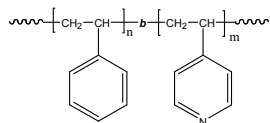


Sample Name: Poly(styrene-b-4-vinyl pyridine)

Electronic grade

Sample #: P5544P-S4VP

Structure:



Composition:

| | |
|-------------------------------------|----------------------|
| Mn x 10 ³ PS-b-4VP | PDI |
| 1,700.0-b-40.0 | 1.20 |
| T _g for PS block: 108 °C | 4VP block: Not found |

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 1556 cm⁻¹. From titration it shows the **presence of 3 wt % 4VP component and by FTIR 2%**

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.

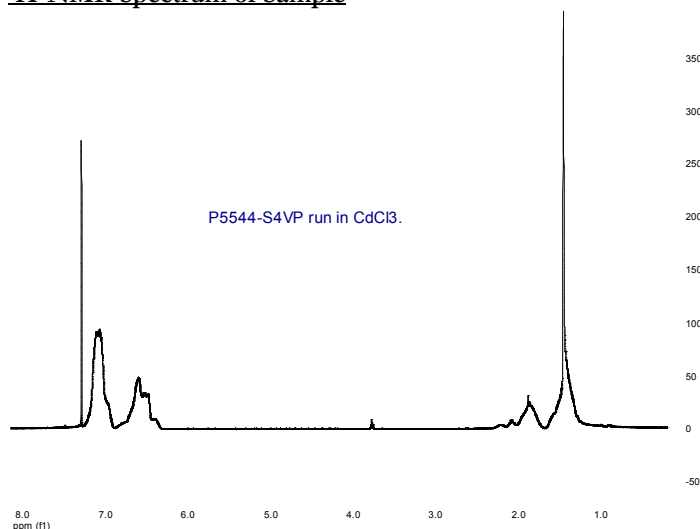
Solubility:

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

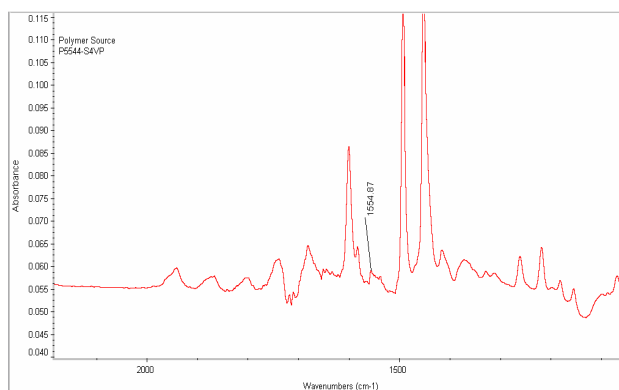
Purification of the obtained polymer was carried out rigorously as follows to ensure the removal of the catalyst side product:

1. First the polymer soxhlet in Cyclohexane to remove unreacted homiopolystyrene fraction.
2. Dissolved the polymer in 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 Al₂O₃.
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.

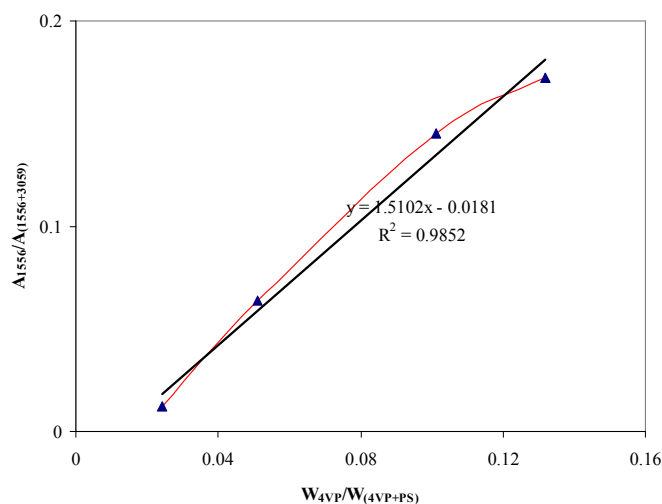
¹H-NMR Spectrum of Sample



FTIR spectrum:

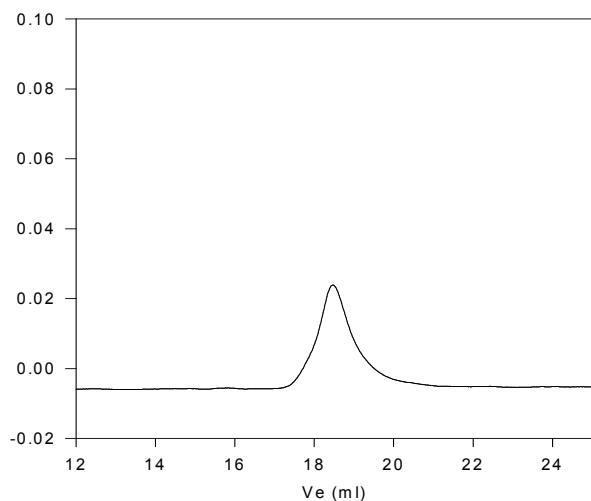


Relationship between weight fraction and area fraction of PS and 4VP



SEC of Sample:

P5554-S4VP

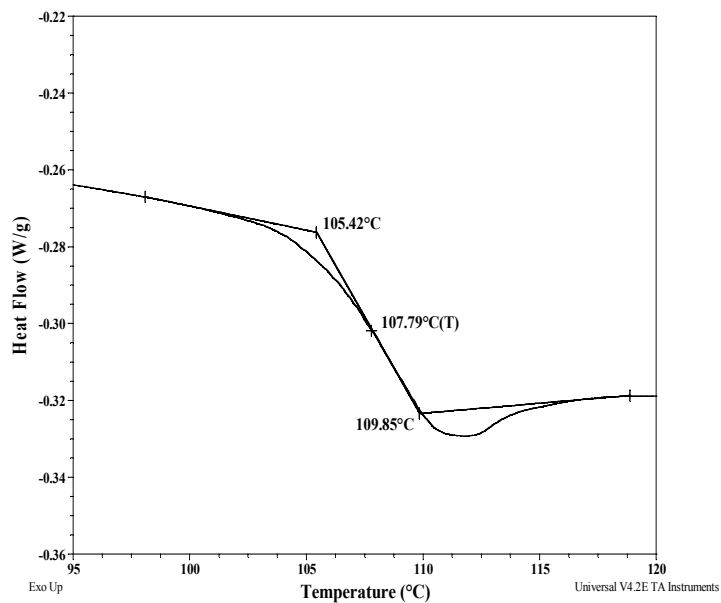


Size exclusion chromatography of P(s-b-4VP) in DMF at 40 °C:

—— PS block: $M_n=1700,000$, $M_w=2000,000$, $PI=1.19$

—— Block Copolymer PS-4VP (1700,000)-b-4VP(40,000), (from FTIR) $PI=1.20$
From FTIR 4VP wt % = 2.94

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.