

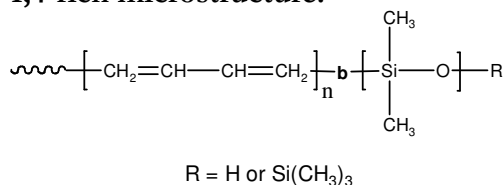
**Sample Name:** Poly(butadiene-b-dimethylsiloxane)

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

**Polybutadiene rich in 1,4 microstructure**

**Sample #: P2088-2BdDMS**

**1,4-rich microstructure:**

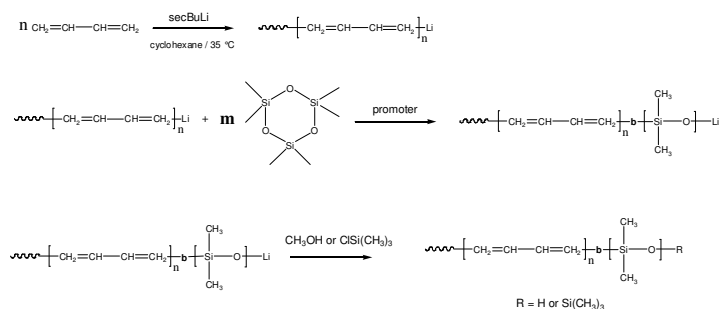


**Composition:**

Mn × 10 <sup>3</sup>	PDI
Bd-b-DMS	
17.0-b-31.0	1.14

**Synthesis Procedure:**

Poly(butadiene(1,4 or 1,2 addition)-b-dimethyl siloxane) is prepared by living anionic polymerization with sequence addition of butadiene (Bd) followed by addition of hexamethylcyclotrisiloxane (D3) monomer. The diblock copolymer is prepared by the polymerization of Bd in toluene followed by medium polarity modification through the introduction of freshly distilled THF followed by the addition of D3. The reaction polymerization scheme is illustrated below:

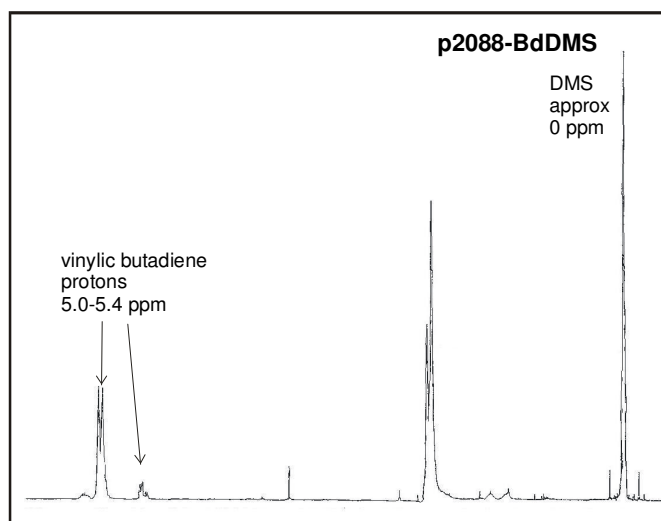


**Characterization:**

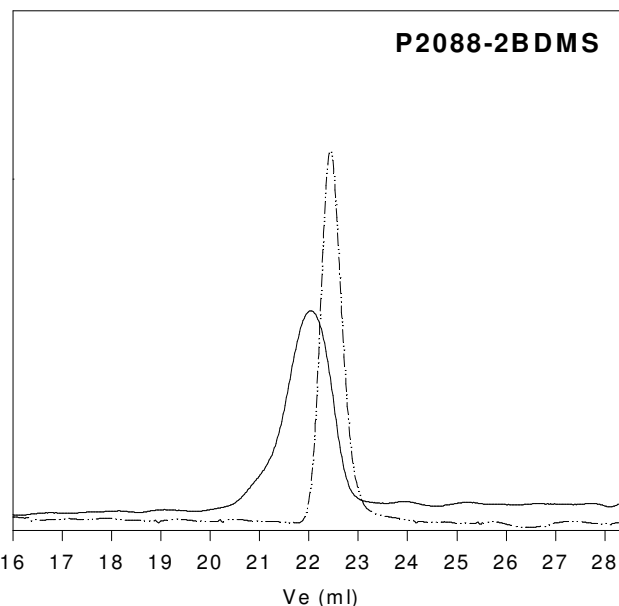
An aliquot of the anionic polybutadiene block was terminated before addition of D3 and analyzed by size exclusion chromatography (SEC) to obtain the molecular weight and polydispersity index (PDI). The final block copolymer composition was calculated from <sup>1</sup>H-NMR spectroscopy by comparing the peak area of the vinylic butadiene protons between about 5.0-5.4 ppm with the siloxane (SiCH<sub>3</sub>) protons at 0.8-0.9 ppm. The block copolymer PDI was 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 also present at 5.4 ppm.

**Solubility:**

Poly(butadiene-b-dimethylsiloxane) block copolymer is soluble in toluene, cyclohexane, hexane, THF, CHCl<sub>3</sub>. The polymer can be precipitated from ethanol, methanol, water.



**SEC of the block copolymer:**



----- Polybutadiene, M<sub>n</sub>=17000, M<sub>w</sub>=17850, PI=1.05

———— Block Copolymer PBd(17000)-b-PDMS(31000), Composition from H NMR PI=1.14

Thermal analysis of the sample# P2088-BdDMS

Thermal analysis of the samples was carried out on a TA Q100 differential scanning calorimeter at a heating rate of 10°C/min. The midpoint of the slope change of the heat flow plot of the second heating scan was considered as the glass transition temperature ( $T_g$ ).

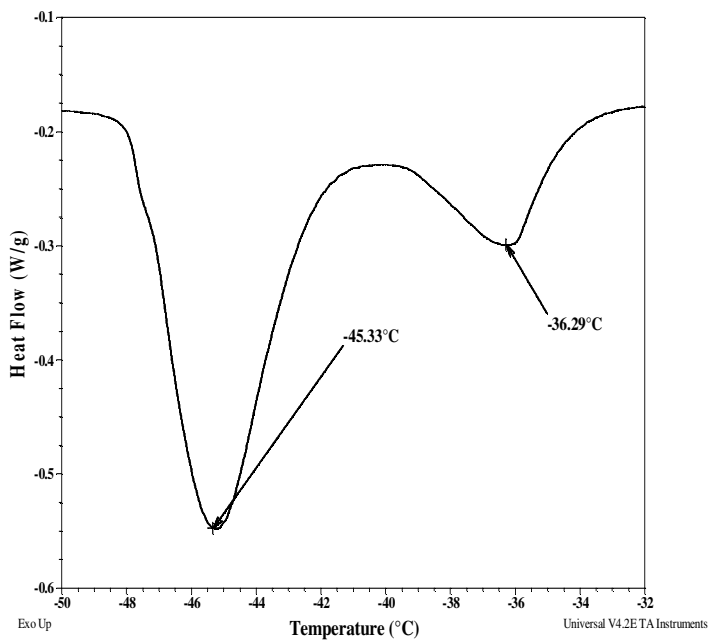
Melting and crystallization curve for the sample

The melting temperature ( $T_m$ ) was taken as the maximum of the endothermic peak where as the crystallization temperature ( $T_c$ ) was considered as the minimum of the exothermic peak.

Thermal analysis results at a glance

For Bd block		
$T_g$ : -121°C (lit.)	$T_m$ : -	$T_c$ : -
For DMS block		
$T_g$ : Not distinct	$T_m$ : -45 & -36 °C	$T_c$ : -71°C

Melting curve for DMS block



Crystallization curve For PEO block

