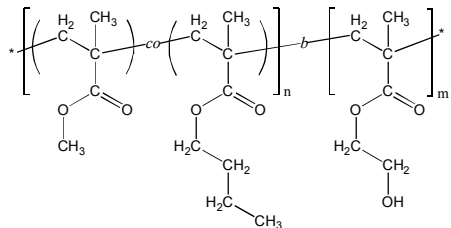


### Sample Name:

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

### Sample #: P10582-MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA

#### Structure:



#### Composition:

$M_n \times 10^3$ (g/mol)	33.0- <i>b</i> -41.0
$M_w/M_n$	1.25
Molar ratio MMA : nBuMA	55 : 45 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	21 : 24 : 55 (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.

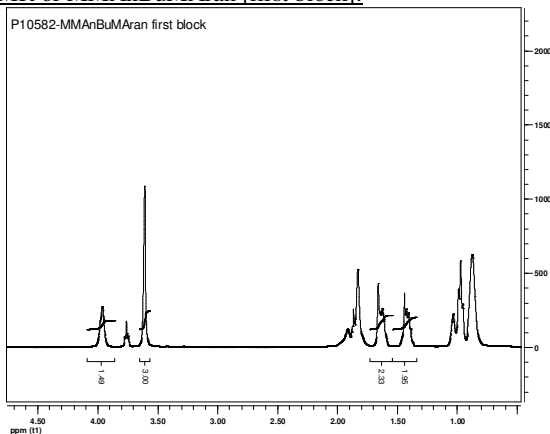
#### Characterization:

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.

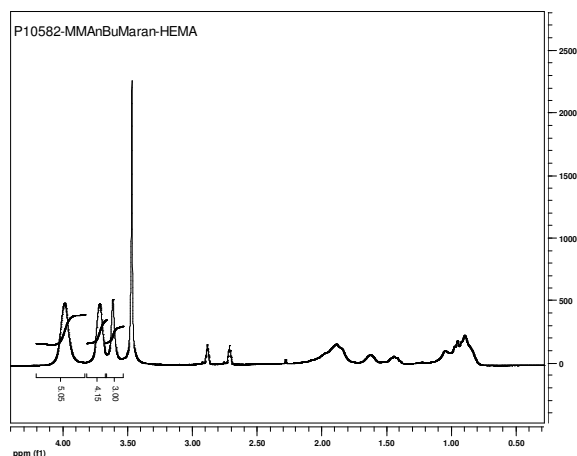
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA<sub>n</sub>BuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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]:



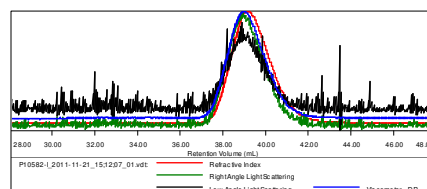
#### <sup>1</sup>H NMR of MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA diblock copolymer:



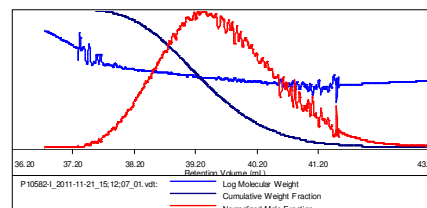
#### SEC of MMA<sub>n</sub>BuMA<sub>r</sub>an [first block]:

Sample ID: P10582-I-MMA<sub>n</sub>BuMA

Concentration (mg/mL)	15.9022
Sample dn/dc (mL/g)	0.0800
Method File	PS80K-Oct-0000.vcm
Column Set	3x PL 1113-6300
System	System 1

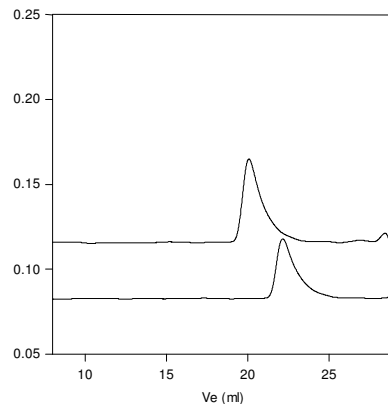


Sample	Mn (Da)	Mw (Da)	Mp (Da)	Mw/Mn	IV (dL/g)
P10582-I_2011-11-21_15:12:07_01.vdt	33,236	36,388	36,051	1.095	0.2594



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

P10582-MMA<sub>n</sub>BuMA<sub>r</sub>anHEMA



Size exclusion chromatography of  
1. Poly MMA<sub>n</sub>BuMA<sub>r</sub>an: Mn 33,000 Mw: 39,000 Mw/Mn 1.2  
Poly MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMATMS: Mn 33,000 -b- 64,000 Mw/Mn 1.25  
After Deprotection : MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA Mn 33,000-b-41,000  
It shows no micellization in THF