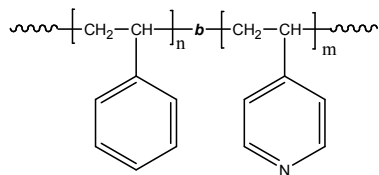


Sample Name: **Poly(styrene-b-4-vinyl pyridine)**

Sample #: **P5728-S4VP**

**Structure:**



**Composition:**

Mn x 10 <sup>3</sup> PS-b-4VP	PDI
274.0-b-7.0	1.15
T <sub>g</sub> for PS block:101°C	T <sub>g</sub> for 4VP block: not clear

**Synthesis Procedure:**

Poly(styrene-b-4-vinyl pyridine) is prepared by living anionic polymerization in THF or THF-DMF solvent mixtures at -78 °C. Polystyrene macroanions were end capped with a unit of diphenyl ethylene (DPE) before adding 4-vinylpyridine (4VP) monomer. For further details please see our published articles.<sup>1,2</sup>

**Characterization:**

An aliquot of the anionic polystyrene block was terminated before addition of 4-vinyl pyridine and analyzed by size exclusion chromatography (SEC) in DMF to obtain the molecular weight and polydispersity index (PDI). The block copolymer composition was then calculated from <sup>1</sup>H-NMR spectroscopy by comparing the peak area of the two aromatic 4-VP protons at about 8.5 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/HClO<sub>4</sub> using crystal violet indicator. Copolymer PDI is determined by SEC.

**Difficulties in determination of chemical compositions of such high molecular weights product:**

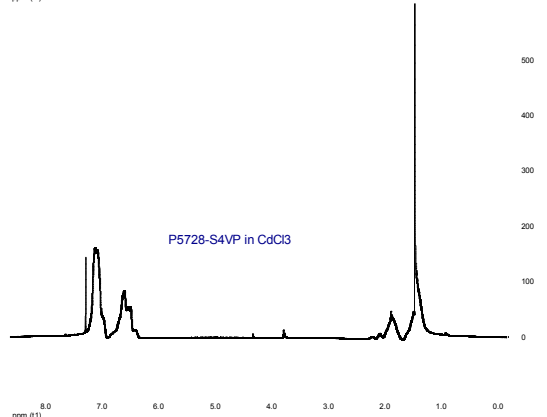
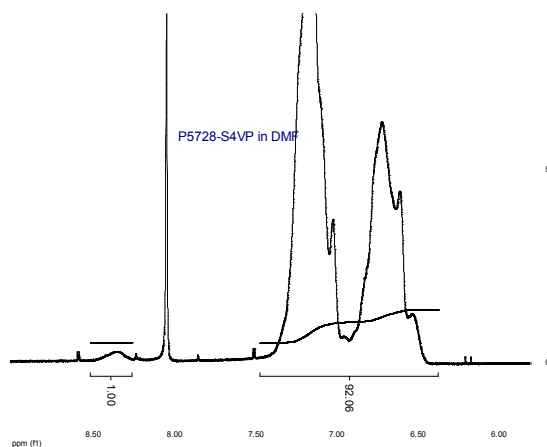
These high molecular weights polymer by HNMR in CdCl<sub>3</sub> do not gives the correct compositions. These polymers were characterized by HNMR in DMF at room temperature and at 50°C. In CdCl<sub>3</sub>, HNMR chemical shift occurs at 8.4 ppm. The product compositions were verified by titration in acetic acid using crystal violet and HClO<sub>4</sub> (per chloric acid) acid-base titration. The Compositions were also verified by FTIR taking the comparison of styrene characteristics at 3059 cm<sup>-1</sup> and for 4VP at 1558 Cm<sup>-1</sup>. From titration it shows the **presence of 24 wt % 4VP component**.

Thermal analysis of the samples was carried out using a differential scanning calorimeter (TA Q100) at a heating rate of 10°C/min. The inflection glass transition temperature (T<sub>g</sub>) of the sample has been considered.

**Solubility:**

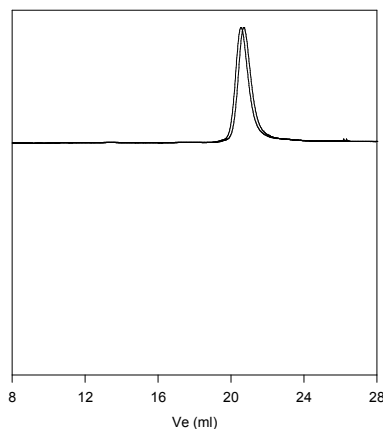
Poly(styrene-b-4-vinyl pyridine) is soluble in DMF, CHCl<sub>3</sub>. The polymer can also be solubilized in THF depending on its chemical composition. The polymer readily precipitates from hexanes and diethyl ether.

**H-NMR Spectrum of Sample:**



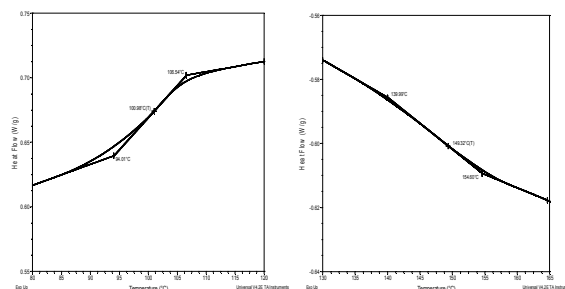
**SEC of Sample #**

**P5728-S4VP**



Size exclusion chromatography of polystyrene-b-poly(4-vinylpyridine)  
— Polystyrene, M<sub>n</sub>=274,000, M<sub>w</sub>=315,000, PI=1.09  
— Block Copolymer PS(274,000)-b-P4VP(7000), PI=1.15 Run in DMF

**Thermogram of sample:**



**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.