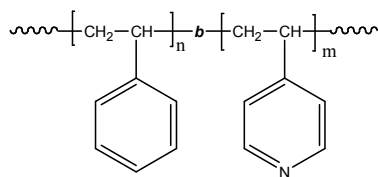


Sample Name: Poly(styrene-b-4-vinyl pyridine)

Sample #: P5731-S4VP

Structure:



Composition:

Mn x 10 ³ PS-b-4VP	PDI
235.0-b-23.0	1.15
T _g for PS block: 101°C	T _g 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.^{1,2}

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 ¹H-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/HClO₄ using crystal violet indicator. Copolymer PDI is determined by SEC.

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

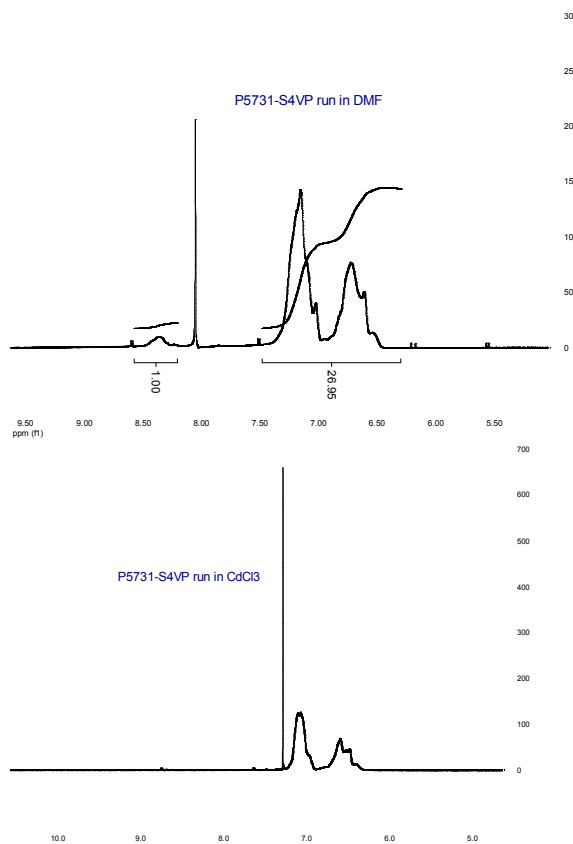
These high molecular weights polymer by HNMR in CdCl₃ do not gives the correct compositions. These polymers were characterized by HNMR in DMF at room temperature and at 50°C. In CdCl₃, HNMR chemical shift occurs at 8.4 ppm. The product compositions were verified by titration in acetic acid using crystal violet and HClO₄ (per chloric acid) acid-base titration. The Compositions were also verified by FTIR taking the comparison of styrene characteristics at 3059 cm⁻¹ and for 4VP at 1558 Cm⁻¹. 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_g) of the sample has been considered.

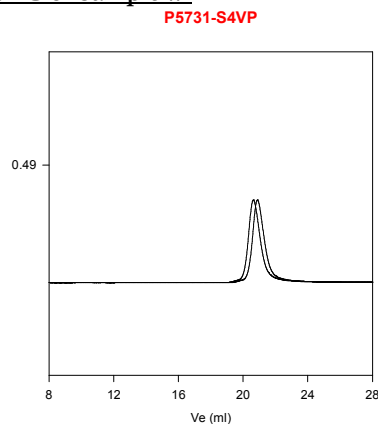
Solubility:

Poly(styrene-b-4-vinyl pyridine) is soluble in DMF, CHCl₃. 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:

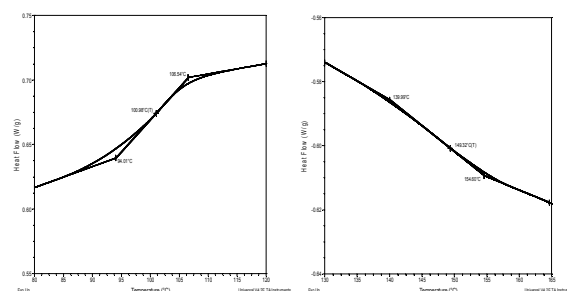


SEC of Sample #



Size exclusion chromatography of polystyrene-b-poly(4-vinylpyridine)
— Polystyrene, M_n=235,000, M_w=258,000, PI=1.10
— Block Copolymer PS(235,000)-b-P4VP(23000), 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.