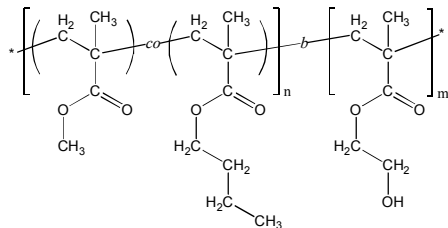


Sample Name:

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

Sample #: P19402-MMA_nBuMA_ran-b-HEMA

Structure:



Composition:

$M_n \times 10^{-3}$ (g/mol)	23.5- <i>b</i> -19.0
M_w/M_n	1.08
Molar ratio MMA : nBuMA	52 : 48 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	24 : 31 : 45 (wt%)
T_g (MMA _n BuMA)	77 °C
T_g (HEMA)	116 °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.

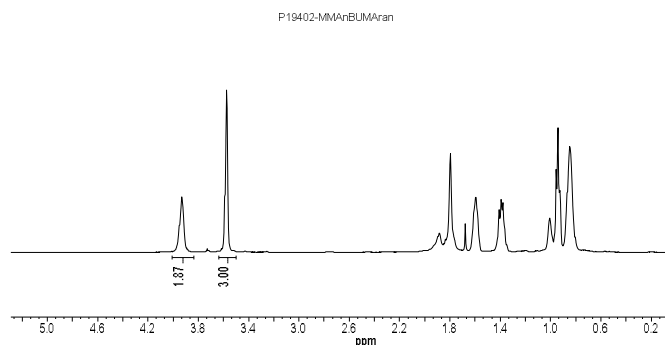
Characterization:

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 δ = 3.9 ppm) to the integration of methoxy group of MMA (at δ = 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.

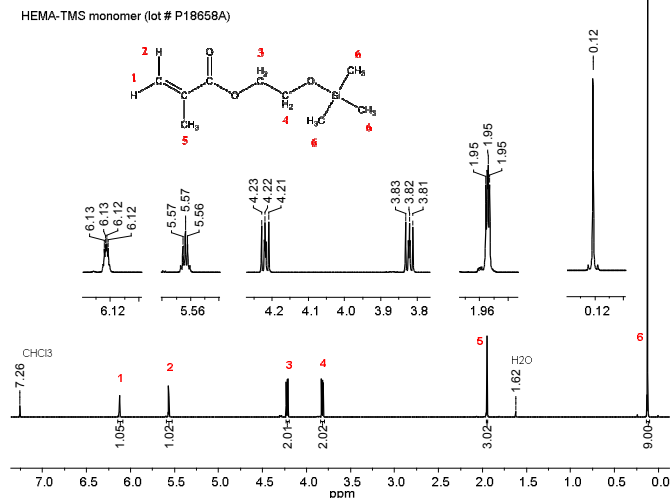
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA_nBuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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.

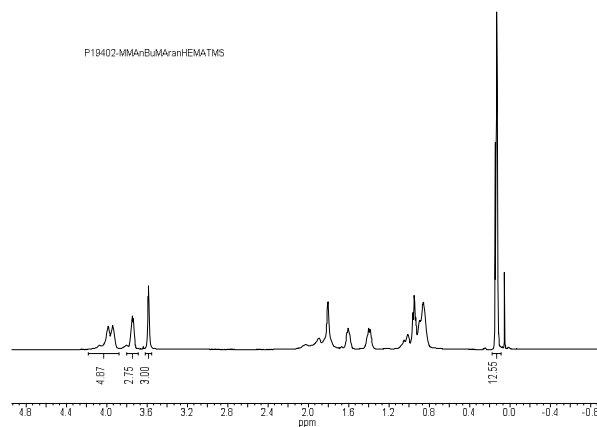
¹H NMR of MMA_nBuMA_ran [first block]:



¹H NMR of HEMATMS monomer (500 MHz, CDCl₃):



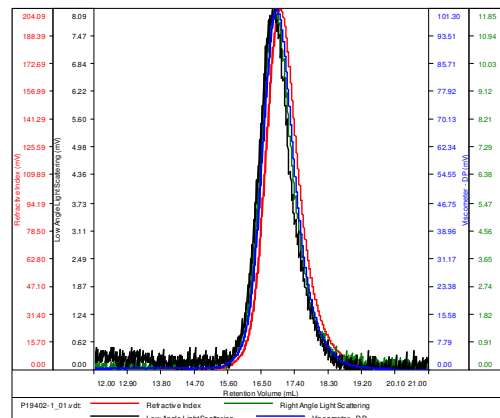
¹H NMR of MMA_nBuMA_ran-b-HEMATMS:



SEC of MMA_nBuMA_ran [first block]:

SAMPLE ID: P19402-1-MMA_nBuMA_ran

Conc (mg/mL)	10.6813
dn/dc (mL/g)	0.0850
Method	ps-B0k-July2015-0000.vcm
Solvent	DMF w 0.03M LiBr
Column	PSS

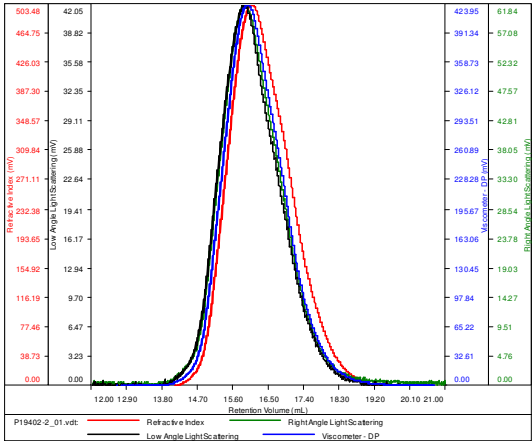


Sample	Mn	Mw	Mp	Mw/Mn	IV
P19402-1_01.vdt	23,582	25,077	23,947	1.063	0.1159

SEC of MManBuMAran-b-HEMATMS:

SAMPLE ID:
P19402-MManBuMAranHEMATMS

Conc (mg/mL)	46.4215
dn/dc (mL/g)	0.0600
Method	ps80kJuly2015-0000.vcm
Solvent	DMF w 0.03MLiBr
Column	PSS



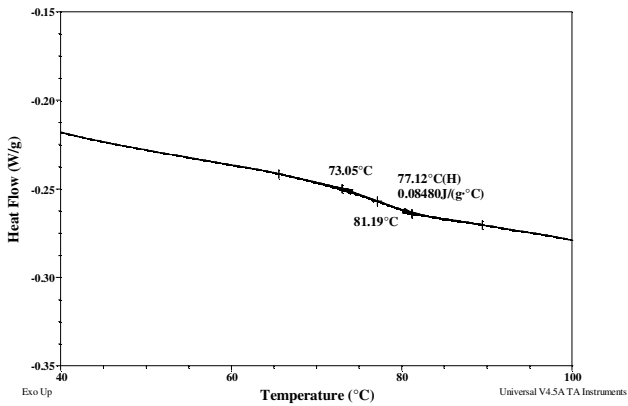
Sample	Mn	Mw	Mp	Mw/Mn	IV
P19402-2_01.vdt	52,677	56,857	56,206	1.079	0.1729

DSC of MManBuMAran-b-HEMA:

Sample: P19402-MManBuMA-HEMA
Size: 6.9000 mg

DSC

File: P19402.001



Sample: P19402-MManBuMA-HEMA
Size: 6.9000 mg

DSC

File: P19402.001

