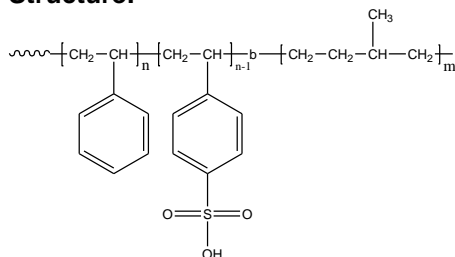


Sample Name: Sulfonated Poly(styrene-b-methyl butylene)

Polymer obtained by the hydrogenation of (Poly (styrene -b- isoprene rich in 1,4-addition) and its sulfonation on Polystyrene fraction

Sample #: P5478A-SSO3HMB

Structure:



Composition:

Mn x 10 ³ SSO3H-b-MB	Mw/Mn (PDI)
1.8-b-1.6	1.08

Degree of sulfonation on Polystyrene block is 38% by HNMR and 44% by titration:

By variation of one unit of styrene sulfonation gives about 7% variation. **We think that titration values are more accurate in such case.**

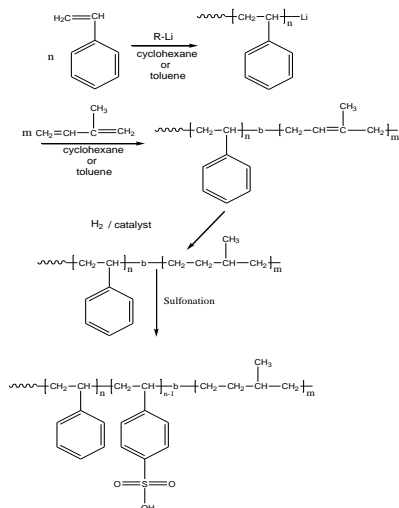
Mn of the Poly(S-b-IP) before Hydrogenation : 1400-b-1600 Mw/Mn=1.08

Degree of polymerization: P(S)₁₃-b-(IP)₂₃ Mw/Mn 1.08

Degree of sulfonation on Polystyrene block is 38% by HNMR and by titration 44%

Synthesis Procedure:

Poly(styrene-b-isoprene) is prepared by living anionic polymerization in non-polar solvent with sequence addition of styrene followed by isoprene and catalytic hydrogenation followed by sulfonation:



Characterization:

An aliquot of the anionic polystyrene block was terminated before addition of isoprene and analyzed by size exclusion chromatography (SEC) 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 vinylic isoprene (before hydrogenation) proton at about 5.1 ppm with the aromatic protons of polystyrene at about 6.3-7.2 ppm. Copolymer PDI is determined by SEC.

FTIR: After the hydrogenation the product was characterized by FTIR and the disappearance of absorbance at 885 and 846 cm⁻¹ indicate the quantitative hydrogenation.

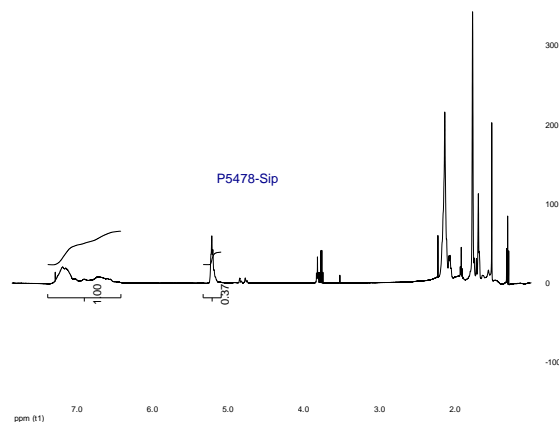
HNMR of the product also confirm the quantitative hydrogenation (> 99%) of poly isoprene block.

Solubility: Sulfonated Poly(styrene-b-hydrogenated isoprene) is soluble in THF, Acetone.

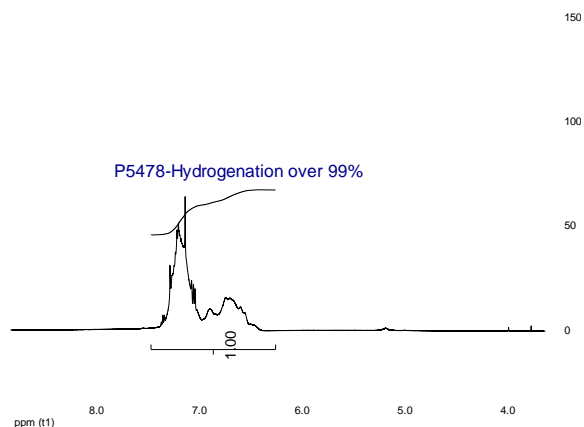
Purification the Obtained polymer after sulfonation:

Polymer after sulfonation the excess of H₂SO₄ and acetic anhydride was removed by dialysis in water. Polymer was dissolved after removing dichloroethane used for the sulfonation and dissolved polymer in water. Polymer was dialyzed for 3 days in water using 1000 molecular cut cellulose membrane obtained from Spectrum Co. The polymer solution than concentrated and freeze dried from water. Polymer was dried further under vacuum for 48h at room temperature.

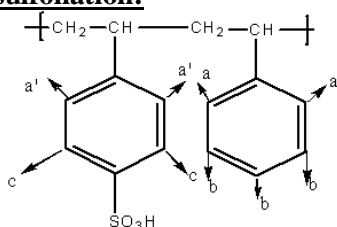
¹H-NMR Spectrum of the block copolymer Poly (styrene-b-isoprene)



After Hydrogenation:

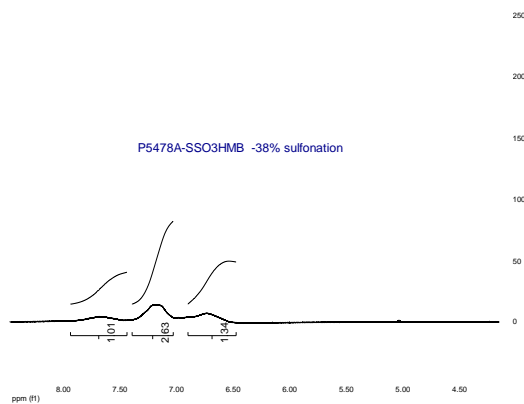


HNMR after sulfonation:



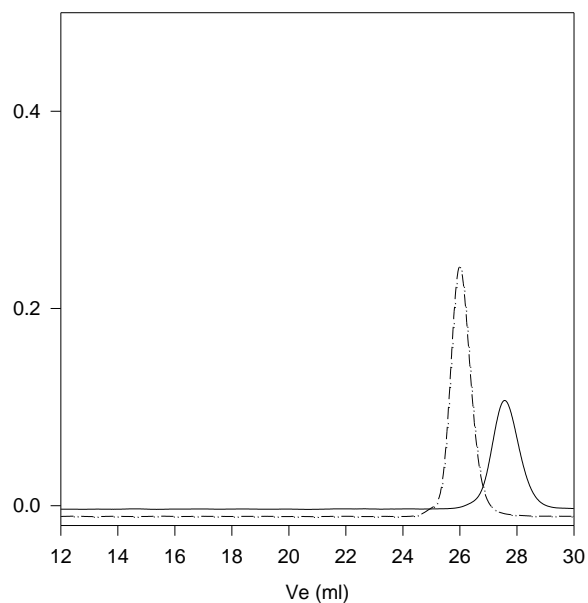
$$\% \text{ sulfonation} = \frac{\text{moles of styrene sulfonate}}{\text{moles of styrene} + \text{moles of styrenesulfonate}}$$

$$\% \text{ sulfonation} = \frac{\text{integrals of peak c/2}}{\text{integrals of (peak c/2 + peak b/3)}}$$



SEC of Sample of the block copolymer:

P5478-SIP (precursor for PSSO3HMB)

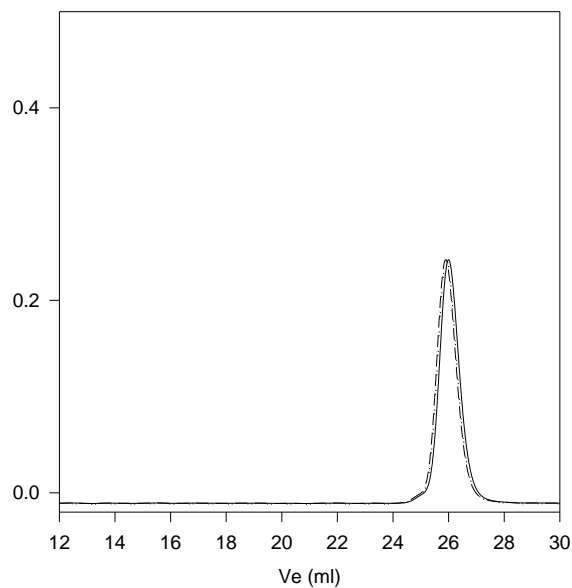


Size exclusion chromatography of polystyrene-b-polyisoprene_{1,4} addition

— Polystyrene, $M_n=1400$, $M_w=1500$ $PI=1.08$

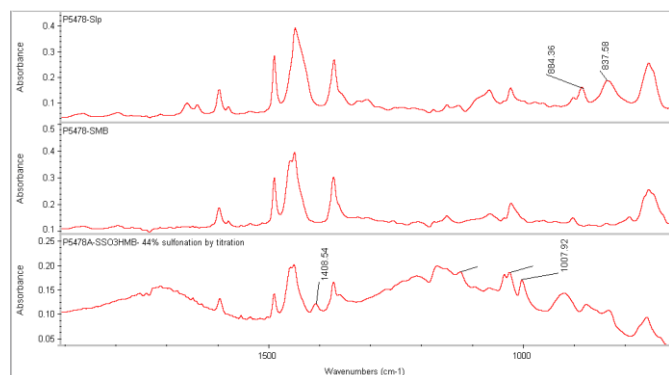
- - - Block Copolymer:
PS-IP(1400)-b-PI(1600), $PI=1.08$ (by H NMR)

P5478SMB (after hydrogenation of polyisoprene block)



Size exclusion chromatography of polystyrene-b-polyisoprene_{1,4} addition

FTIR spectra of the polymer before and after hydrogenation and sulfonation:



In Hydrogenation: The characteristics at 885 and 846cm⁻¹ should be disappeared.

In sulfonation on the styrene ring: the characteristics at around 1411, 1126, 1033 and 1001 cm⁻¹ must be observed these are characteristics at the benzene ring.

The characteristics at 1411cm⁻¹ in particular is a characteristics for the styrene at para position is sulfonated