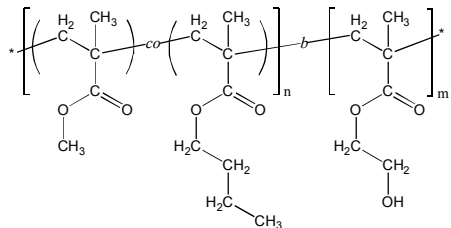


**Sample Name:**

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

**Sample #: P11498p-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> -25.0
$M_w/M_n$	1.15
Molar ratio MMA : nBuMA	60 : 40 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	24 : 22 : 54 (wt%)

**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.

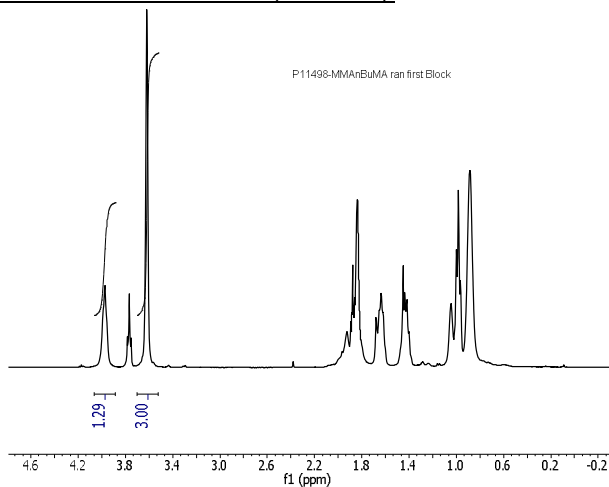
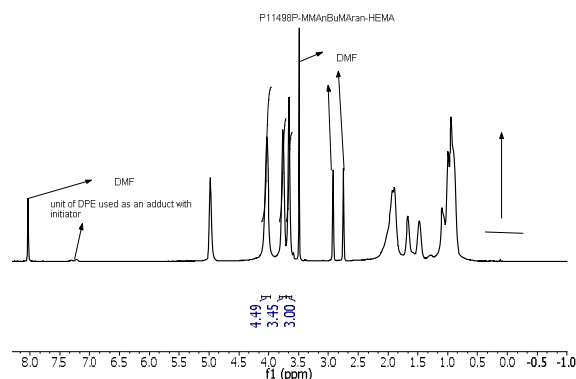
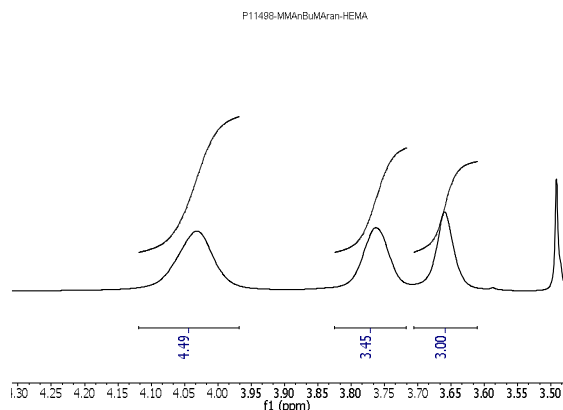
**Solubility:** The polymer is soluble in THF, DMF.

**Characterization:**

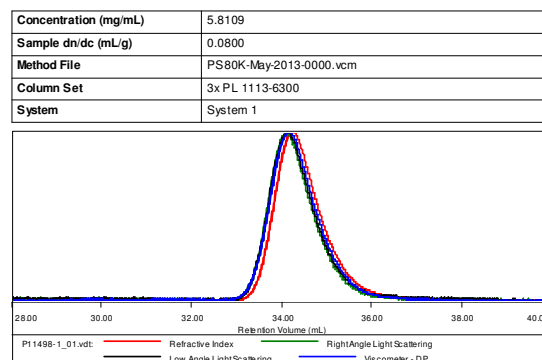
The polymer composition was determined by  $^1\text{H}$  NMR. MMA:nBuMA molar ratio was calculated by comparing the integration of the  $-\text{OCH}_2-$  protons of nBuMA (at  $\delta = 3.9$  ppm) to the integration of methoxy group of MMA (at  $\delta = 3.6$  ppm). Molecular weight of the second (HEMA) block was calculated by comparing the integration of  $-\text{OCH}_2-$  protons of 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.

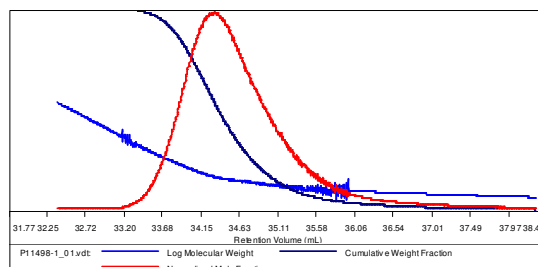
Thermal analysis of the sample was done on a TA Q100 differential scanning calorimeter (DSC) at a heating rate of  $10^\circ\text{C}/\text{min}$ . The glass transition temperature ( $T_g$ ) was determined as a midpoint of step change in heat flow curve for the second heating scan.

 **$^1\text{H}$  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 diblock copolymer:****SEC of MMA<sub>n</sub>BuMA<sub>r</sub>an [first block]:**

**Sample ID: P11498-1-MMA<sub>n</sub>BuMA**

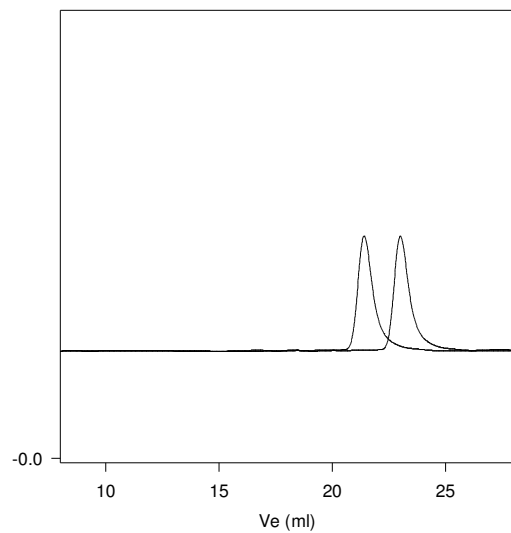


Concentration (mg/mL)	5.8109
Sample dn/dc (mL/g)	0.0800
Method File	PS80K-May-2013-0000.vcm
Column Set	3x PL 1113-6300
System	System 1



SEC of MManBuMAran and MManBuMAran-b-HEMATMS:

**P11498-MManBuMAranHEMA**



Size exclusion chromatography of

1. Random copolymer of MMA and nBuMA: Mn 21,500 Mw/Mn=1.07

Poly(MMA-nBuMAran)-b- Poly 2-Hydroxy ethyl methacrylate (Protected with TMS)

Mn 21,500-b-39,000 Mw/Mn 1.15

After Deprotection of HEMA TMS : Mn 21,500-b-25,000 Mw/Mn 1.15

In THF after deprotection, the SEC profile shows no micellization