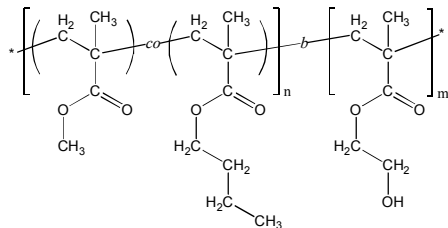


**Sample Name:**

**Poly(methyl methacrylate-*co*<sub>(random)</sub>-n-butyl methacrylate)-*block*-poly(2-hydroxyethyl methacrylate)**

**Sample #: P9333-MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA****Structure:****Composition:**

$M_n \times 10^{-3}$ (g/mol)	23.0- <i>b</i> -22.0
$M_w/M_n$	1.10
Molar ratio MMA : nBuMA	65 : 35 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	29 : 22 : 49 (wt%)
$T_g$ (MMA <sub>n</sub> BuMA)	85 °C
$T_g$ (HEMA)	120 °C

**Synthesis Procedure:**

Poly([methyl methacrylate-*co*-n-butyl methacrylate]-*b*-2-hydroxyethyl methacrylate) block copolymer was synthesized by living anionic polymerization. First, methyl methacrylate (MMA) and n-butyl methacrylate (n-BuMA) were co-polymerized; and then 2-[trimethylsilyloxy]ethyl methacrylate (hydroxyprotected HEMA monomer) was added. The obtained block copolymer was precipitated in acidic methanol solution to deprotect the hydroxyl group.

**Solubility:** The polymer is soluble in THF, DMF.

**Characterization:**

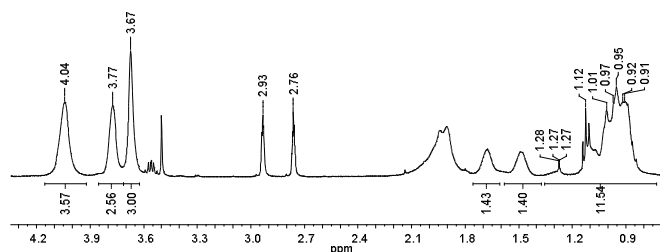
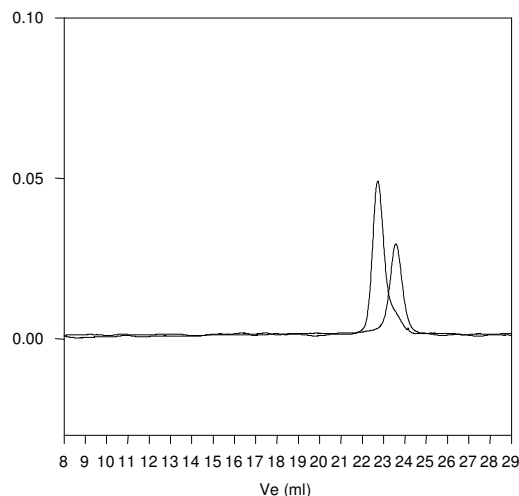
The polymer composition was determined by <sup>1</sup>H NMR. MMA:nBuMA molar ratio was calculated by comparing the integration of the -OCH<sub>2</sub>- protons of nBuMA (at  $\delta$  = 3.9 ppm) to the integration of methoxy group of MMA (at  $\delta$  = 3.6 ppm). Molecular weight of the second (HEMA) block was calculated by comparing the integration of -OCH<sub>2</sub>- protons of HEMATMS to the integration of methoxy group of MMA and using SEC data for the first (MMA<sub>n</sub>BuMA) block.

The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA<sub>n</sub>BuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

Thermal analysis of the sample was done on a TA Q100 differential scanning calorimeter (DSC) at a heating rate of 10°C/min. The glass transition temperature ( $T_g$ ) was determined as a midpoint of step change in heat flow curve for the second heating scan.

**<sup>1</sup>H NMR of MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA in DMF-d<sub>7</sub>:**

P9333-HMMA<sub>n</sub>BuMA-HEMA in DMF

**SEC of MMA<sub>n</sub>BuMA<sub>r</sub>an and MMA<sub>n</sub>BuMA-b-HEMATMS:****P9333--MMA<sub>n</sub>BuMA<sub>r</sub>anHEMA**

Size exclusion chromatography of

1. Random copolymer of MMA and nBuMA:  $M_n$  23,000  $M_w$ : 24,300  $M_w/M_n$  1.06  
Poly(MMA-nBuMA<sub>r</sub>an)-b- Poly 2-Hydroxy ethyl methacrylate (Protected with TMS)  
 $M_n$  23,000-*b*-34,000  $M_w/M_n$  1.10

After Deprotection of HEMA TMS :  $M_n$  23,000-*b*-22,000  $M_w/M_n$  1.10

**DSC thermogram of MMA<sub>n</sub>BuMA-b-HEMA:**