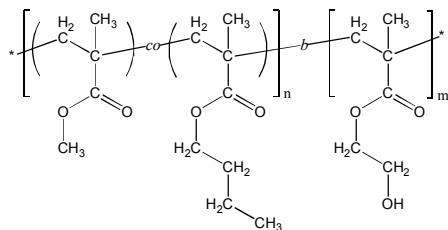


Sample Name:

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

Sample #: P19398-MMA_nBuMA_ran-b-HEMA**Structure:****Composition:**

$M_n \times 10^{-3}$ (g/mol)	30.0- <i>b</i> -30.5
M_w/M_n	1.5
Molar ratio MMA : nBuMA	50 : 50 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	21 : 29 : 50 (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.

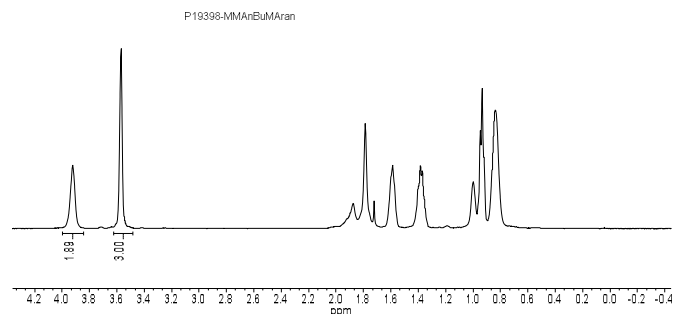
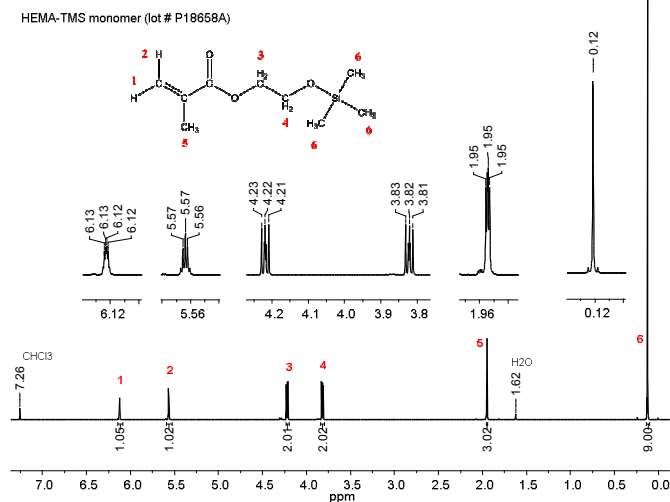
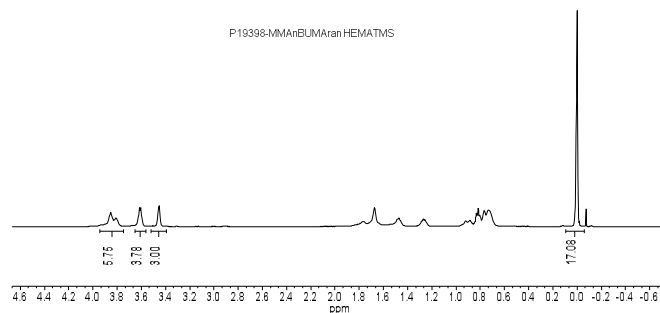
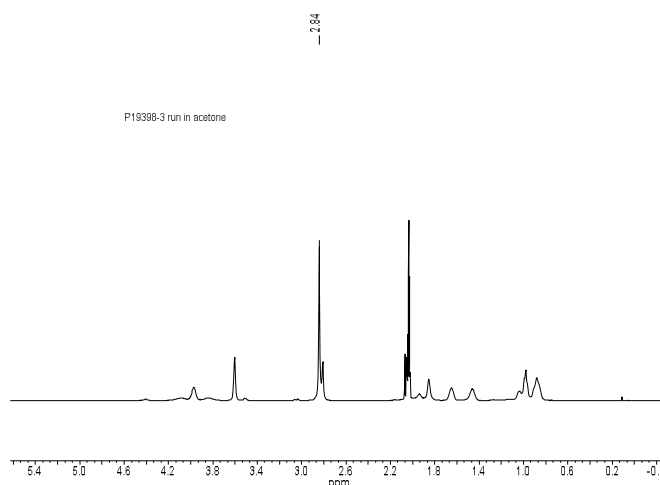
Solubility: The polymer is soluble in THF, DMF.

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.

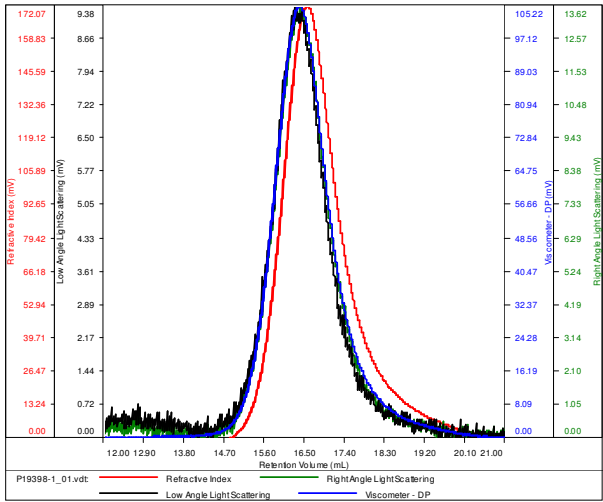
Thermal analysis of the sample was done on a TA Q100 differential scanning calorimeter (DSC) at a heating rate of 10°C/min. The glass transition temperature (T_g) was determined as a midpoint of step change in heat flow curve for the second heating scan.

 ^1H NMR of MMA_nBuMA_ran [first block]: **^1H NMR of HEMATMS monomer (500 MHz, CDCl_3):** **^1H NMR of MMA_nBuMA_ran-b-HEMATMS in CDCl_3 :** **^1H NMR of MMA_nBuMA_ran-b-HEMA in acetone- d_6 :**

SEC of MManBuMAran [first block]:

SAMPLE ID: P19398-MMA nBuMAran

Conc (mg/mL)	11.9412
dn/dc (mL/g)	0.0650
Method	ps80k-July242015-0000.vcm
Solvent	DMF w 0.03M LiBr
Column	PSS

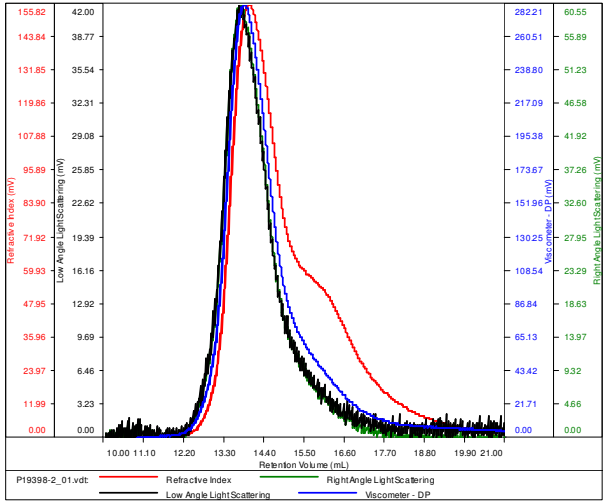


Sample	Mn	Mw	Mp	Mw/Mn	IV
P19398-1_01.vdt	29,768	34,598	33,737	1.162	0.1483

SEC of MManBuMAran-b-HEMATMS:

SAMPLE ID:
P19398-MMA nBuMAranHEMATMS

Conc (mg/mL)	13.7958
dn/dc (mL/g)	0.0700
Method	ps80k-July2015-0000.vcm
Solvent	DMF w 0.03M LiBr
Column	PSS



Sample	Mn	Mw	Mp	Mw/Mn	IV
P19398-2_01.vdt	79,559	122,829	148,819	1.544	0.3764