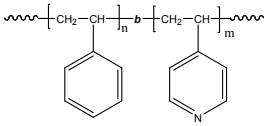
Sample Name: **Poly(styrene-b-4-vinyl pyridine) Electronic grade**

Sample #: **P5635P-S4VP**

Structure:



Composition:

Mn x 10^3 PS-b-4VP	PDI
1,100.0-b-285.0	1.13
T_g for PS block: 103°C	T_g for 4VP block: 154°C

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 ^{1}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/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 $HClO_4$ (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 22 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.

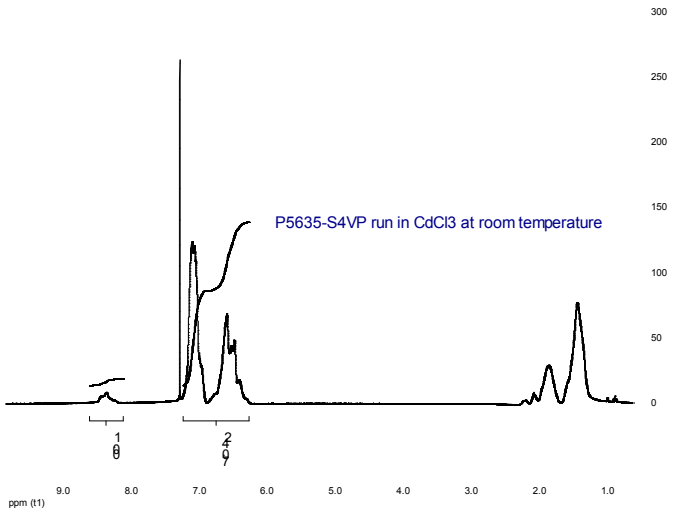
Solubility:

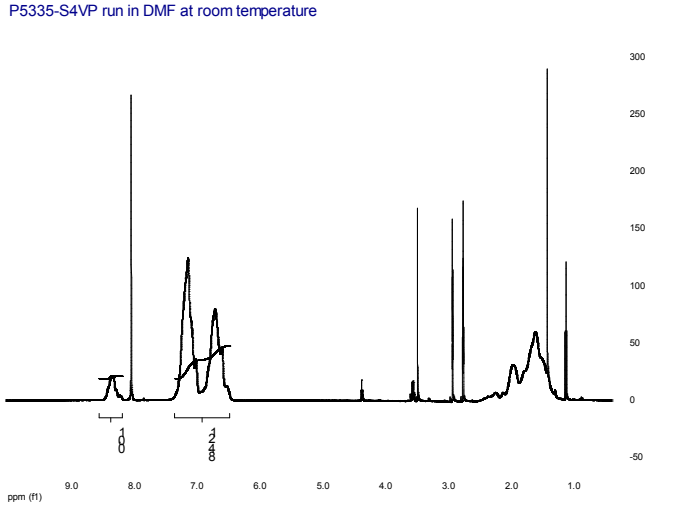
Poly(styrene-b-4-vinyl pyridine) is soluble in DMF, $CHCl_3$.

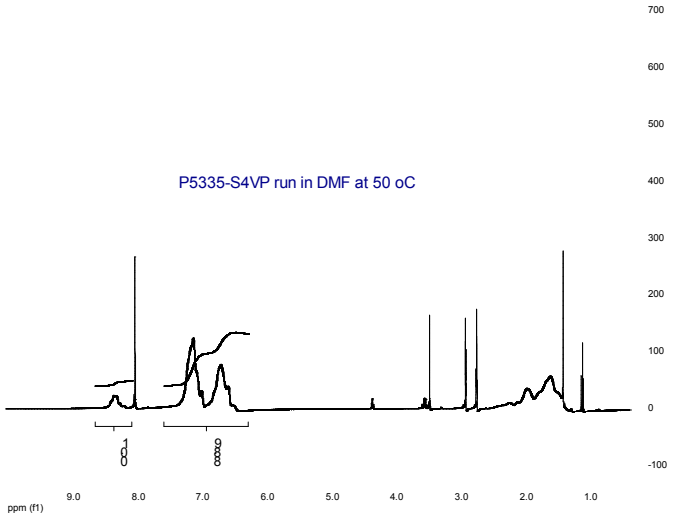
Purification of the obtained polymer was carried out rigorously as follows to ensure the removal of the catalyst side product:

1. First the polymer soxhlet in Cylcohexane to remove unreacted homiopolystyrene fraction.
2. Dissolved the polymer in CHCl3 and wash with de-ionized distilled water to remove the any soluble organic catalyst side product.
3. Polymer extracted from water with chloroform.
4. Polymer solution in CHCl3 was dried over anhydrous sodium sulfate.
5. Solution filtered and than passed through a column packed with basic Al_2O_3 .
6. Solution concentrated on rota-evaporator
7. Solution precipitated in cold hexane and redissolved in benzene and freeze dried.
8. Final dried under vacuum for 48h at 50°C.

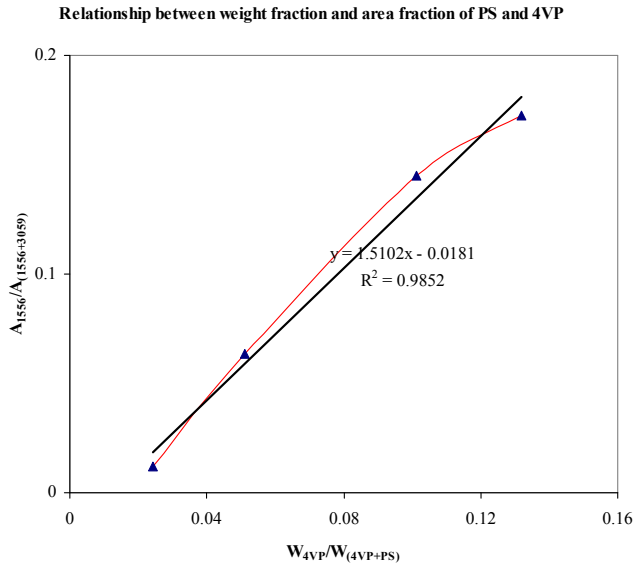
^{1}H-NMR Spectrum of Sample



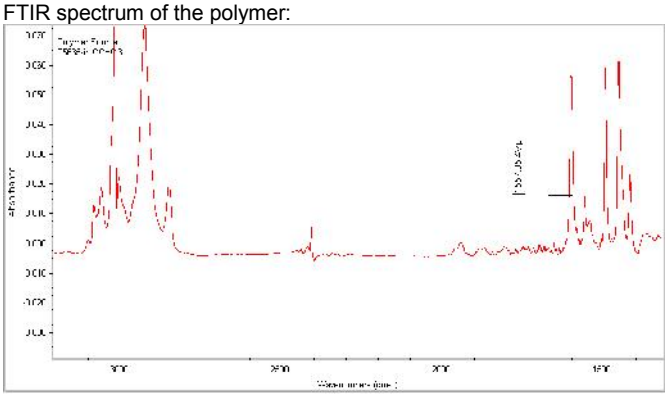




FTIR study:

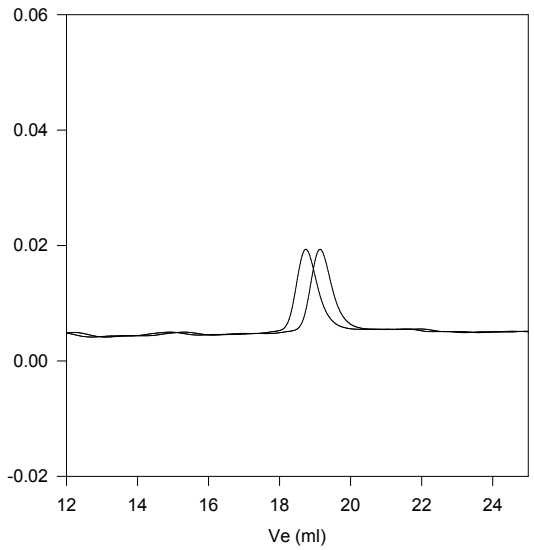


FTIR spectrum of the polymer:



SEC of Sample:

P5635-S4VP



Size exclusion chromatography of P(s-b-4VP) in DMF at 40 oC:

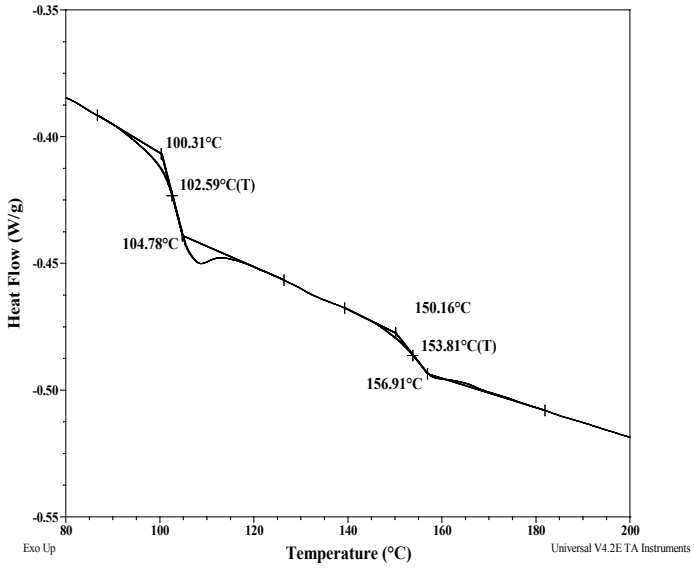
—— PS block: M_n=1100,000, M_w=1230,000, PI=1.12

—— Block Copolymer PS-4VP (1100,000)-b-4VP(285,000), PI=1.13

Running the sample polymer in THF at 35 oC :

The elution count show micellization and the molecular weight over 20 million

`Thermograms 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.