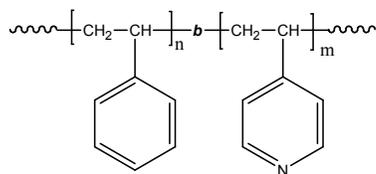


Sample Name: **Poly(styrene-b-4-vinyl pyridine)**

Sample #: **P9849-S4VP**

Structure:



Composition:

$M_n \times 10^3$ PS-b-4VP	PDI
18.5-b-40.5	1.10
$T_g$ 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  $-78^\circ\text{C}$ . 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  $^1\text{H-NMR}$  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/ $\text{HClO}_4$  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  $15^\circ\text{C}/\text{min}$ . The inflection glass transition temperature ( $T_g$ ) of the sample has been considered.

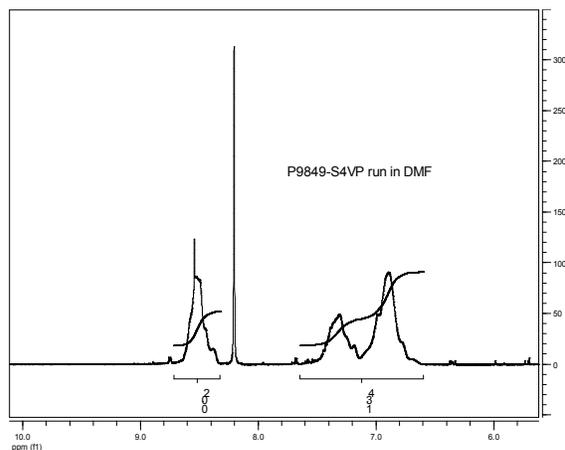
Solubility:

Poly(styrene-b-4-vinyl pyridine) is soluble in DMF,  $\text{CHCl}_3$ . 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:

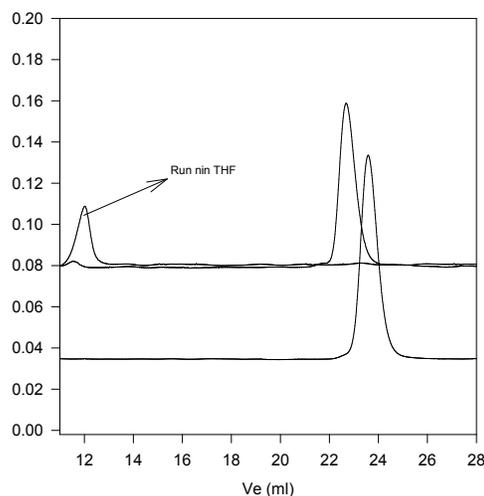
1. Dissolved the polymer in  $\text{CHCl}_3$  and wash with de-ionized distilled water to remove the any soluble organic catalyst side product.
2. Polymer extracted from water with chloroform.
3. Polymer solution in  $\text{CHCl}_3$  was dried over anhydrous sodium sulfate.
4. Solution filtered and than passed through a column packed with basic  $\text{Al}_2\text{O}_3$ .
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  $50^\circ\text{C}$ .

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



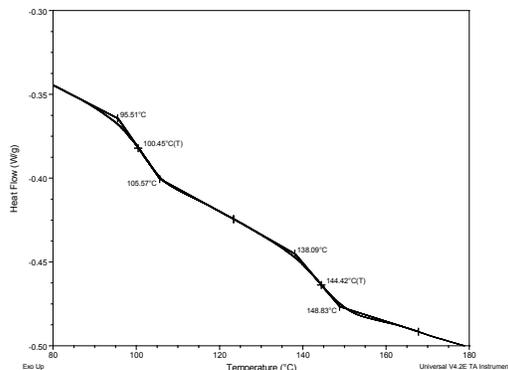
SEC of the polymer:

P9849-S4VP



Size exclusion chromatography of P(s-b-4VP) in DMF at 40 °C:  
— PS block:  $M_n=18,500$ ,  $M_w=20,000$ ,  $PI=1.08$   
— Block Copolymer PS-4VP (18,500)-b-4VP(40,500),  $PI=1.10$   
Showing Micellization in THF

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.