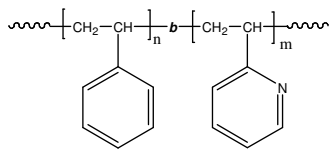


Sample Name: Poly(styrene-*b*-2-vinyl pyridine)

Sample #: P18220-S2VP

Structure:

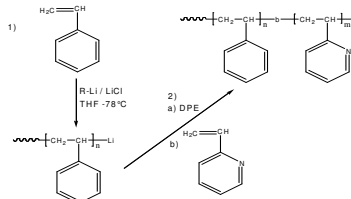


Composition:

$M_n \times 10^3$ S- <i>b</i> -2VP	PDI
25.0- <i>b</i> -25.0	1.06
T_g for 2VP block: Not distinct 93°C for 200k homopolymer)	T_g for PS block: 104 °C

Synthesis Procedure:

Poly(styrene-*b*-2-vinyl pyridine) is prepared by living anionic polymerization in THF at -78°C in the presence of LiCl additive. Polystyrene macroanions were end capped with a unit of diphenyl ethylene (DPE) before adding 2-vinylpyridine (2VP) monomer. For further details please see our published articles^{1,2} The scheme of the reaction is illustrated below:



Characterization:

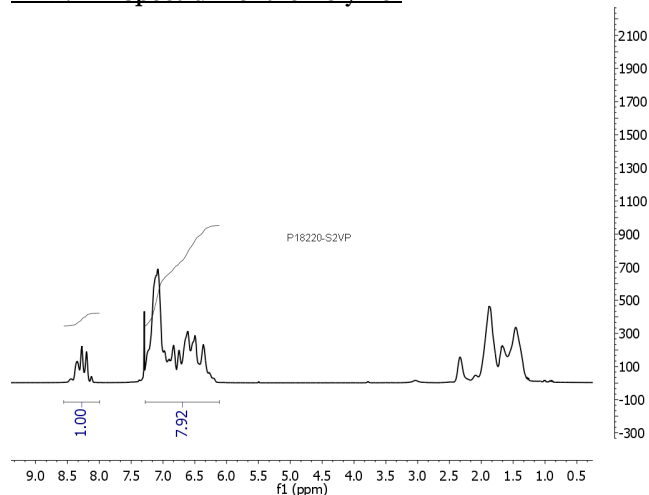
An aliquot of the anionic polystyrene block was terminated before addition of 2VP and analyzed by size exclusion chromatography (SEC) to obtain the molecular weight and polydispersity index (PDI). The Block copolymer composition was then calculated from $^1\text{H-NMR}$ spectroscopy by comparing the 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).

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.

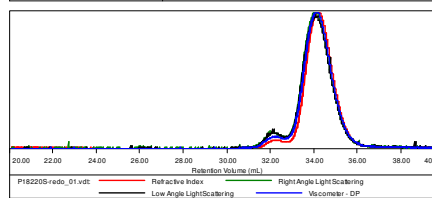
$^1\text{H-NMR}$ Spectrum of the Polymer



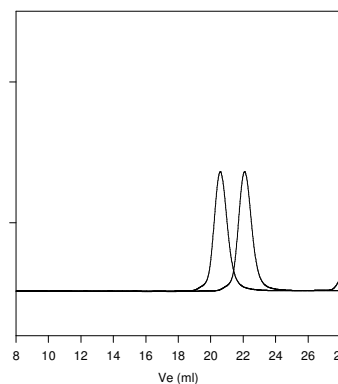
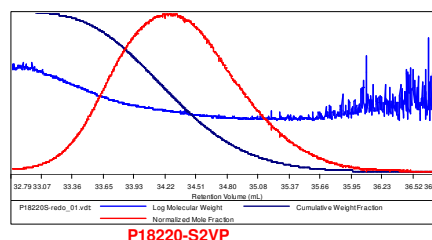
SEC for the polymer:

Sample ID: P18220-S

Concentration (mg/mL)	22.6794
Sample dn/dc (mL/g)	0.1850
Method File	PS80K-Sep26-2013-0000.vcm
Column Set	3x PL 1113-6300
System	System 1



Sample	M_n	M_w	M_p	M_w/M_n	IV
P18220S-redo_01.vdt	25,033	25,599	24,790	1.023	0.2207

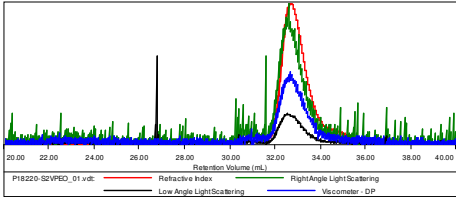


Size exclusion chromatography of poly(styrene-*b*-2-vinyl pyridine)
 — Polystyrene, $M_n=25,000$ $M_w=25,600$ $PI=1.02$
 — Polystyrene(25,000)-*b*-Poly(2-vinyl pyridine)(25,000), $PI=1.06$

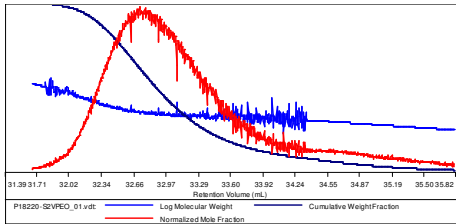
SEC for the polymer:

Sample ID: P18220-S2VP

Concentration (mg/mL)	0.6085
Sample dn/dc (mL/g)	0.1580
Method File	PS80K-Sep26-2013-0000.vcm
Column Set	3x PL 1113-6300
System	System 1



Sample	Mn	Mw	Mp	Mw/Mn	IV
P18220-S2VPEO_01.vdt	50,083	52,275	53,668	1.044	0.2576



DSC thermogram for the PS block:

