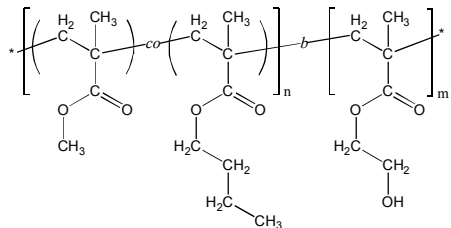


### Sample Name:

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

### Sample #: P10608-MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA

#### Structure:



#### Composition:

$M_n \times 10^3$ (g/mol)	22.5- <i>b</i> -15.5
$M_w/M_n$	1.12
Molar ratio MMA : nBuMA	53 : 47 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	26 : 33 : 41 (wt%)
$T_g$ (MMA <sub>n</sub> BuMA)	65 °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.

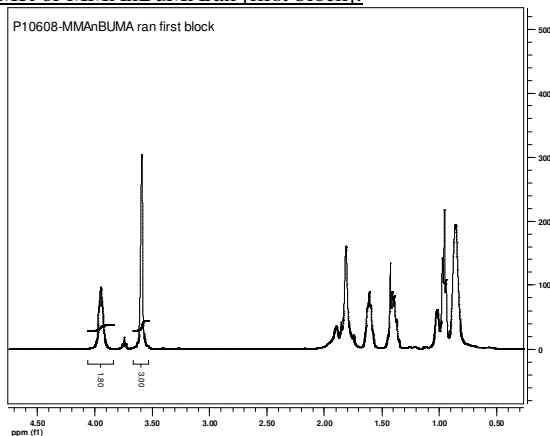
#### Characterization:

The polymer composition was determined by <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.

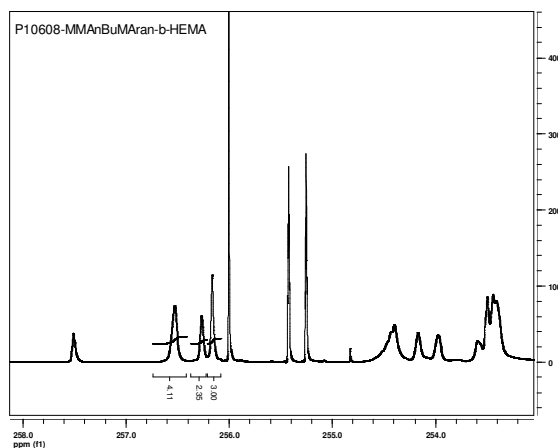
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA<sub>n</sub>BuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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 [first block]:



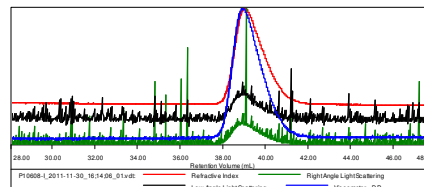
#### <sup>1</sup>H NMR of MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA diblock copolymer:



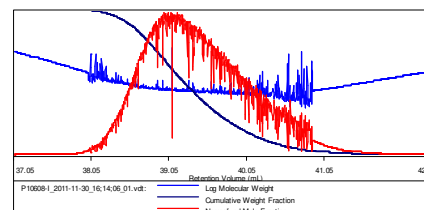
#### SEC of MMA<sub>n</sub>BuMA<sub>r</sub>an [first block]:

Sample ID: P10608-I-MMA<sub>n</sub>BuMA

Concentration (mg/mL)	8.2405
Sample dn/dc (mL/g)	0.0800
Method File	PS80K-Oct-0000.vcm
Column Set	3x PL 1113-6300
System	System 1

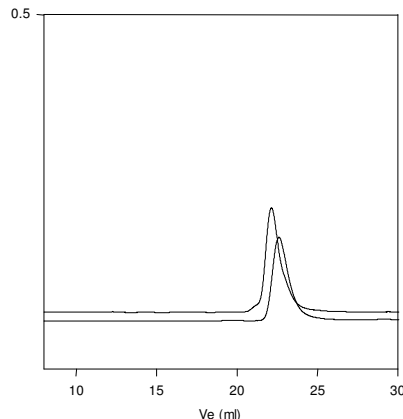


Sample	Mn (Da)	Mw (Da)	Mp (Da)	Mw/Mn	IV (dL/g)
P10608-I_2011-11-30_16:14:06_01.vdt	22,651	24,410	22,832	1.078	0.1930



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

P10608-MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA



Size exclusion chromatography of

- MMA<sub>n</sub>BuMA<sub>r</sub>an block Mn 22,500 Mw: 23,800 Mw/Mn 1.08
- MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMATMS: 22,500-24,100 MW/Mn : 1.12

After deprotection Mn 22,500-b-15,500 Mw/Mn 1.12