

## Sample Name:

**Poly(methyl methacrylate-*co*(*random*)-n-butyl methacrylate)  
-*block*-poly(2-hydroxyethyl methacrylate)**

## Sample #: P10513-MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA

### Structure:



### Composition:

$M_n \times 10^3$ (g/mol)	111.0- <i>b</i> -16.0
$M_w/M_n$	1.15
Molar ratio MMA : nBuMA	50 : 50 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	36 : 51 : 13 (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.

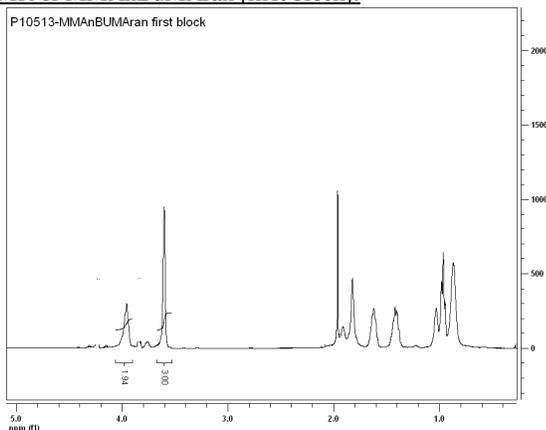
### Characterization:

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.

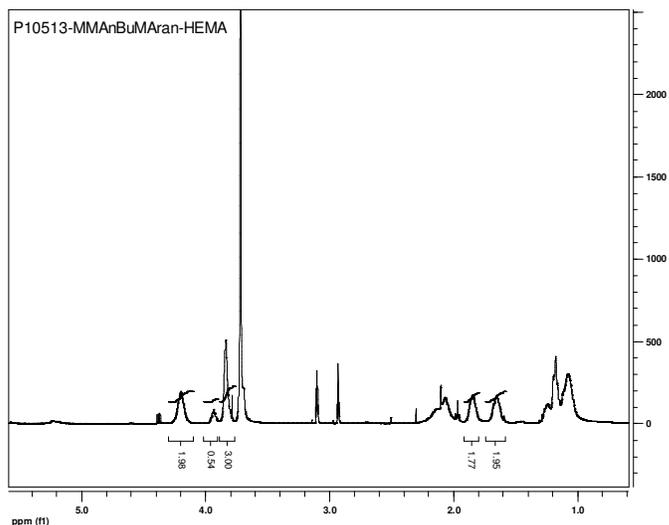
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA<sub>n</sub>BuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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.

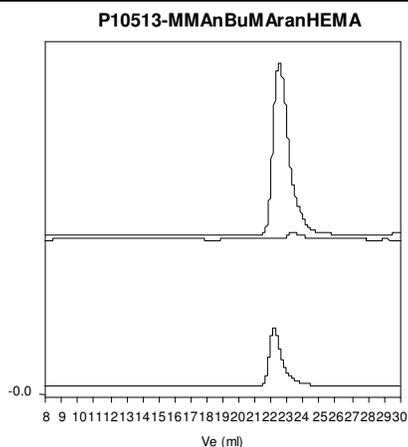
### <sup>1</sup>H NMR of MMA<sub>n</sub>BuMA<sub>r</sub>an [first block]:



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



Size exclusion chromatography of  
1. Random copolymer of MMA and nBuMA: Mn 111,000 Mw: 127,500 Mw/Mn 1.15  
Poly(MMA-nBuMA<sub>r</sub>an)-b- Poly 2-Hydroxy ethyl methacrylate (Protected with TMS)  
Mn 111,000-b-25,000 Mw/Mn 1.15  
After Deprotection of HEMA TMS : Mn 111,000-b-16,000 Mw/Mn 1.15  
In THF after deprotection, the SEC profile shows no micellization