

## Sample Name:

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

**Sample #: P6748-MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA**

**Structure:**



## Composition:

$M_n \times 10^3$ (g/mol)	18.0- <i>b</i> -8.0
$M_w/M_n$	1.1
Molar ratio MMA : nBuMA	60 : 40 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	36 : 34 : 31 (wt%)
$T_g$ (MMA <sub>n</sub> BuMA)	86 °C
$T_g$ (HEMA)	117 °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.

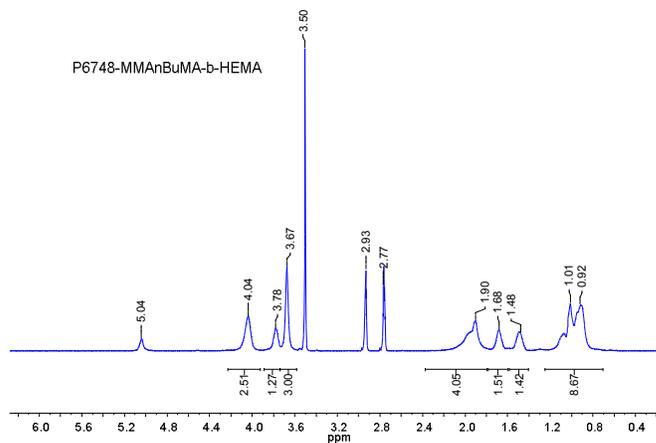
## Characterization:

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.

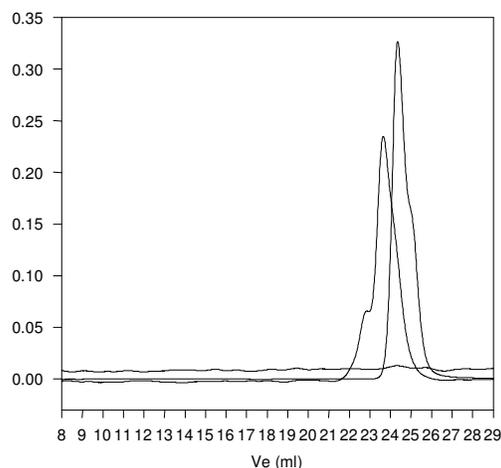
Thermal analysis of the sample was done on a TA Q100 differential scanning calorimeter (DSC) at a heating rate of 10°C/min. The glass transition temperature ( $T_g$ ) was determined as a midpoint of step change in heat flow curve for the second heating scan.

## <sup>1</sup>H NMR of MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA in DMF-d<sub>7</sub>:



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

**P6748-MMA<sub>n</sub>BuMA<sub>r</sub>anHEMA**



Size exclusion chromatography of

1. Random copolymer of MMA and nBuMA:  $M_n$  18000  $M_w$ : 19500  $M_w/M_n$  1.08  
Poly(MMA-*n*BuMA<sub>r</sub>an)-*b*- Poly 2-Hydroxy ethyl methacrylate (Protected with TMS)  
 $M_n$  18,000-*b*-12,500  $M_w/M_n$  1.10  
After Deprotection of HEMA TMS :  $M_n$  18,000-*b*-8,000  $M_w/M_n$  1.10  
In THF after deprotection, the SEC profile shows no micellization and can not be eluted

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

