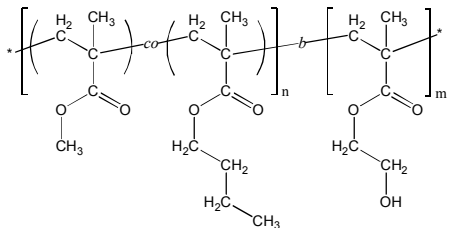


Sample Name:

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

Sample #: P11496p-MMA_nBuMA_ran-b-HEMA

Structure:



Composition:

| | |
|-----------------------------|----------------------|
| $M_n \times 10^3$ (g/mol) | 20.0- <i>b</i> -27.0 |
| M_w/M_n | 1.15 |
| Molar ratio MMA : nBuMA | 50 : 50 (mol/mol) |
| Weight ratio MMA:nBuMA:HEMA | 18 : 25 : 57 (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.

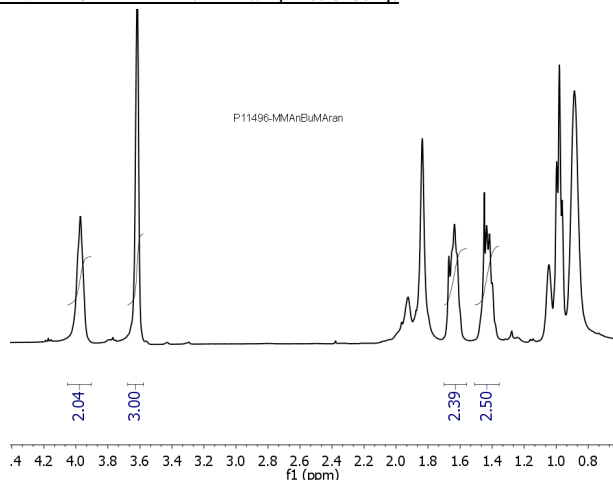
Characterization:

The polymer composition was determined by ^1H 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_nBuMA) block.

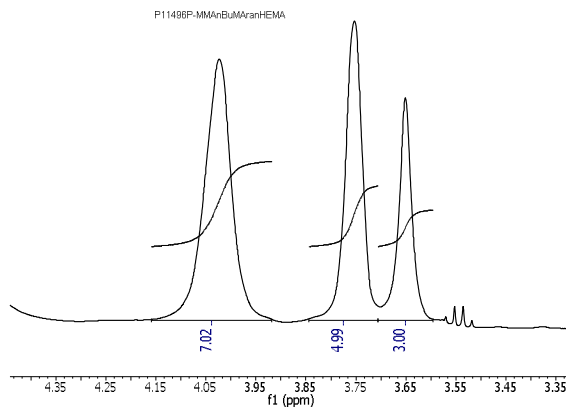
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA_nBuMA-*b*-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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.

^1H NMR of MMA_nBuMA_ran [first block]:



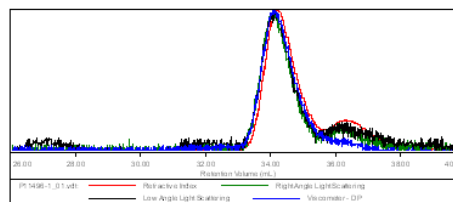
^1H NMR of MMA_nBuMA_ran-*b*-HEMA diblock copolymer:



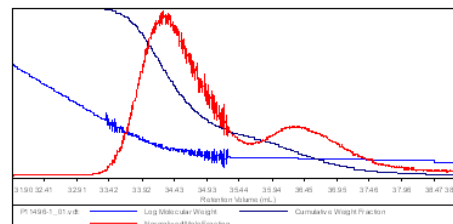
SEC of MMA_nBuMA_ran [first block]:

Sample ID: P11496-1-MMA_nBuMA

| | |
|-----------------------|---------------------------|
| Concentration (mg/mL) | 1.5150 |
| Sample dilution (mL) | 0.0800 |
| Method File | PS801-11496-2013-0000.zen |
| Column Set | 3x PL 1113-6300 |
| System | System 1 |

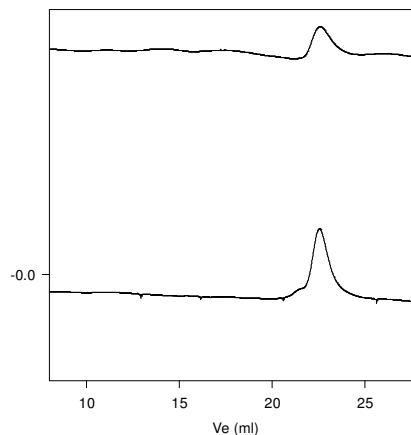


| Sample | Mn | Mw | Mp | Mw/Mn | PDI |
|-------------------|--------|--------|--------|-------|--------|
| P11496-1, 0.1 wt% | 20,304 | 21,802 | 22,819 | 1.074 | 0.2615 |



SEC of MMA_nBuMA_ran-*b*-HEMATMS:

P11496-MMA_nBuMA_ran-b-HEMA



Size exclusion chromatography of
1. MMA_nBuMA_ran block Mn 20,000 Mw/Mn 1.05
2. MMA_nBuMA_ran-*b*-HEMATMS: 20,000-42,000 MW/Mn : 1.15
After deprotection Mn 20,000-*b*-27,000 Mw/Mn 1.15