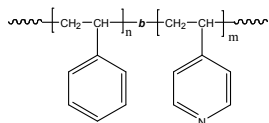


Sample Name: Poly(styrene-b-4-vinyl pyridine)

Electronic grade

Sample #: P5552P-PS4VP

Structure:



Composition:

Mn x 10 <sup>3</sup> PS-b-4VP	PDI
925.0-b-310.0	1.18
T <sub>g</sub> for PS block: 103°C	T <sub>g</sub> 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.<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 16 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.

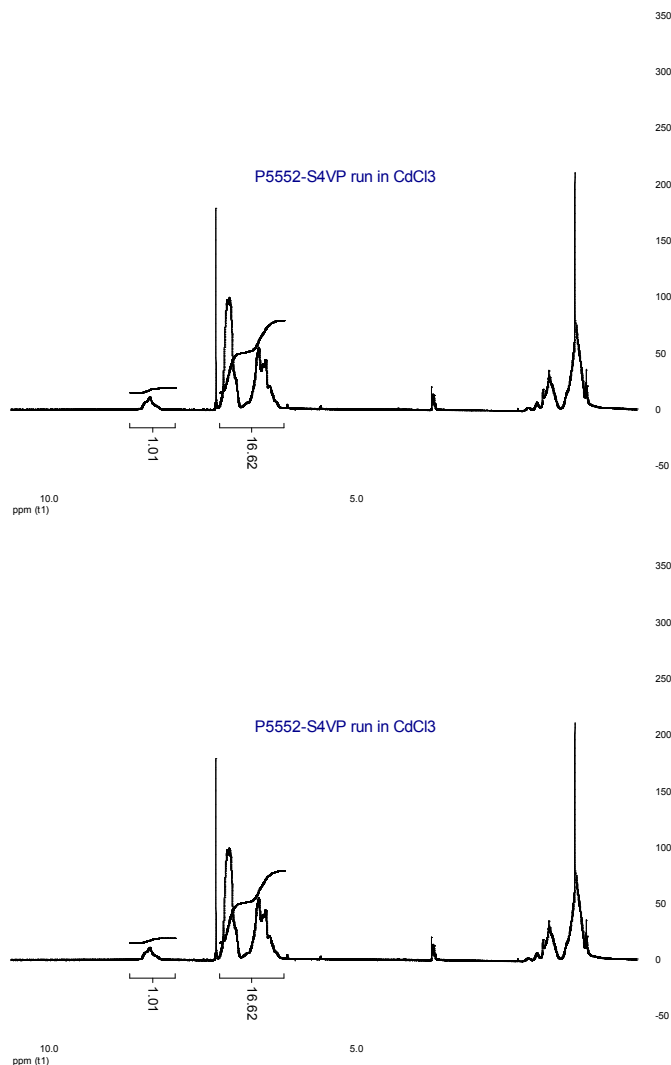
#### Solubility:

Poly(styrene-b-4-vinyl pyridine) is soluble in DMF, CHCl<sub>3</sub>.

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

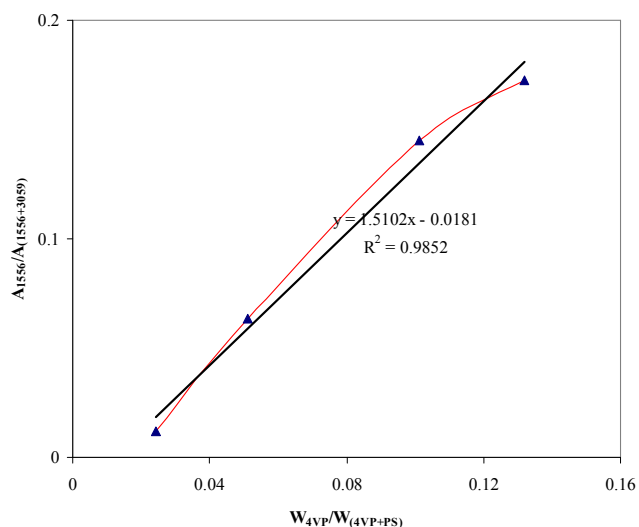
1. First the polymer soxhlet in Cyclohexane to remove unreacted homiopolystyrene fraction.
2. Dissolved the polymer in CHCl<sub>3</sub> and wash with de-ionized distilled water to remove the any soluble organic catalyst side product.
3. Polymer extracted from water with chloroform.
4. Polymer solution in CHCl<sub>3</sub> was dried over anhydrous sodium sulfate.
5. Solution filtered and than passed through a column packed with basic Al<sub>2</sub>O<sub>3</sub>.
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.

#### <sup>1</sup>H-NMR Spectrum of Sample

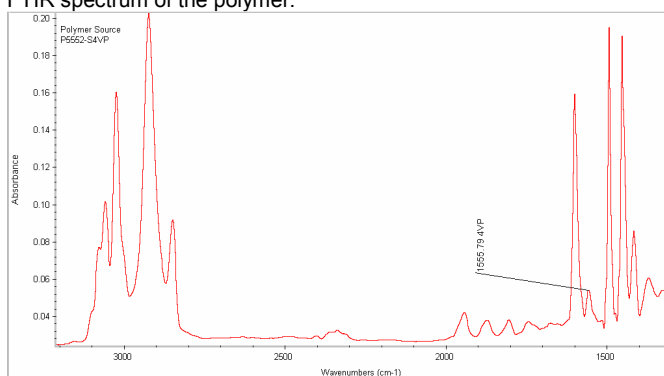


## FTIR study:

Relationship between weight fraction and area fraction of PS and 4VP

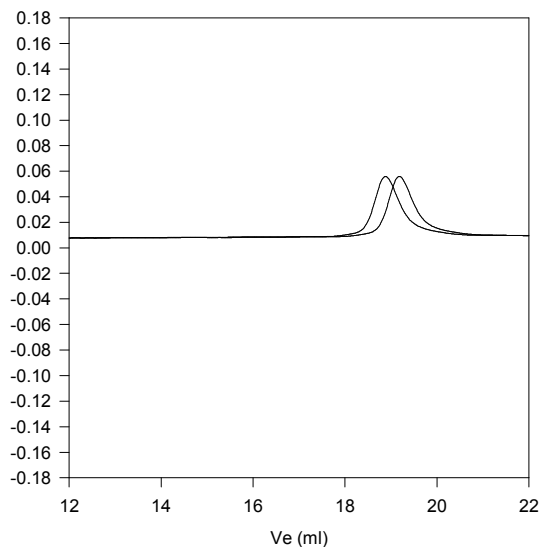


FTIR spectrum of the polymer:



## SEC of Sample:

P5552-S4VP



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

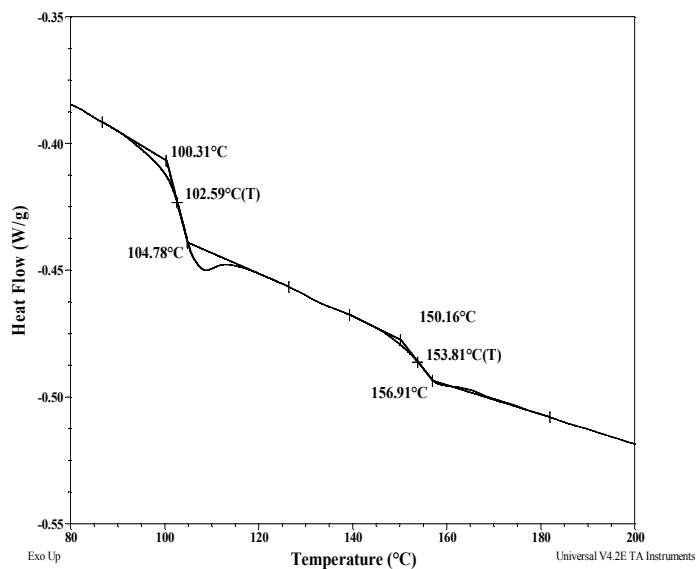
— PS block:  $M_n=925,000$ ,  $M_w=1070,000$ ,  $PI=1.16$

— Block Copolymer PS-4VP (925,000)-b-4VP(310,000),  $PI=1.18$

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.