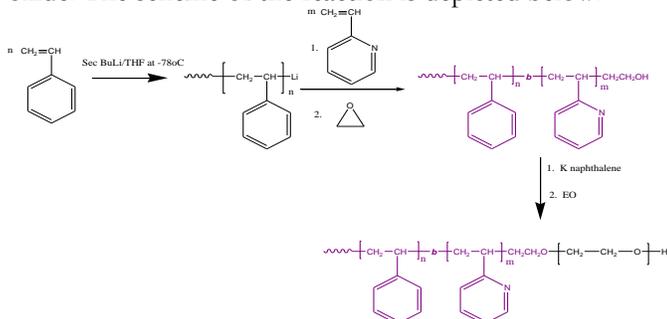


### Composition:

Mn x 10 <sup>3</sup>	PDI
S-b-2VP-b-EO	
45.0-b-26.0-82.0	1.12

### Synthesis Procedure:

Poly(styrene-b-2-vinyl pyridine-ethylene oxide) triblock copolymer is prepared by living anionic polymerization. The triblock is synthesized in 2 steps: 1<sup>st</sup> OH terminated Poly(S-b-2VP) is synthesized in THF at  $-78^\circ\text{C}$  using LiCl as an additive. Polystyrene macroanions were end capped with a unit of diphenyl ethylene (DPE) before adding 2-vinylpyridine (2VP) monomer. The reaction was terminated with ethylene oxide. The OH terminated Poly(S-b-2VP) was converted to potassium salt by addition of K-naphthalene and freshly distilled ethylene oxide. The scheme of the reaction is depicted below:



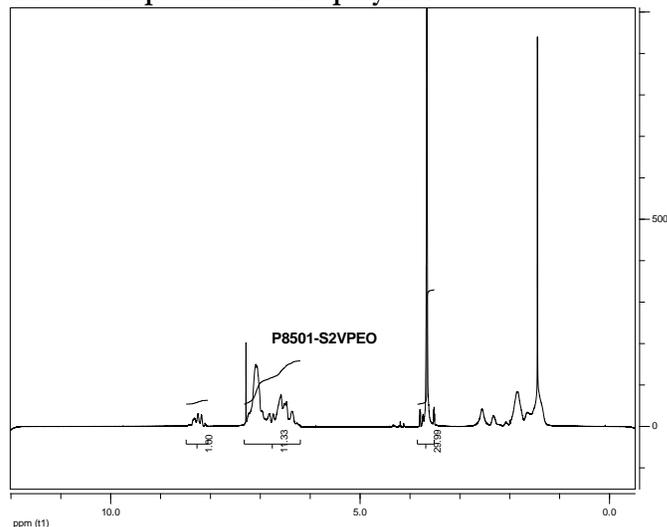
### Characterization:

An aliquot of the anionic polystyrene block was terminated before addition of 2VP and analyzed by size exclusion chromatography (SEC) to obtain the molecular weight and polydispersity index (PDI). The Block copolymer composition was then calculated from  $^1\text{H-NMR}$  spectroscopy by comparing the peak area of the 2VP proton at 8.2 ppm with the peak area of the aromatic protons of polystyrene at 6.3-7.2 ppm and EO protons at 3.6 ppm. The composition of the block copolymer can also be determined by titration in acetic acid/ $\text{HClO}_4$  using crystal violet indicator. Copolymer PDI is determined by SEC.

### Solubility:

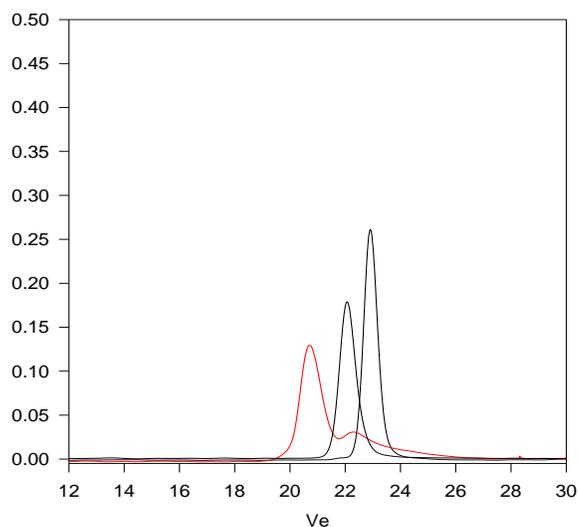
Poly(styrene-b-2 vinylpyridine-b-ethylene oxide) is soluble in THF, toluene, and  $\text{CHCl}_3$ . The triblock copolymer can also be solubilized in methanol, ethanol depending on its composition. The polymer readily precipitates from hexanes, ether and water.

### $^1\text{H-NMR}$ Spectrum of the polymer:



### SEC for triblock polymer:

#### P8501-S2VPEO



#### Size Exclusion Chromatography :

- First PS block,  $M_n=45000$ ,  $M_w/M_n=1.15$
- PS2VP, the diblock PS(45000)-b-P2VP(26,000),  $M_w/M_n=1.10$
- PS2VPEO, the triblock PS(45,000)-b-P2VP(26,000)-b-PEO(82,000)  $M_w/M_n=1.12$  (composition from H NMR)

### References:

1. S. K. Varshney, X. F. Zhong and A. Eisenberg *Macromolecules* **1993**, 26, 701-706.
2. Gohy J.-F., Willet N., Zhang J.-X., Varshney S., Jerome, , *pH dependence of the morphology of aqueous micelles formed by poly(styrene)-block-poly(2-vinylpyridine)-block-poly(ethylene oxide) copolymers*, e-polymers 2002, 35.
3. Gohy, J.-F., Lohmeijer, B Varshney S,K, Decamps B., Leroy E., Boileau S., Schubert U. S., *Stimuli-responsive aqueous micelles from an ABC metallo-supramolecular triblock copolymer*, *Macromolecules* 2002, 35, 9748-9755.
4. Gohy, J.-F., Mores S., Varshney S. K., Jerome, R., *Self-organization of water-soluble complexes of a poly(2-vinylpyridinium)-block-poly(ethylene oxide) diblock and a fluorinated anionic surfactant*, *Macromolecules* 2003, 36, 2579-2581.
5. Leil L., Gohy J.-F., Willet N., Zhang J.-X., Varshney S., Jerome R., *Tuning of the morphology of core-shell-corona aqueous micelles: I. sphere-to-cylinder transition*, *Macromolecules* 2004, 37, 1089-1094.
6. Jean-Francois Gohy, Bas G. G. Lohmeijer, Sunil K. Varshney, and Ulrich S. Schubert, *Covalent vs Metallo-supramolecular Block Copolymer Micelles* *Macromolecules* 2002, 35, 7427-7435.

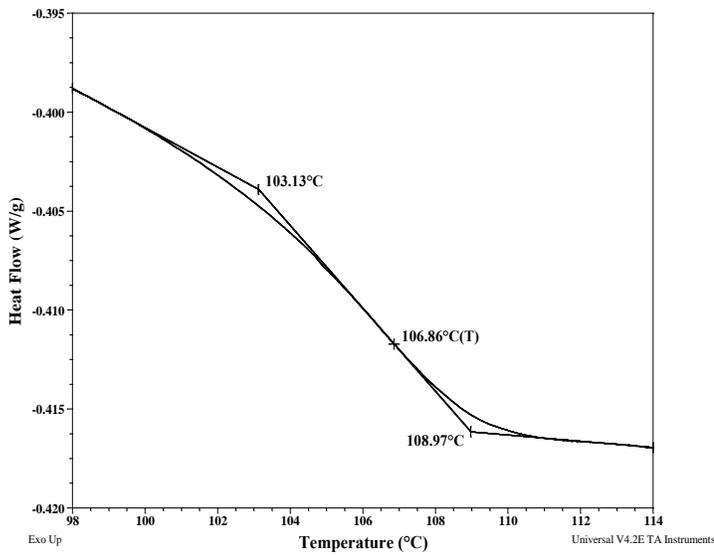
## Thermal Analysis of the sample P8501-S2VPEO

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 ( $T_g$ ).

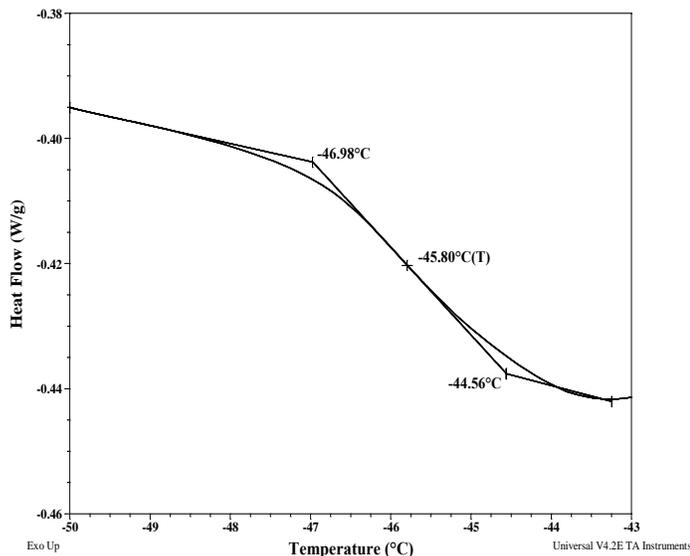
### Thermal analysis results at a glance

For PS block: $T_g$ : 107°C		For 2VP block: $T_g$ : Not distinct
For PEO block		
$T_g$ : -46°C	$T_m$ : 63°C	$T_c$ : 42°C

### Thermogram for PS block:



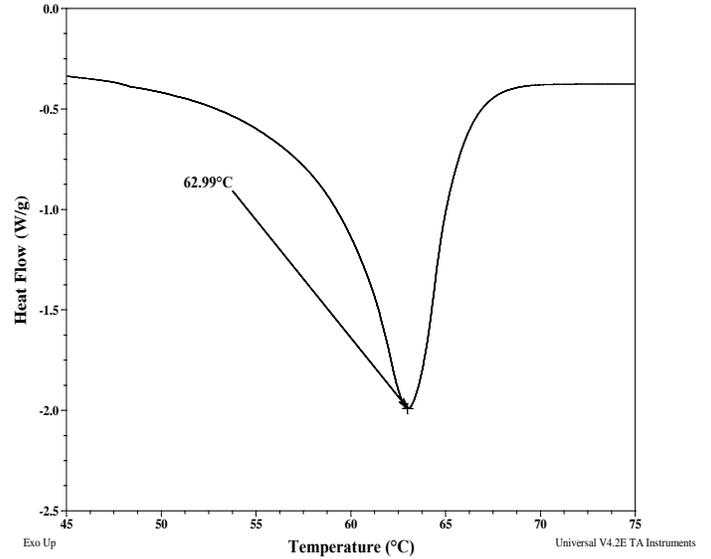
### Thermogram for PEO block:



## 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



### Crystallization curve For PEO block:

