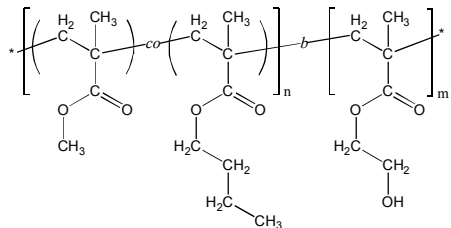


Sample Name:

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

Sample #: P18660-MMA_nBuMA_ran-b-HEMA

Structure:



Composition:

$M_n \times 10^{-3}$ (g/mol)	29.5- <i>b</i> -33.5
M_w/M_n	1.4
Molar ratio MMA : nBuMA	67 : 33 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	28 : 19 : 53 (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.

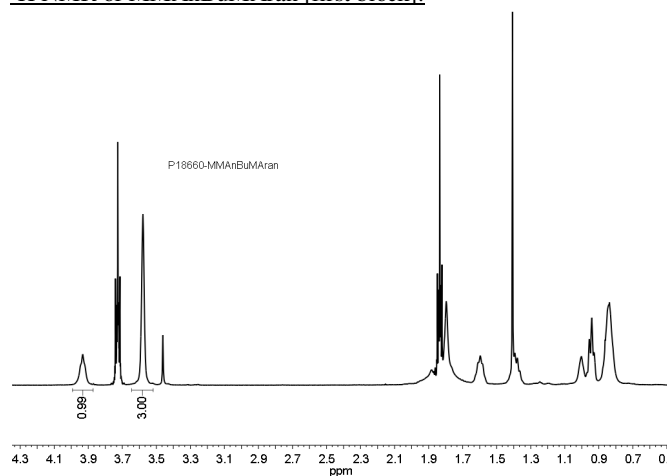
Characterization:

The polymer composition was determined by ^1H NMR. MMA:nBuMA molar ratio was calculated by comparing the integration of the -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.

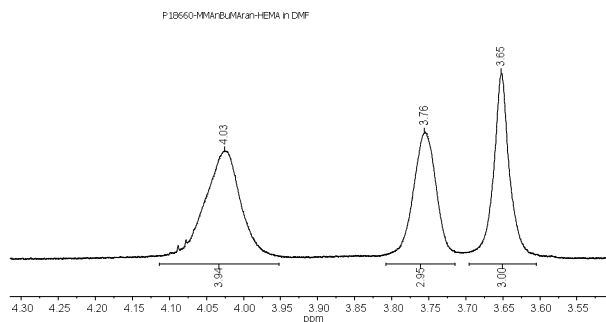
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA_nBuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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]:



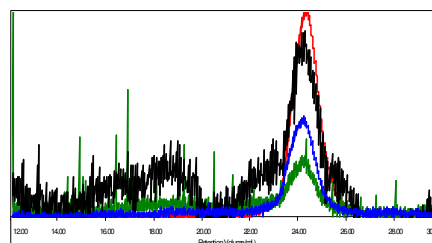
^1H NMR of MMA_nBuMA_ran-b-HEMA in DMF-d₇:



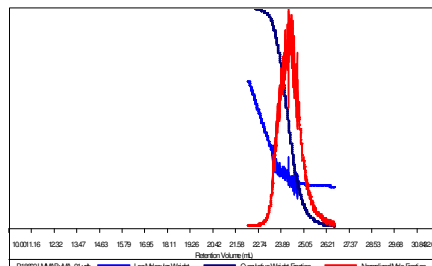
SEC of MMA_nBuMA_ran [first block]:

Sample ID: P18660-MMA_nBuMA_ran

Concentration (mg/mL)	1.6334
Sample dn/dc (mL/g)	0.0940
Method File	PS80K-Apr 15 2014-0000.vcm
Column Set	3x PL 1113-6300
Solvent	THF



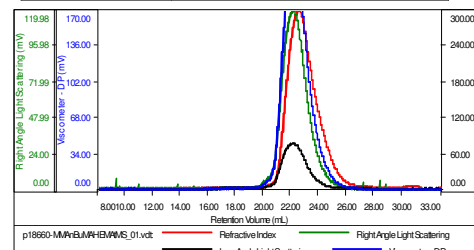
Sample	Mn	Mw	Mp	Mw/Mn	IV
P18660-MMA _n BuMA _r an_01.vct	29,785	33,099	29,099	1.111	0.0720



SEC of MMA_nBuMA_ran-b-HEMATMS:

Sample ID: P18660-MMA_nBuMA_ran-b-HEMATMS

Concentration (mg/mL)	55.7216
Sample dn/dc (mL/g)	0.0700
Method File	PS80K-0923 2014-0000.vcm
Column Set	3x PL 1113-6300
Solvent	THF



Sample	MW Number Average (Da)	MW Weight Average (Da)	MW at Peak (Da)	Polydispersity	Intrinsic Viscosity (dL/g)
p18660-MMA _n BuMA _r an-b-HEMATMS_01.vct	69,372	100,459	110,880	1.459	0.1646