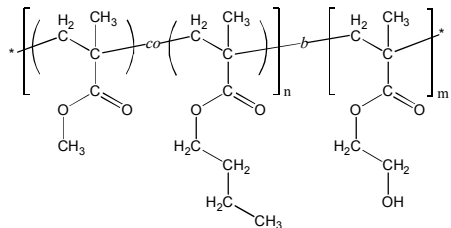


### Sample Name:

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

### Sample #: P15010-MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA

#### Structure:



#### Composition:

$M_n \times 10^{-3}$ (g/mol)	26.5- <i>b</i> -21.0
$M_w/M_n$	1.10
Molar ratio MMA : nBuMA	65 : 35 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	32 : 24 : 44 (wt%)
$T_g$ (MMA <sub>n</sub> BuMA)	80 °C
$T_g$ (HEMA)	112 °C

#### Synthesis Procedure:

Poly([methyl methacrylate-*co*-n-butyl methacrylate]-*b*-2-hydroxyethyl methacrylate) block copolymer was synthesized by **GTP process** polymerization with sequential addition of a mixture of MMA and n-BuMA followed by adding HEMA with protected hydroxyl (trimethyl siloxy ethyl methacrylate monomer). The obtained polymer was precipitated in methanol/acidic to deprotect the hydroxyl group.

**Solubility:** The polymer is soluble in THF, DMF.

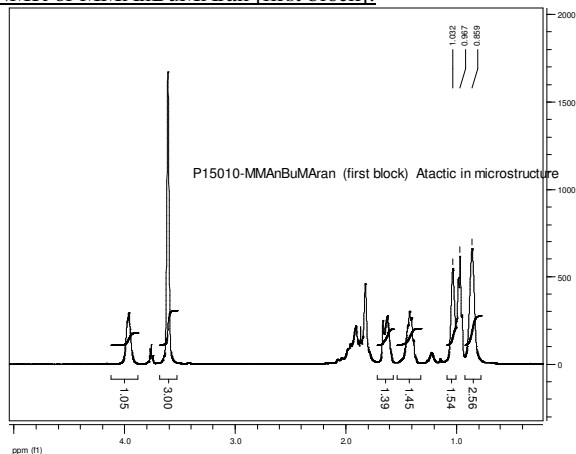
#### Characterization:

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 HEMA to the integration of methoxy group of MMA and using SEC data for the first (MMA<sub>n</sub>BuMA) block.

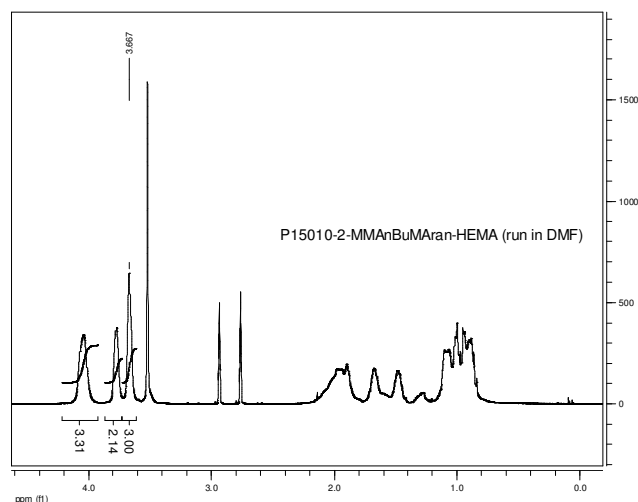
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA<sub>n</sub>BuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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.

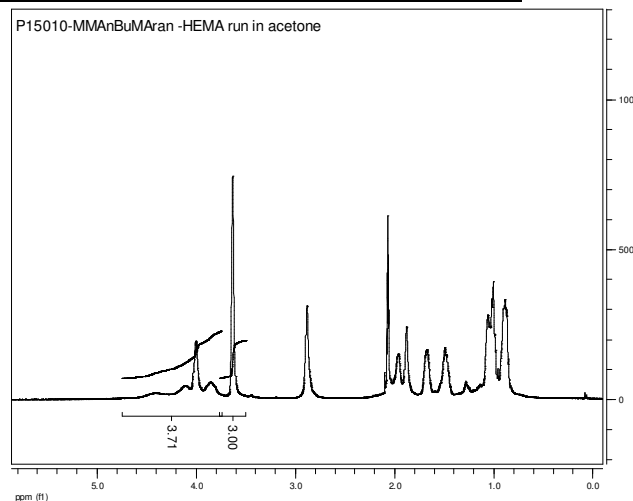
#### $^1\text{H}$ NMR of MMA<sub>n</sub>BuMA<sub>r</sub>an [first block]:



#### $^1\text{H}$ NMR of MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA in DMF-d<sub>7</sub>:

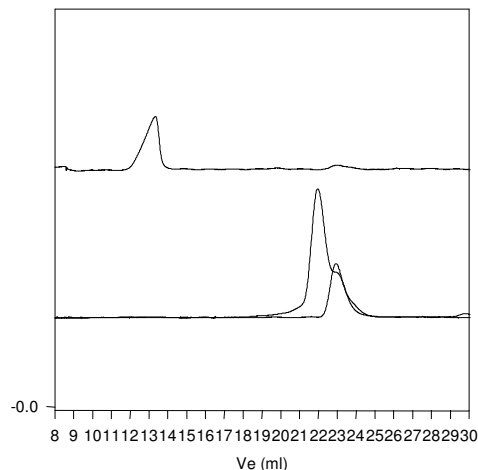


#### $^1\text{H}$ NMR of MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA in acetone-d<sub>6</sub>:



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

##### P15010-MMA<sub>n</sub>BuMA<sub>r</sub>anHEMA



Size exclusion chromatography of  
1. Random copolymer of MMA and nBuMA:  $M_n$  26,500  $M_w$  28,500  $M_w/M_n$  1.08  
Poly(MMA-nBuMA<sub>r</sub>an)-b-Poly(2-Hydroxy ethyl methacrylate (Protected with TMS))  
 $M_n$  26,500-*b*-32,600  $M_w/M_n$  1.10  
After Deprotection of HEMA TMS :  $M_n$  26,000-*b*-21,000  $M_w/M_n$  1.10  
In THF After deprotection, the SEC profile shows micellization

DSC of MManBuMAran-b-HEMA:

