

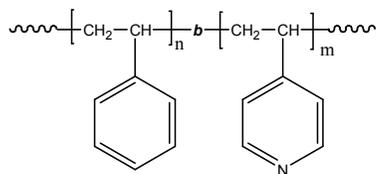
¹H-NMR Spectrum of Sample #: P5546-S4VP:

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

Electronic Grade

Sample #: **P5546P-S4VP**

Structure:



Composition:

Mn x 10 ³ PS-b-4VP	PDI
160.0-b-21.0	1.07
T _g for PS block: 100°C	T _g for 4VP block: 144°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 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.

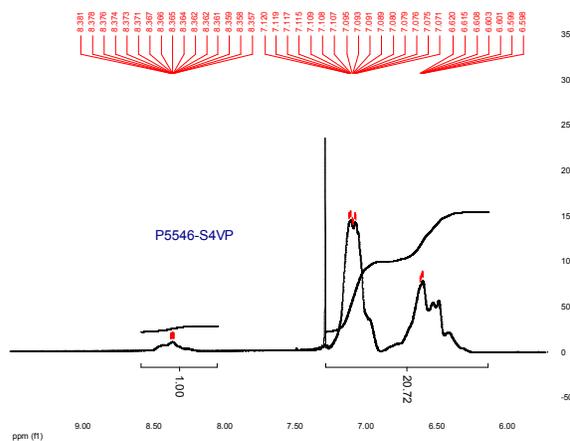
Thermal analysis of the samples was carried out using a differential scanning calorimeter (TA Q100) at a heating rate of 10°C/min. The inflection glass transition temperature (T_g) of the sample has been considered.

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.

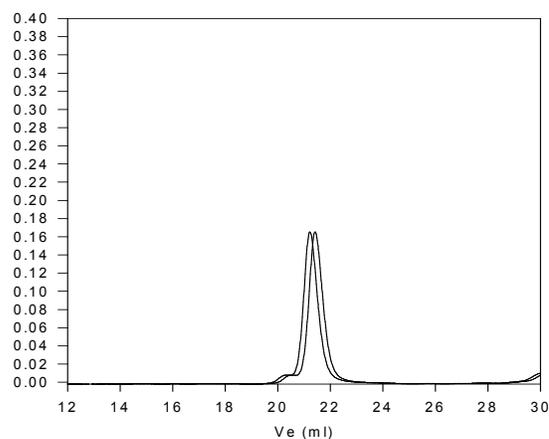
Purification of the obtained polymer was carried out rigorously as follows to ensure the removal of the catalyst side product:

1. Dissolved the polymer in CHCl₃ 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 CHCl₃ was dried over anhydrous sodium sulfate.
4. Solution filtered and then passed through a column packed with basic Al₂O₃.
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°C.



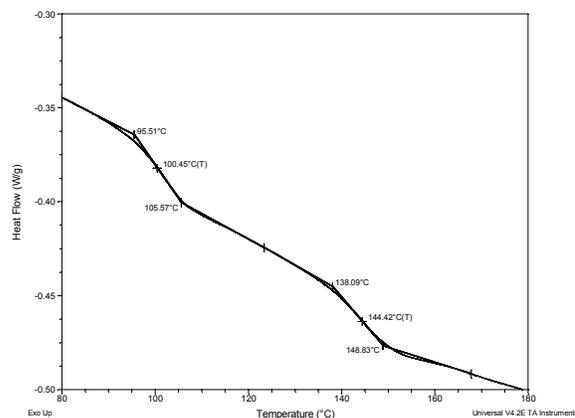
SEC of Sample:

P 5546-S4VP



Size exclusion chromatography of P(s-b-4VP) in DMF at 40 °C:
— PS block: M_n=160,000, M_w=168,000, PI=1.05
— Block Copolymer PS-4VP (160,000)-b-4VP(21,000), PI=1.07

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.