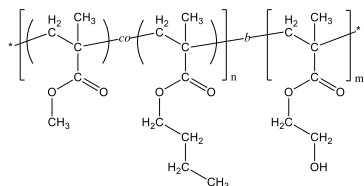


**Sample Name: Poly (methyl methacrylate–
co(random)–n-butyl methacrylate) –block–poly(2-
hydroxyethyl methacrylate)**

Sample #: P10610A-MMA_nBuMA_ran-b-HEMA

Structure:



Composition:

$M_n \times 10^3$ (g/mol)	32.0- <i>b</i> -15.0
$M_n \times 10^3$ (g/mol) (MMA- <i>co</i> -nBuMA)- <i>b</i> - HEMA	(13.0- <i>co</i> -19.0)- <i>b</i> - 15.0
M_w/M_n	1.12

Molar ratio MMA : nBuMA	50 : 50 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	28 : 40 : 32 (wt%)
TMS protected product ((MMA- <i>co</i> -nBuMA)- <i>b</i> - HEMATMS)	< 5 %

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.

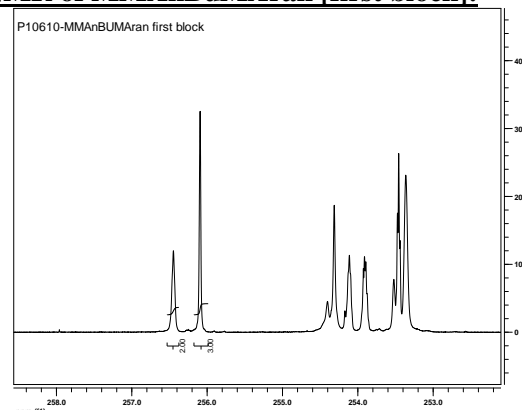
Characterization:

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).

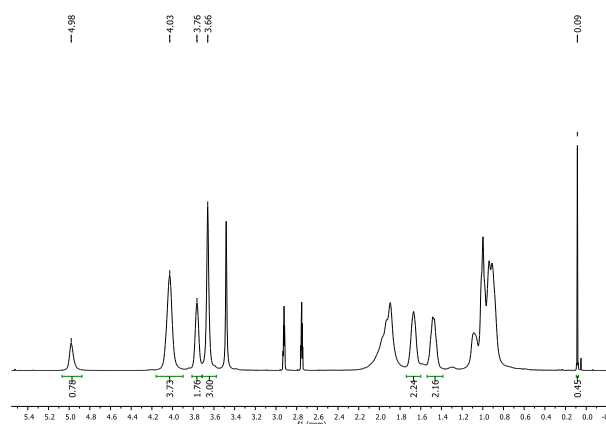
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMAnBuMA-*b*-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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 MManBuMAran [first block]:



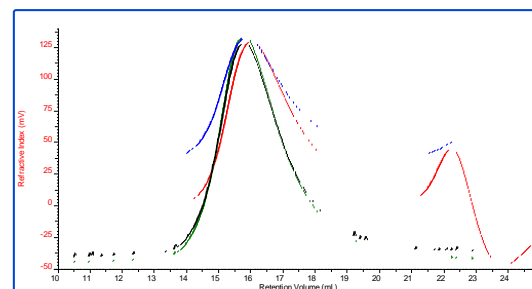
¹HNMR of MManBuMAran-b-HEMA in DMF-d₇:



SEC of MManBuMAran-b-HEMA:

P10601A-MMA_nBuMA-b-HEMA

dn/dc	0.0650
Flow	0.7000
Solvent	DMF with LiBr
Method	PSS column-PMMA60K-Jan3-2019-0002.vcm



Sample	Mn	Mw	Mz	IV	Mw/Mn
P10610A_1_20'	47,002	52,710	63,309	0.1913	1.121