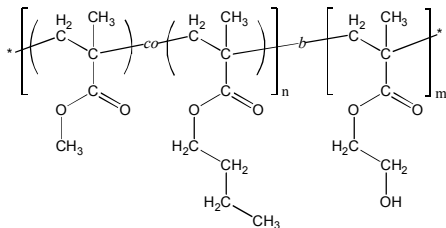


Sample Name:

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

Sample #: P10443-MMA_nBuMA_ran-b-HEMA

Structure:



Composition:

$M_n \times 10^3$ (g/mol)	38.0- <i>b</i> -21.5
M_w/M_n	1.10
Molar ratio MMA : nBuMA	50 : 50 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	26 : 38 : 36 (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.

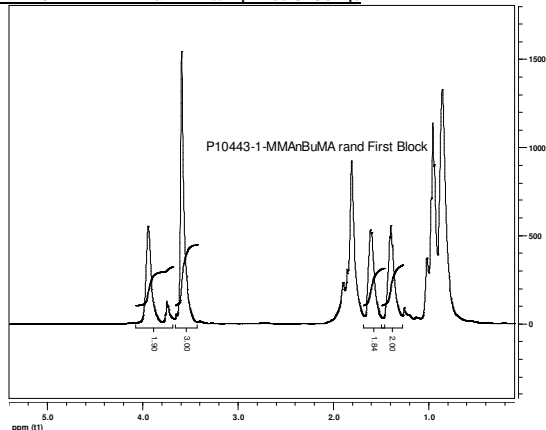
Characterization:

The polymer composition was determined by ¹H NMR. MMA:nBuMA molar ratio was calculated by comparing the integration of the -OCH₂- 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 -OCH₂- protons of HEMATMS to the integration of methoxy group of MMA and using SEC data for the first (MMA_nBuMA) block.

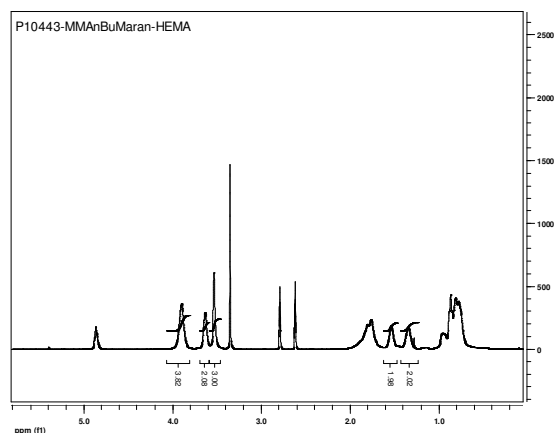
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA_nBuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

Thermal analysis of the sample was done on a TA Q100 differential scanning calorimeter (DSC) at a heating rate of 10°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 [first block]:



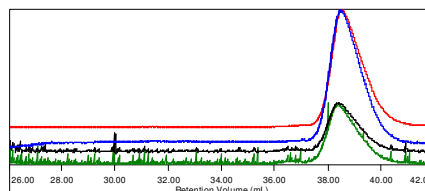
¹H NMR of MMA_nBuMA_ran-b-HEMA in DMF-d₇:



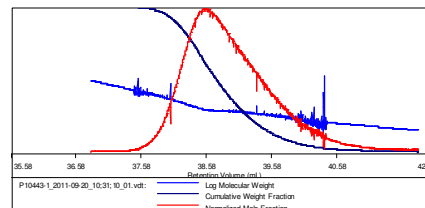
SEC of MMA_nBuMA_ran [first block]:

Sample ID: P10443-1

Concentration (mg/mL)	5.6778
Sample dn/dc (mL/g)	0.0800
Method File	PS80K-July-0000.vcm
Column Set	3x PL 1113-6300
System	System 1

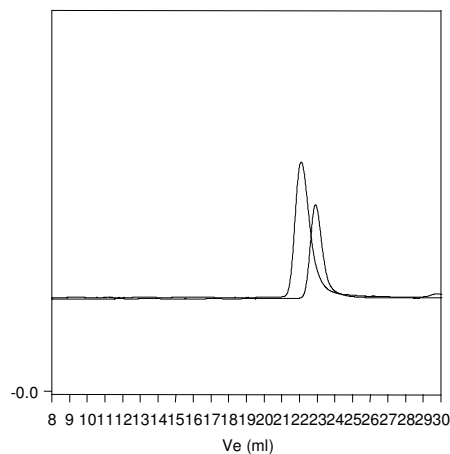


Sample	Mn (Da)	Mw (Da)	Mp (Da)	Mw/Mn	IV (dL/g)
P10443-1_2011-09-20_10:31:10_01.vdt	38,295	40,032	39,638	1.045	0.2989



SEC of MMA_nBuMA_ran and MMA_nBuMA_ran-b-HEMATMS:

P10443-MMA_nBuMA_ranHEMA



Size exclusion chromatography of

1. Random copolymer of MMA and nBuMA: Mn 38,000 Mw: 36,000 Mw/Mn 1.05
2. Poly(MMA-nBuMA_ran)-b- Poly 2-Hydroxy ethyl methacrylate (Protected with TMS)
Mn 38,000-b-33,500 Mw/Mn 1.10
After Deprotection of HEMA TMS : Mn 38,000-b-21,500 Mw/Mn 1.10