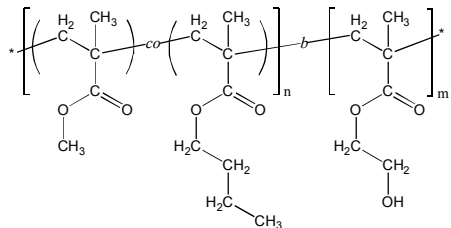


**Sample Name:**

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

**Sample #: P5960-MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA****Structure:****Composition:**

$M_n \times 10^{-3}$ (g/mol)	15.0- <i>b</i> -9.5
$M_w/M_n$	1.10
Molar ratio MMA : nBuMA	90 : 10 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	53 : 8 : 39 (wt%)
$T_g$	105 °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.

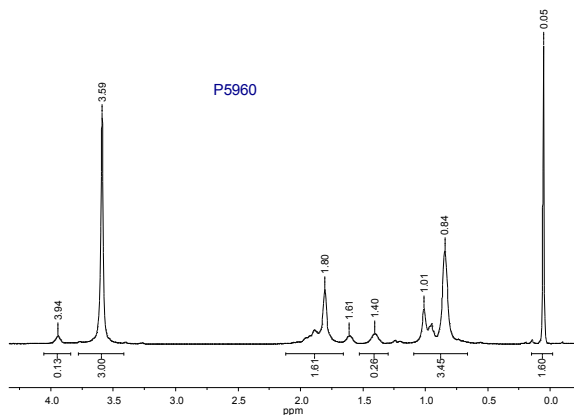
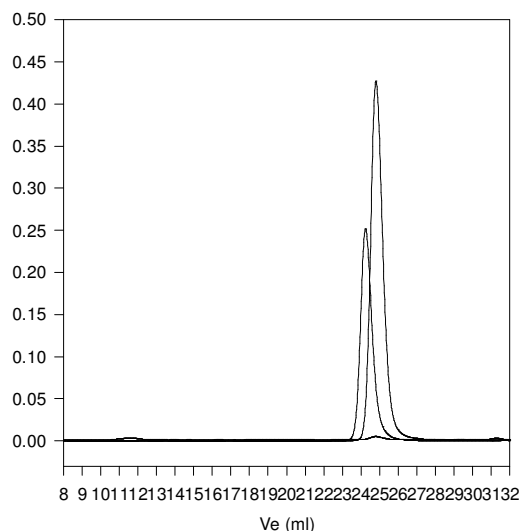
**Solubility:** The polymer is soluble in THF, DMF.

**Characterization:**

The polymer composition was determined by  $^1\text{H}$  NMR. MMA:nBuMA molar ratio was calculated by comparing the integration of the  $-\text{OCH}_2-$  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  $-\text{OCH}_2-$  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.

 **$^1\text{H}$  NMR of MMA<sub>n</sub>BuMA<sub>r</sub>an (400 MHz,  $\text{CDCl}_3$ ):****SEC of MMA<sub>n</sub>BuMA<sub>r</sub>an and MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMATMS:****P5960--MMA<sub>n</sub>BuMA<sub>r</sub>anHEMA**

Size exclusion chromatography of

1. Random copolymer of MMA and nBuMA:  $M_n$  15000  $M_w$ : 16500  $M_w/M_n$  1.09  
Poly(MMA-nBuMA<sub>r</sub>an)-b- Poly 2-Hydroxy ethyl methacrylate (Protected with TMS)  
 $M_n$ : 15000-*b*-14500  $M_w/M_n$  1.10  
After Deprotection of HEMA TMS :  $M_n$  15000-*b*-9500  $M_w/M_n$  1.10  
In THF After deprotection, the SEC profile shows no micellization and can not be eluted

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