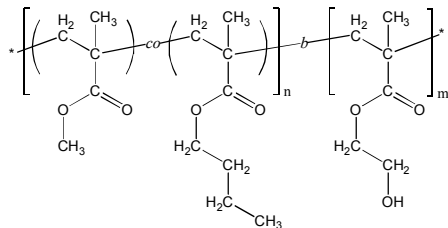


### Sample Name:

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

### Sample #: P11177A-MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA

#### Structure:



#### Composition:

$M_n \times 10^3$ (g/mol)	28.0- <i>b</i> -19.5
$M_w/M_n$	1.15
Molar ratio MMA : nBuMA	20 : 80 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	9 : 50 : 41 (wt%)
$T_g$ (MMA <sub>n</sub> BuMA)	49 °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.

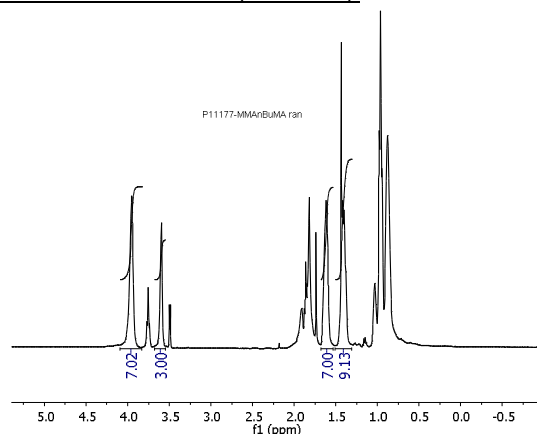
#### Characterization:

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

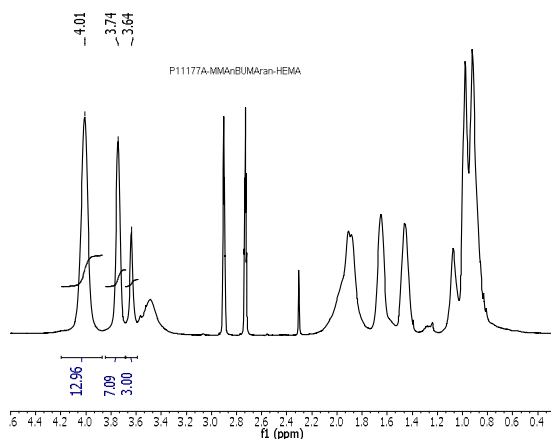
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA<sub>n</sub>BuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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 [first block]:



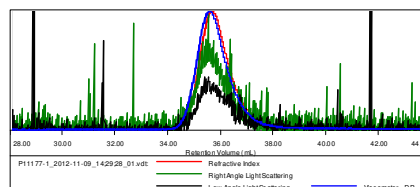
#### $^1\text{H}$ NMR of MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA in DMF-d7:



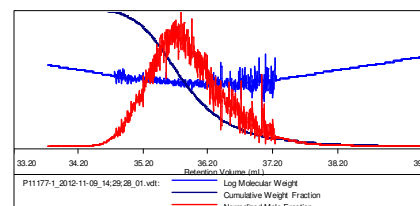
#### SEC of MMA<sub>n</sub>BuMA<sub>r</sub>an [first block]:

Sample ID: P11177-1-MMA<sub>n</sub>BuMA

Concentration (mg/mL)	12.3229
Sample dn/dc (mL/g)	0.0800
Method File	PS80K-Nov-2012-0000.vcm
Column Set	3x PL 1113-6300
System	System 1

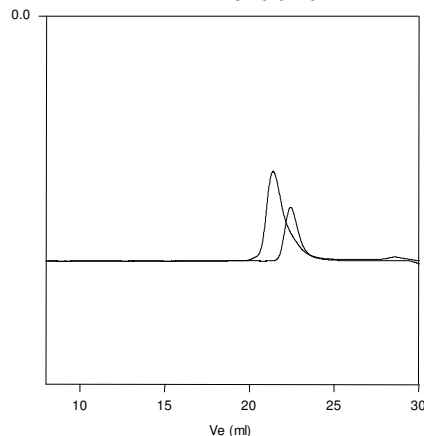


Sample	Mn (Da)	Mw (Da)	Mp (Da)	Mw/Mn	IV (dL/g)
P11177-1_2012-11-09_142928_01.vcl	27,823	29,607	28,854	1.064	0.1720



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

P11177A-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 28,000 Mw/Mn 1.06  
2. MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMATMS: 28,000-30,300 Mw/Mn : 1.15  
After deprotection Mn 27,800-b-19,500 Mw/Mn 1.15