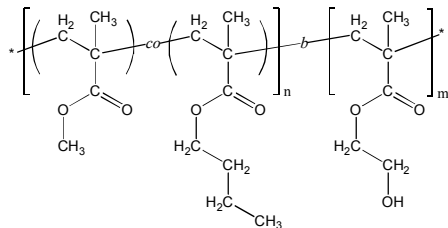


**Sample Name:**

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

**Sample #: P9769A-MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA****Structure:****Composition:**

$M_n \times 10^3$ (g/mol)	21.5- <i>b</i> -20.0
$M_w/M_n$	1.15
Molar ratio MMA : nBuMA	60 : 40 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	27 : 25 : 48 (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.

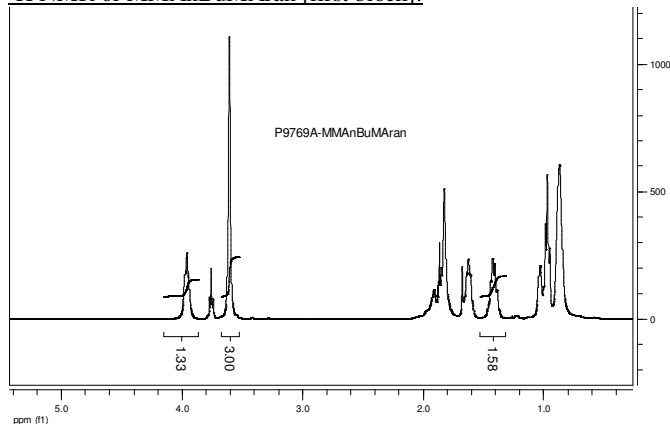
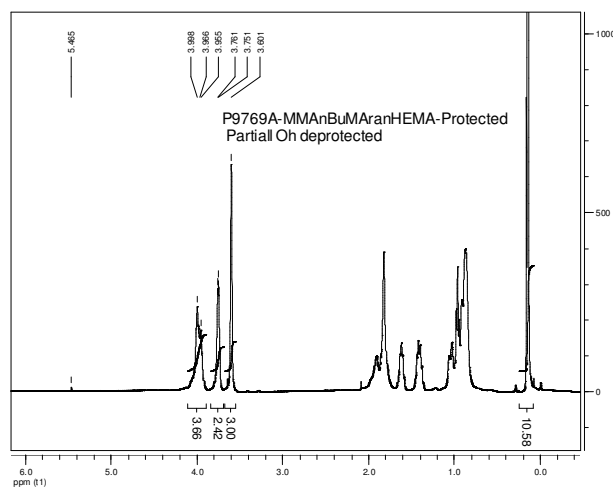
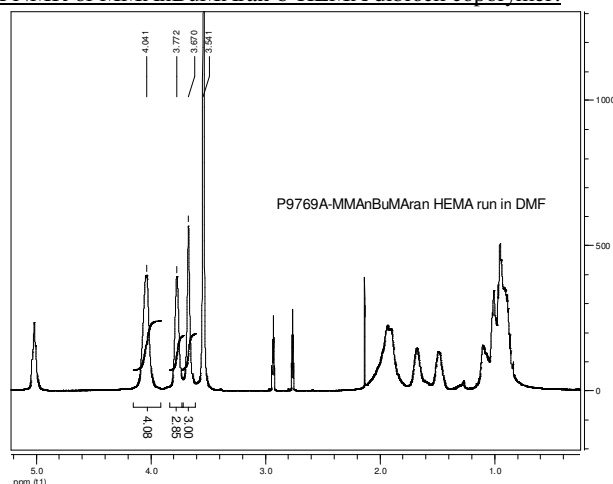
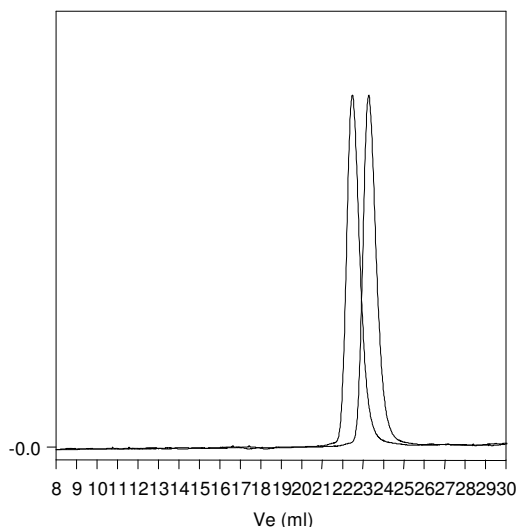
**Solubility:** The polymer is soluble in THF, DMF.

**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:****P9769A-3 MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA**

Size exclusion chromatography of

1. MMA<sub>n</sub>BuMA ran block  $M_n$  21,500  $M_w$ : 24,800  $M_w/M_n$  1.15
2. MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMATMS: 21,500-31,100  $M_w/M_n$  : 1.15

DSC of MManBuMAran-b-HEMA:

