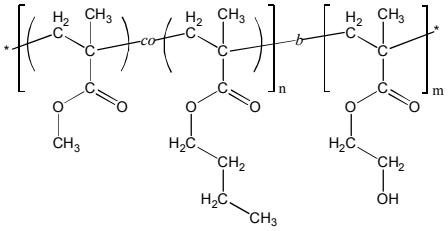
Sample Name:

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

Sample #: P19399-MMAnBuMAran-b-HEMA

Structure:



Composition:

M_n x 10^3 (g/mol)	18.5-*b*-21.0
M_w/M_n	1.08
Molar ratio MMA : nBuMA	52 : 48 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	20 : 27 : 53 (wt%)
T_g (MMAnBuMA)	79 °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.

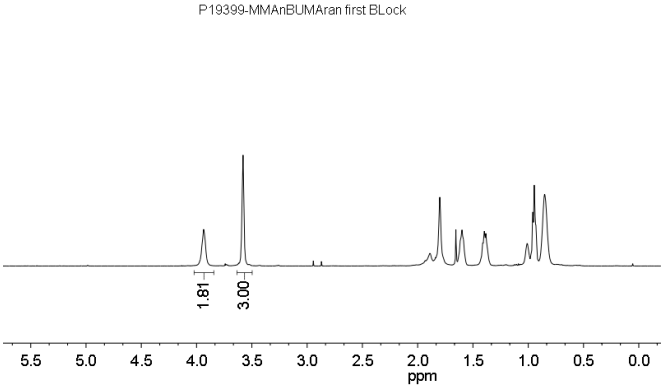
Characterization:

The polymer composition was determined by ^{1}H NMR. MMA:nBuMA molar ratio was calculated by comparing the integration of the -OCH_2- 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 -OCH_2- protons of HEMATMS to the integration of methoxy group of MMA and using SEC data for the first (MMAnBuMA) block.

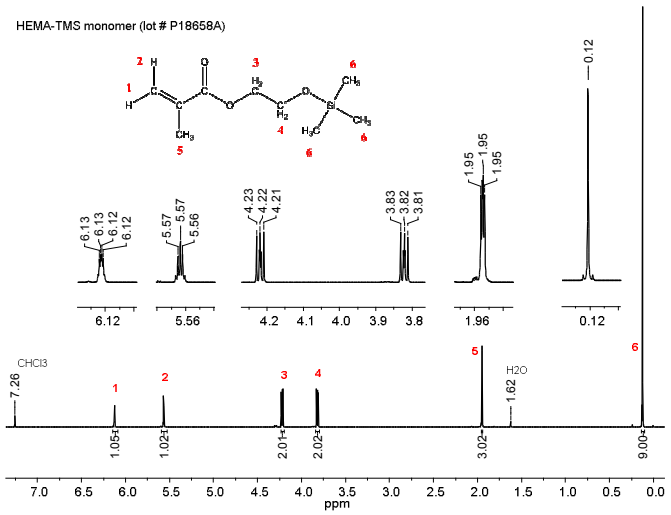
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMAnBuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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.

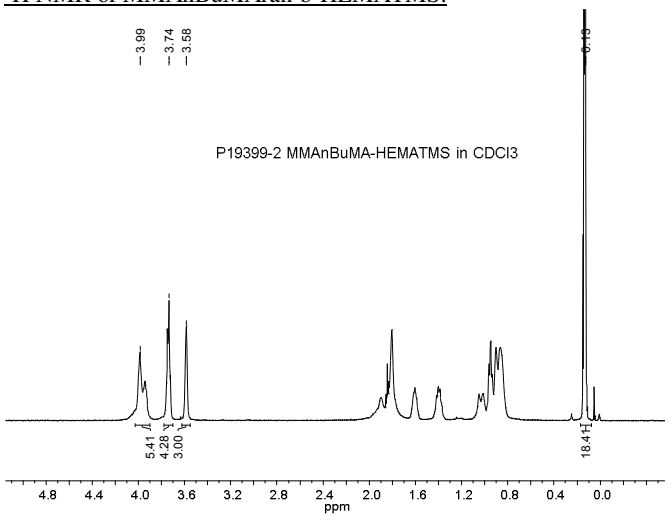
^{1}H NMR of MMAnBuMAran [first block]:



^{1}H NMR of HEMATMS monomer (500 MHz, $CDCl_3$):



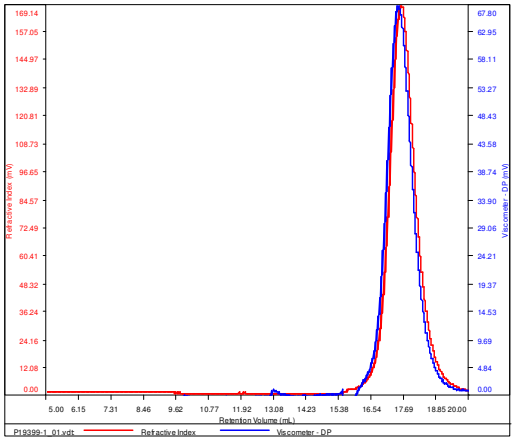
^{1}H NMR of MMAnBuMAran-b-HEMATMS:



SEC of MMAnBuMAran [first block]:

SAMPLE ID: P19399-MMAnBUMAran

Conc (mg/mL)	8.9017
dn/dc (mL/g)	0.0650
Method	ps80k-July2015-0000.vcm
Solvent	DMF w 0.03M LiBr
Column	PSS

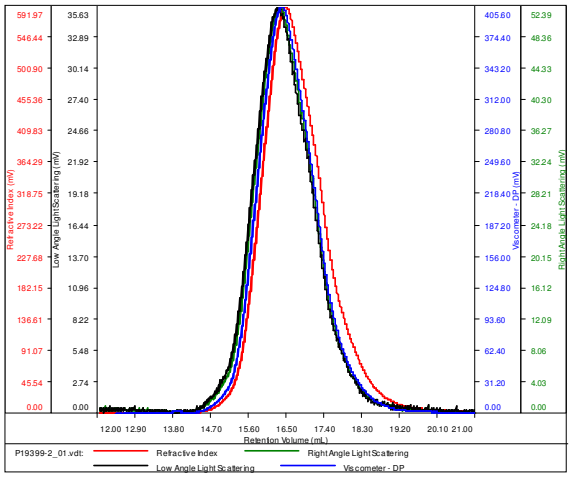


Sample	Mn	Mw	Mp	Mw/Mn	IV
P19399-1_01.vdt	18,322	19,948	17,653	1.089	0.0942

SEC of MMAnBuMAran-b-HEMATMS:

SAMPLE ID:
P19399-MMAnBuMAranHEMATMS

Conc (mg/mL)	65.6750
dn/dc (mL/g)	0.0450
Method	ps80k-July2015-0000.vcm
Solvent	DMF w 0.03M LiBr
Column	PSS



Sample	Mn	Mw	Mp	Mw/Mn	IV
P19399-2_01.vdt	51,193	55,438	54,208	1.083	0.1052

DSC of MMAnBuMAran-b-HEMA: