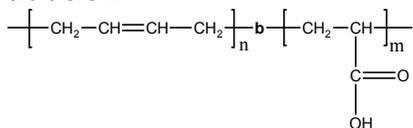
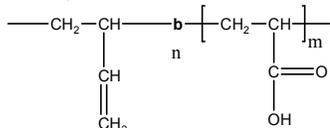


Sample Name:

Poly(Butadiene -b- acrylic acid) poly butadiene microstructure rich in 1,4 addition



or 1,2 addition



Sample #: **P5533A-BdAA (rich in 1, 4 addition)**
1, 4 addition > 89%

Structure:

Composition:

Mn x 10 ³ PBd-b-AA	PDI
9.0-b-3.5	1.10

Synthesis Procedure:

Poly(1,4-butadiene -b- acrylic acid) is prepared by living anionic polymerization with sequence addition of butadiene followed by t-butyl acrylate and hydrolysis of the t-butyl group. The solvents for the polymerization selected to get the polybutadiene with microstructure rich in 1,4 addition or 1,2 addition.

Characterization:

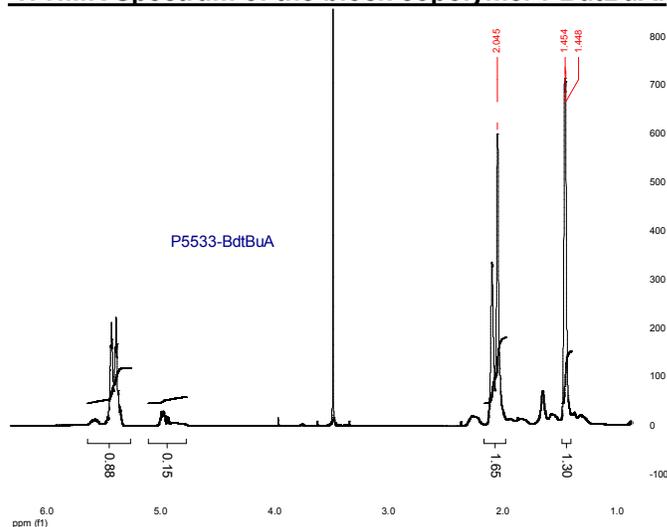
An aliquot of the anionic poly(butadiene) block was terminated before addition of t-butyl acrylate and analyzed by size exclusion chromatography (SEC) to obtain the molecular weight and polydispersity index (PDI). The final block copolymer composition was calculated from ¹H-NMR spectroscopy by comparing the peak area of the vinylic butadiene protons between about 5.0-5.4 ppm with the t-butyl acrylate protons at 1.43 ppm. Block copolymer PDI is determined by SEC. **Note:** The ¹H-NMR of 1,2-polybutadiene is composed of 1 proton signal at 5.4 ppm and 2 proton signals at 5.0 ppm. Signals due to vinylic 1,4-polybutadiene are present at 5.4 ppm.

Hydrolysis of the ester was followed by FTIR for the disappearance of ter-butyl ester at 1362cm⁻¹.

Purification of the polymer:

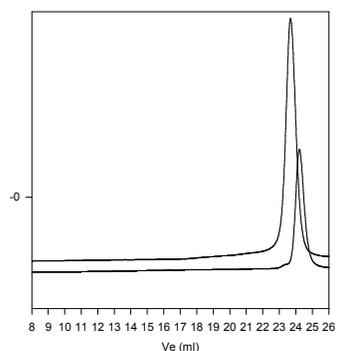
After the Hydrolysis the solvent was removed under vacuum and the obtained polymer was dissolved in THF and neutralized with NaHCO₃ to get pH around 6. The product was filtered and the filtrate was treated for 2days with Mixed bed exchange resin, IONA NM -60 H⁺/OH⁻ form (16-50 mesh). The product was filtered and the clear solution was passed through a column packed with basic Al₂O₃. The Filtrate was concentrated under vacuum and dried at room temperature.

¹H-NMR Spectrum of the block copolymer PBdTBuA:



SEC of the block copolymer:

P5533-Bd_{1,4 rich addition}-tBuA (for P5333A-BdAA)



— SEC profile of Poly(Butadiene_{1,4 addition}-b-tert. butylacrylate):
— Polybutadiene, M_n=9,000, M_w=9,500, PI=1.05
— Block Copolymer PBd(9,000)-b-PIBuA(6,000), PI=1.10
(Composition from ¹H-NMR)
after Hydrolysis of tert.butyl ester:
Bd-b-AA Mn 9000-b-3500