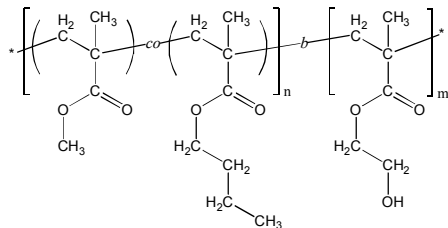


**Sample Name:**

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

**Sample #: P11176A-MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA****Structure:****Composition:**

$M_n \times 10^3$ (g/mol)	26.0- <i>b</i> -22.5
$M_w/M_n$	1.15
Molar ratio MMA : nBuMA	30 : 70 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	12 : 41 : 47 (wt%)
$T_g$ (MMA <sub>n</sub> BuMA)	52 °C
$T_g$ (HEMA)	112 °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.

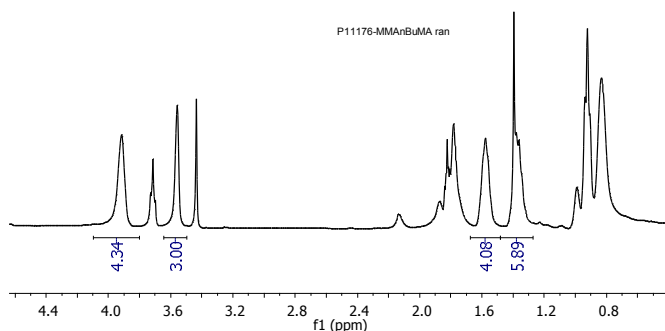
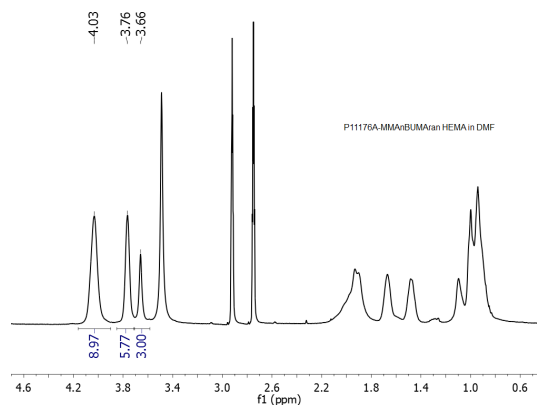
**Solubility:** The polymer is soluble in THF, DMF.

**Characterization:**

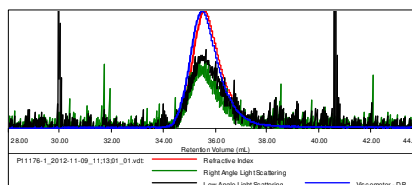
The polymer composition was determined by  $^1\text{H}$  NMR. MMA:nBuMA molar ratio was calculated by comparing the integration of the -OCH<sub>2</sub>-protons of nBuMA (at  $\delta = 3.9$  ppm) to the integration of methoxy group of MMA (at  $\delta = 3.6$  ppm). Molecular weight of the second (HEMA) block was calculated by comparing the integration of -OCH<sub>2</sub>- protons of HEMA 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.

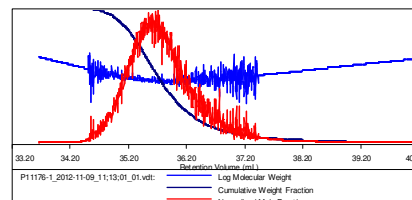
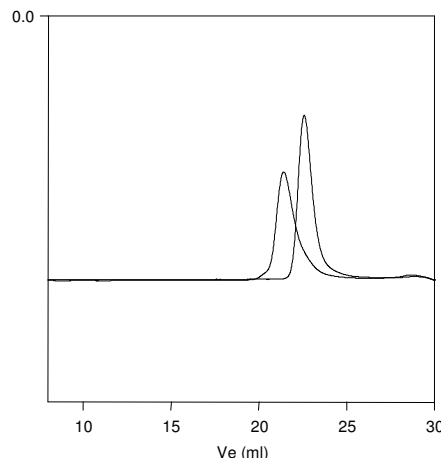
Thermal analysis of the sample was done on a TA Q100 differential scanning calorimeter (DSC) at a heating rate of 10°C/min. The glass transition temperature ( $T_g$ ) was determined as a midpoint of step change in heat flow curve for the second heating scan.

 **$^1\text{H}$  NMR of MMA<sub>n</sub>BuMA<sub>r</sub>an [first block]:** **$^1\text{H}$  NMR of MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA in DMF-d<sub>7</sub>:****SEC of MMA<sub>n</sub>BuMA<sub>r</sub>an [first block]:**Sample ID: P11176-1-MMA<sub>n</sub>BuMA

Concentration (mg/mL)	14.5807
Sample dn/dc (mL/g)	0.0800
Method File	PS80K-Nov2012-0000.vcm
Column Set	3xPL1113-6300
System	System 1



Sample	Mn (Da)	Mw (Da)	Mp (Da)	Mw/Mn	IV (dL/g)
P11176-1_2012-11-09_11:13:01_01.vdt	26,250	27,698	25,459	1.055	0.1665

**SEC of MMA<sub>n</sub>BuMA<sub>r</sub>an and MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMATMS:**P11176A-MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA

Size exclusion chromatography of  
 1. MMA<sub>n</sub>BuMA<sub>r</sub>an block Mn 26,000 Mw/Mn 1.08  
 2. MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMATMS: 26,000-35,000 MW/Mn : 1.15  
 After deprotection Mn 26,000-b-22,500 Mw/Mn 1.15