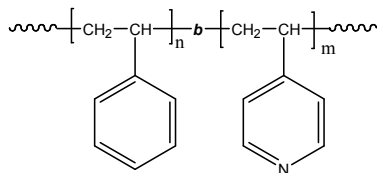


**Sample Name:** Poly(styrene-b-4-vinyl pyridine)

**Sample #:** P10749-S4VP

**Structure:**



**Composition:**

$M_n \times 10^3$ S-b-4VP	PDI
213.0-b-80.0	1.3
Tg for PS block: 104 °C	Tg for 4VP block: 153 °C

**Synthesis Procedure:**

Poly(styrene-b-4-vinyl pyridine) is prepared by living anionic polymerization in THF at  $-78^\circ\text{C}$  in the presence of LiCl as an additive.

**Characterization:**

An aliquot of the anionic polystyrene block was terminated before addition of 4VP 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. 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. Thermal analysis of the samples was carried out on a TA Q100 differential scanning calorimeter at a heating rate of  $10^\circ\text{C}/\text{min}$ . The midpoint of the slope change of the heat flow plot of the second heating scan was considered as the glass transition temperature ( $T_g$ ).

**Solubility:**

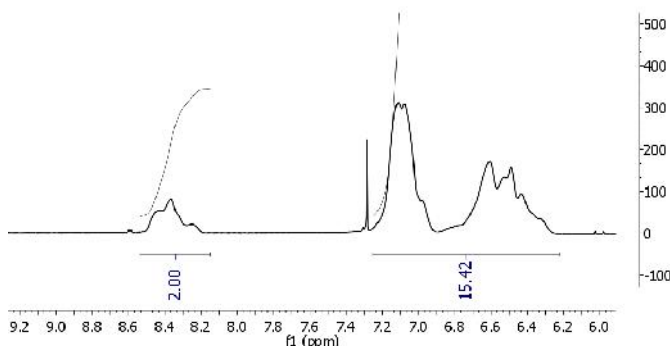
Poly(styrene-b-4-vinylpyridine) is soluble in THF, toluene, and  $\text{CHCl}_3$ . The diblock copolymer can also be solubilized in methanol, ethanol depending on its composition. The polymer readily precipitates from hexanes, ether and water.

**Purification of the obtained polymer was carried out rigorously as follows to ensure the removal of the catalyst side product:**

1. Dissolved the polymer in  $\text{CHCl}_3$  and wash with de-ionized distilled water to remove the any soluble organic catalyst side product.
2. Polymer extracted from water with chloroform.
3. Polymer solution in  $\text{CHCl}_3$  was dried over anhydrous sodium sulfate.
4. Solution filtered and then passed through a column packed with basic  $\text{Al}_2\text{O}_3$ .
5. Solution concentrated on rota-evaporator
6. Solution precipitated in cold hexane and redissolved in benzene and freeze dried.
7. Final dried under vacuum for 48h at  $50^\circ\text{C}$ .

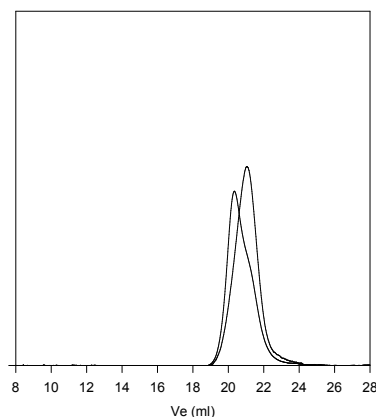
**$^1\text{H}$  NMR Spectrum of the Polymer**

P10749-S4VP



**SEC for the polymer:**

P10749-S4VP

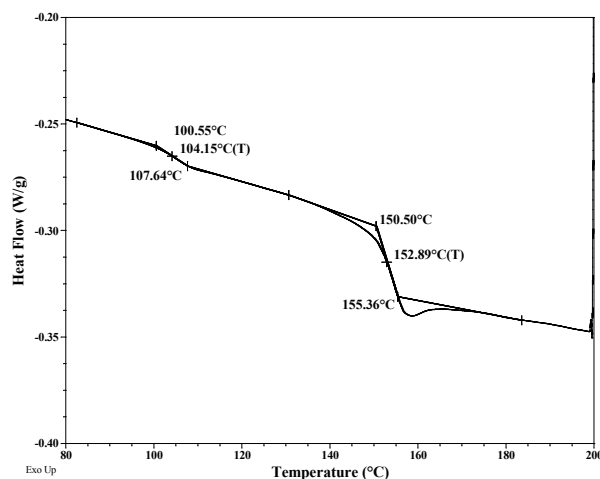


Size exclusion chromatography of poly(styrene-b-2-vinyl pyridine)

— Polystyrene,  $M_n=213,000$  Mw: 245,000 PI=1.15

— Polystyrene(213,000)-b-Poly(80,000), PI=1.3

**DSC thermogram for the PS block:**



**References:**

- (1). S. K. Varshney, X. F. Zhong and A. Eisenberg *Macromolecules*, **1993**, 26, 701-706.
- (2). Z.Gao, S. K. Varshney, S. Wong, A. Eisenberg *Macromolecules*, **1994**, 27, 7923-7927.