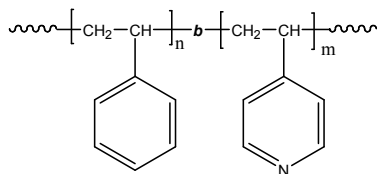


Sample Name: Poly(styrene-b-4-vinyl pyridine)

Sample #: P10710-S4VP

Structure:



Composition:

Mn $\times 10^3$ S-b-4VP	PDI
447-b-110.0	1.09
Tg for PS block: 104 °C	Tg for 4VP block: 153 °C

Synthesis Procedure:

Poly(styrene-b-4-vinyl pyridine) is prepared by living anionic polymerization in THF at -78°C in the presence of LiCl as an additive.

Characterization:

An aliquot of the anionic polystyrene block was terminated before addition of 4VP and analyzed by size exclusion chromatography (SEC) to obtain the molecular weight and polydispersity index (PDI). The block copolymer composition was then calculated from $^1\text{H-NMR}$ spectroscopy by comparing the peak area of the 2VP proton at 8.2 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_4 using crystal violet indicator. Copolymer PDI is determined by SEC.

Thermal analysis of the samples was carried out on a TA Q100 differential scanning calorimeter at a heating rate of $10^\circ\text{C}/\text{min}$. The midpoint of the slope change of the heat flow plot of the second heating scan was considered as the glass transition temperature (T_g).

Solubility:

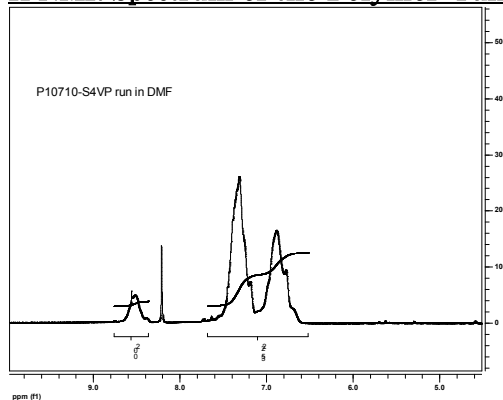
Poly(styrene-b-4-vinylpyridine) is soluble in THF, toluene, and CHCl_3 . The diblock copolymer can also be solubilized in methanol, ethanol depending on its composition. The polymer readily precipitates from hexanes, ether and water.

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 CHCl_3 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 CHCl_3 was dried over anhydrous sodium sulfate.
4. Solution filtered and then passed through a column packed with basic Al_2O_3 .
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 .

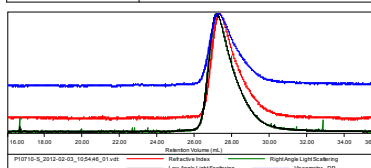
H NMR Spectrum of the Polymer: run in DMF



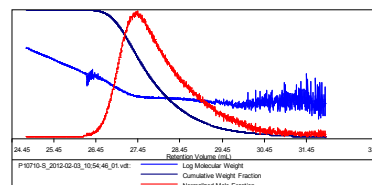
SEC for the polymer:

Sample ID: P10710-S

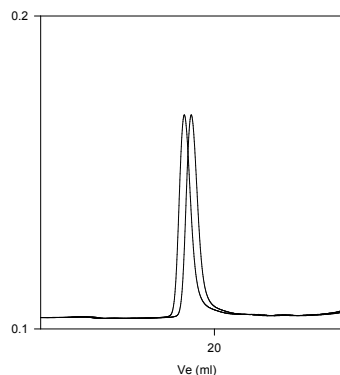
Concentration (mg/mL)	0.6454
Sample dn/dc (mL/g)	0.1850
Method File	PS80K-Jan2012-2-0000.vcm
Column Set	3x PL 1113-6300
System	System 1



Sample	Mn (Da)	Mw (Da)	Mp (Da)	Mw/Mn	IV (dL/g)
P10710-S_2012-02-03_10:54:46_01.vdt	447,210	468,411	470,893	1.047	1.6503

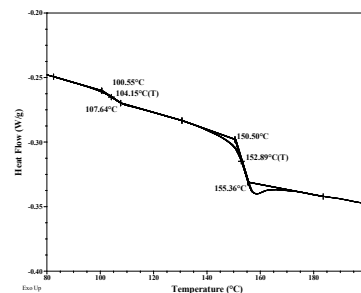


P10710-S4VP



— SEC profile in DMF at 60 °C.
Polystyrene, $M_n=447,000$, $M_w=468,000$ $M_w/M_n=1.04$
— Block Copolymer PS(447,000)-b-P4VP(110,000), $PDI=1.09$
(composition by titration and by $^1\text{H-NMR}$)

DSC thermogram for the PS block:



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.