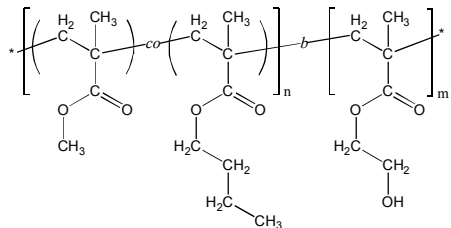


Sample Name:

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

Sample #: P10583-MMA_nBuMA_ran-b-HEMA**Structure:****Composition:**

| | |
|-------------------------------|--------------------|
| $M_n \times 10^3$ (g/mol) | 24.0-25.5 |
| M_w/M_n | 1.16 |
| Molar ratio MMA : nBuMA | 60 : 40 (mol/mol) |
| Weight ratio MMA:nBuMA:HEMA | 25 : 24 : 51 (wt%) |
| T_g (MMA _n BuMA) | 65 °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.

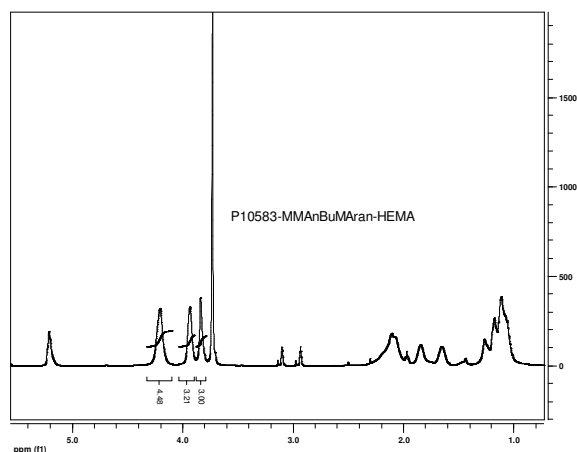
Solubility: The polymer is soluble in THF, DMF.

Characterization:

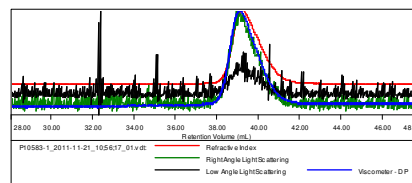
The polymer composition was determined by ^1H NMR. MMA:nBuMA molar ratio was calculated by comparing the integration of the $-\text{OCH}_2-$ protons of nBuMA (at $\delta = 3.9$ ppm) to the integration of methoxy group of MMA (at $\delta = 3.6$ ppm). Molecular weight of the second (HEMA) block was calculated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

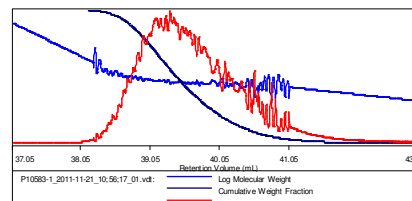
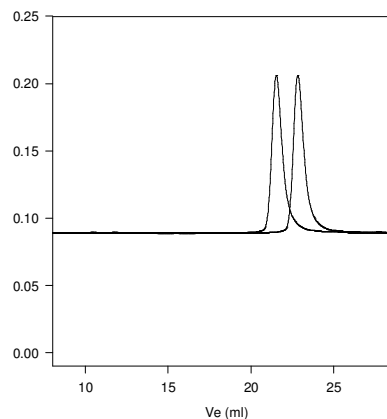
Thermal analysis of the sample was done on a TA Q100 differential scanning calorimeter (DSC) at a heating rate of 10°C/min. The glass transition temperature (T_g) was determined as a midpoint of step change in heat flow curve for the second heating scan.

 ^1H NMR of MMA_nBuMA_ran-b-HEMA diblock copolymer:**SEC of MMA_nBuMA_ran [first block]:**Sample ID: P10583-I-MMA_nBuMA

| | |
|-----------------------|--------------------|
| Concentration (mg/mL) | 8.5106 |
| Sample dn/dc (mL/g) | 0.0800 |
| Method File | PS80K-Oct-0000.vcm |
| Column Set | 3x PL 1113-6300 |
| System | System 1 |



| Sample | Mn (Da) | Mw (Da) | Mp (Da) | Mw/Mn | IV (dL/g) |
|-------------------------------------|---------|---------|---------|-------|-----------|
| P10583-1_2011-11-21_10:56:17_01.vdt | 24,408 | 26,721 | 25,767 | 1.095 | 0.2045 |

**SEC of MMA_nBuMA_ran and MMA_nBuMA_ran-b-HEMATMS:**P10583-MMA_nBuMA_ranHEMA

Size exclusion chromatography of
1. Poly MMA_nBuMA_ran: Mn 24,000 Mw: 25,500 Mw/Mn 1.05