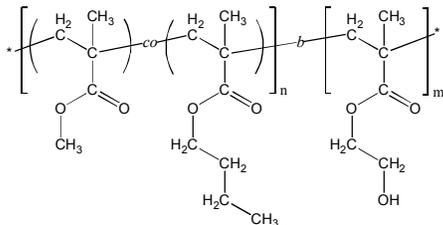


## Sample Name:

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

## Sample #: P9780-MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA

### Structure:



### Composition:

$M_n \times 10^3$ (g/mol)	21.0-23.5
$M_w/M_n$	1.16
Molar ratio MMA : nBuMA	65 : 35 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	27 : 20 : 53 (wt%)
$T_g$ (MMA <sub>n</sub> BuMA)	86 °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.

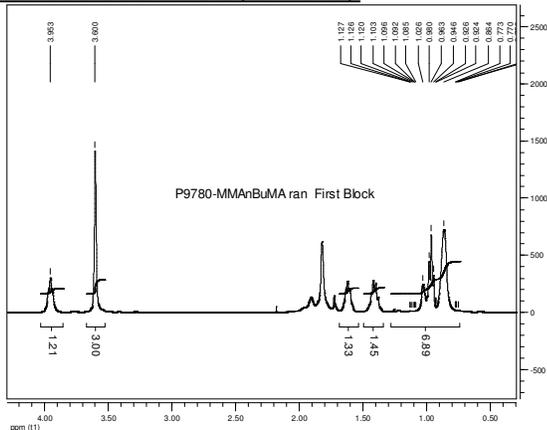
### Characterization:

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.

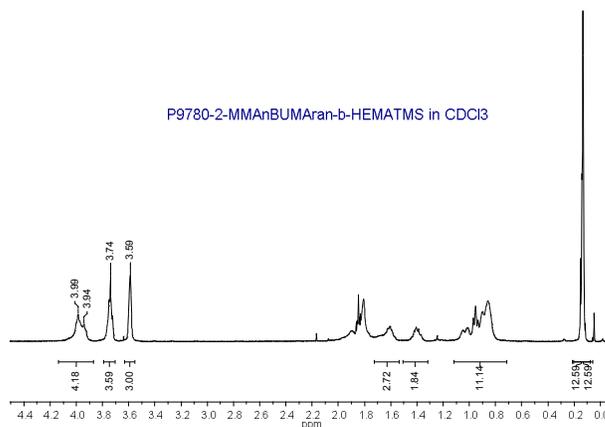
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA<sub>n</sub>BuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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.

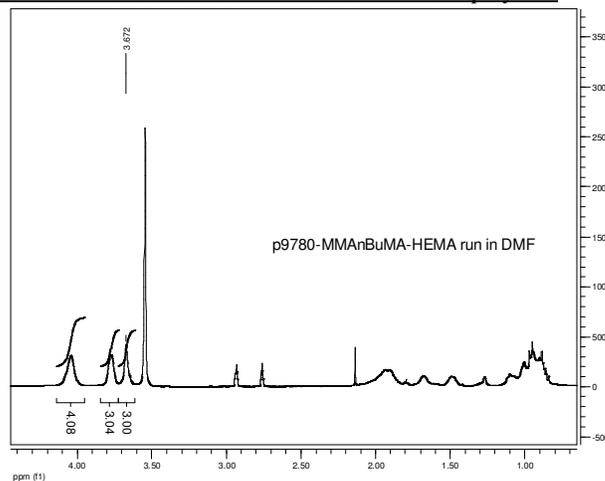
### $^1\text{H NMR}$ of MMA<sub>n</sub>BuMA<sub>r</sub>an [first block]:



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

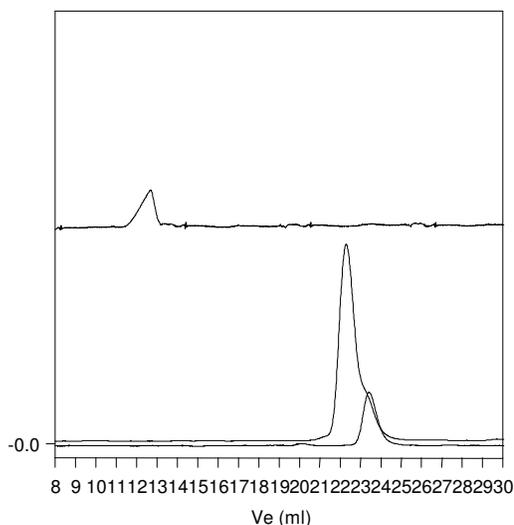


### $^1\text{H NMR}$ of MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA diblock copolymer:



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

#### P9780- MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA



Size exclusion chromatography of

- MMA<sub>n</sub>BuMA<sub>r</sub>an block  $M_n$  21,000  $M_w$ : 22,000  $M_w/M_n$  1.10
  - MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMATMS: 21,000-36,500  $M_w/M_n$  : 1.16
- After deprotection of the hydroxyl group:  
MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA :  $M_n$  21,000-b-23,500  $M_w/M_n$  1.16  
Shows micellization in THF

DSC of MManBuMAran-b-HEMA:

