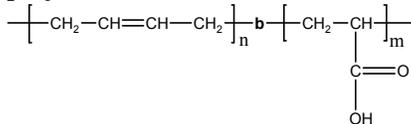
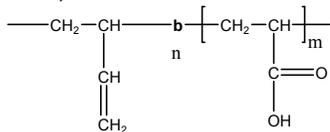


### Sample Name:

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



or 1,2 addition



Sample #: **P5527-BdAA** (rich in 1, 2 addition)  
1, 2 addition > 86%

### Structure:

### Composition:

Mn x 10 <sup>3</sup> PBd-b-AA	PDI
15.0-b-6.5	1.07

### 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:

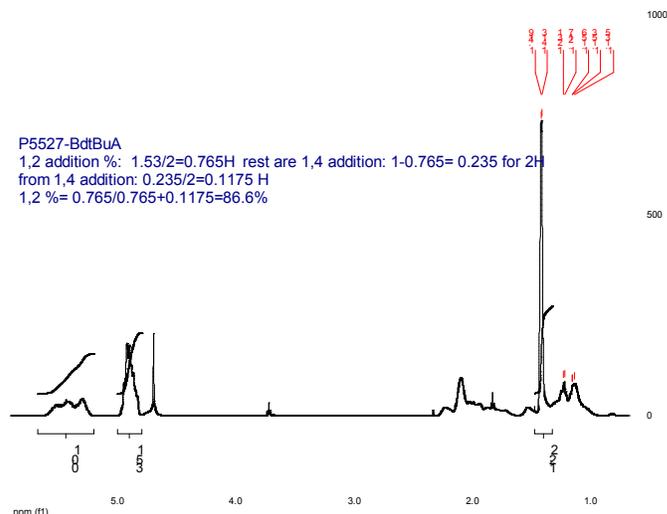
An aliquot of the anionic poly(butadiene) block was terminated before addition of t-butyl acrylate and analyzed by size exclusion chromatography (SEC) to obtain the molecular weight and polydispersity index (PDI). The final block copolymer composition was calculated from <sup>1</sup>H-NMR spectroscopy 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 <sup>1</sup>H-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<sup>-1</sup>.

### Purification of the polymer:

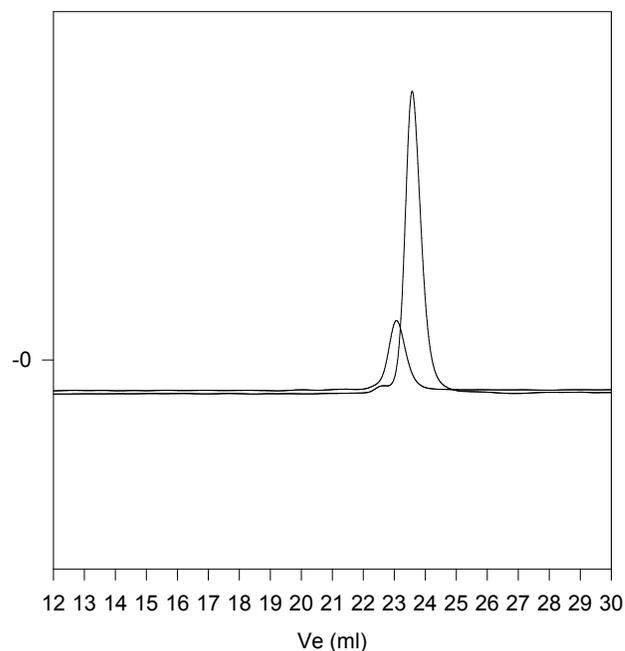
After the Hydrolysis the solvent was removed under vacuum and the obtained polymer was dissolved in THF and neutralized with NaHCO<sub>3</sub> to get pH around 6. The product was filtered and the filtrate was treated for 2 days with mixed bed exchange resin, IONA NM -60 H<sup>+</sup>/OH<sup>-</sup> form (16-50 mesh). The product was filtered and the clear solution was passed through a column packed with basic Al<sub>2</sub>O<sub>3</sub>. The Filtrate was concentrated under vacuum and dried at room temperature.

### <sup>1</sup>H-NMR Spectrum of the block copolymer PBdtBuA:



### SEC of the block copolymer:

**P5527-Bd** <sub>1,2 rich addition</sub> **tBuA** Precursor for Bd-b-AA



— SEC profile of Poly(Butadiene <sub>1,2 addition</sub> -b-tert. butylacrylate):

— Polybutadiene, M<sub>n</sub>=15,000, M<sub>w</sub>=16,000, PI=1.07

— Block Copolymer PBd(15,000)-b-PtBuA(11,500), PI=1.07  
(Composition from <sup>1</sup>H NMR)  
After Hydrolysis of the ester group:  
PBd-b-AA) Mn 15,000-b-6,500 Mw/Mn 1.07