

## Sample Name:

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

## Sample #: P6750-MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA

### Structure:



### Composition:

$M_n \times 10^3$ (g/mol)	20.0- <i>b</i> -12.5
$M_w/M_n$	1.2
Molar ratio MMA : nBuMA	95 : 5 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	57 : 4 : 39 (wt%)
$T_g$	120 °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.

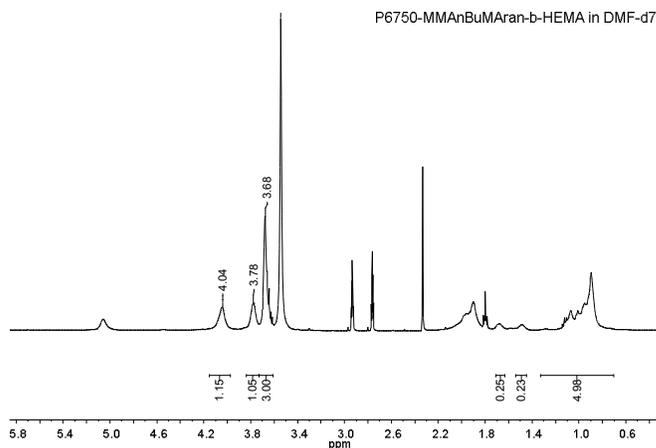
### Characterization:

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.

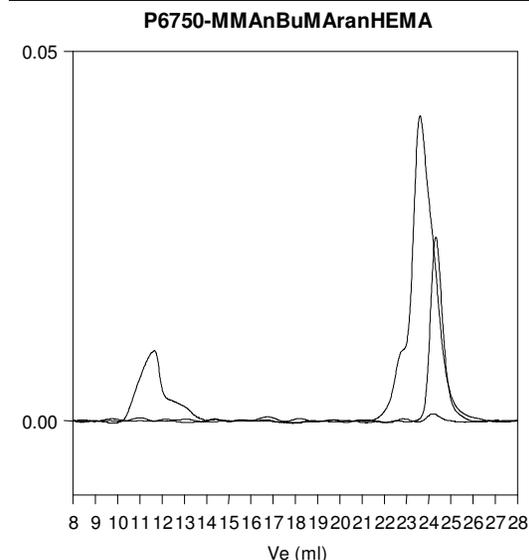
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA<sub>n</sub>BuMA-*b*-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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-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 20000 Mw: 21000 Mw/Mn 1.10  
Poly(MMA-*n*BuMA<sub>r</sub>an)-*b*- Poly 2-Hydroxy ethyl methacrylate (Protected with TMS) Mn 20000-*b*-19400 Mw/Mn 1.20  
After Deprotection of HEMA TMS : Mn 20000-*b*-12500 Mw/Mn 1.20  
In THF after deprotection, the SEC profile shows micellization

## DSC of MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA:

