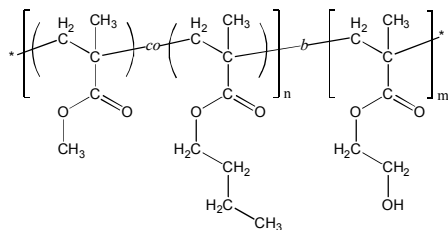


Sample Name:

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

Sample #: P18670-MMA_nBuMA_ran-b-HEMA

Structure:



Composition:

$M_n \times 10^{-3}$ (g/mol)	21.0- <i>b</i> -24.0
M_w/M_n	1.06
Molar ratio MMA : nBuMA	52 : 48 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	20 : 27 : 53 (wt%)
T_g (MMA _n BuMA)	78 °C
T_g (HEMA)	118 °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.

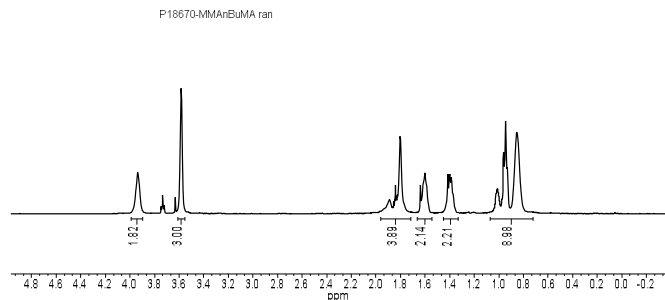
Characterization:

The polymer composition was determined by ^1H NMR. MMA:nBuMA molar ratio was calculated by comparing the integration of the $-\text{OCH}_2-$ 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.

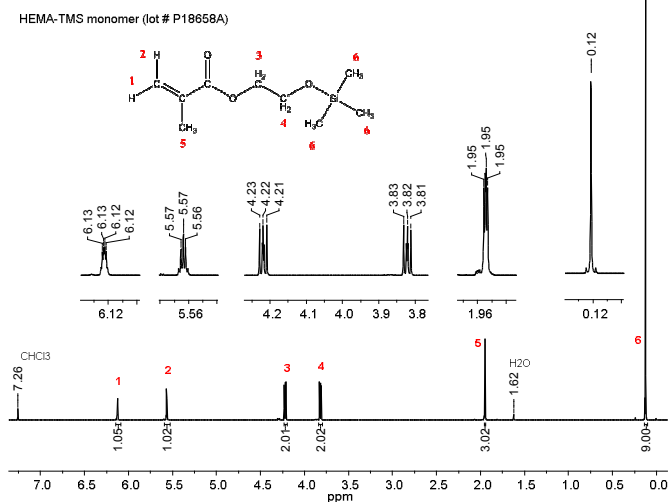
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA_nBuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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.

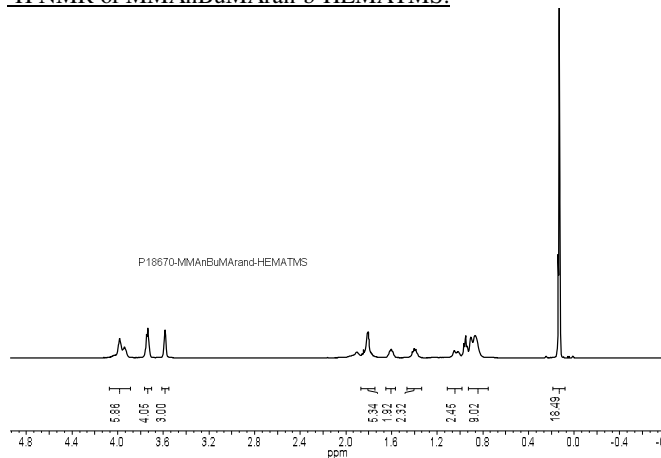
^1H NMR of MMA_nBuMA_ran [first block]:



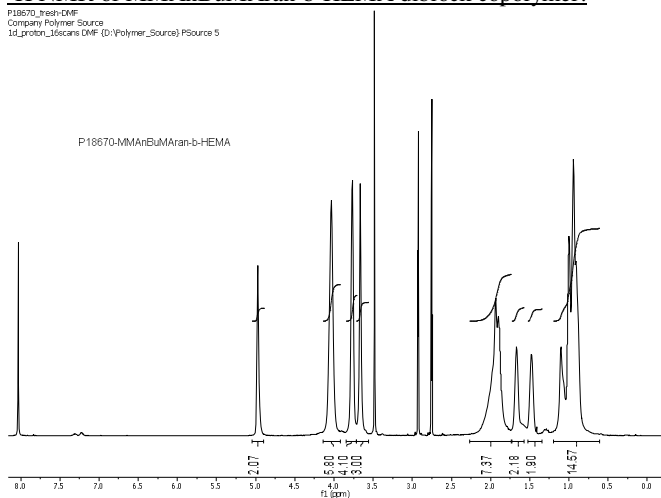
^1H NMR of HEMATMS monomer (500 MHz, CDCl_3):



^1H NMR of MMA_nBuMA_ran-b-HEMATMS:



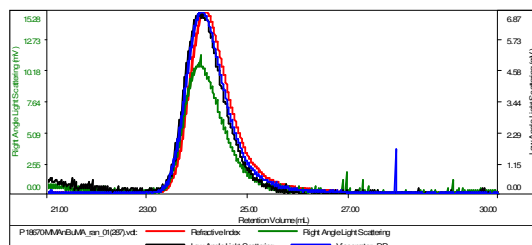
^1H NMR of MMA_nBuMA_ran-b-HEMA diblock copolymer:



SEC of MManBuMAran [first block] in (a) THF and (b) DMF:

(a) Sample ID: P18670-1-MManBuMA

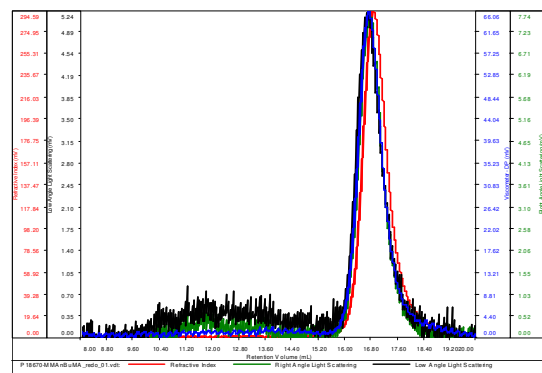
Concentration (mg/mL)	8.3426
Sample dn/dc (mL/g)	0.0840
Method File	PS80K-Apr15-2014-0000.vcm
Column Set	3x PL 1113-6300
Solvent	THF



Sample	Mn	Mw	Mp	Mw/Mn	IV
P18670-MManBuMA_ran_01(28).vdt	21,424	22,676	22,356	1.058	0.0588

(b) SAMPLE ID: P18670-MManBuMAran

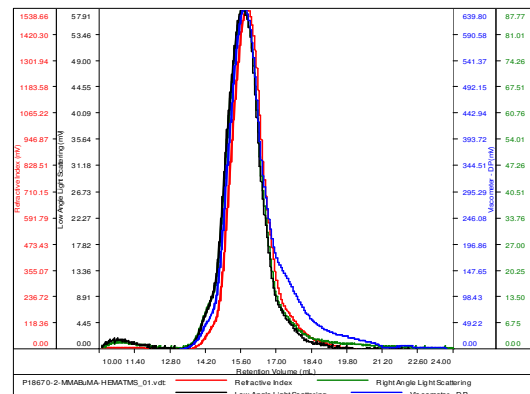
Conc (mg/mL)	6.4164
dn/dc (mL/g)	0.0650
Method	ps80k042014-0000.vcm
Solvent	DMF w 0.03M LiBr
Column	PSS



Sample	Mn	Mw	Mp	Mw/Mn	IV
P18670-MManBuMA_ran_01.vdt	20,594	22,214	22,719	1.079	0.1092

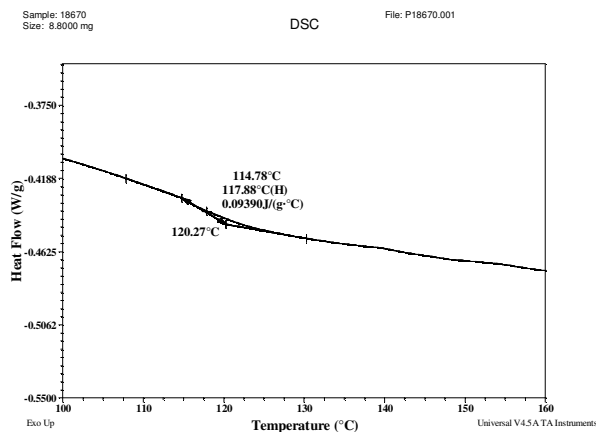
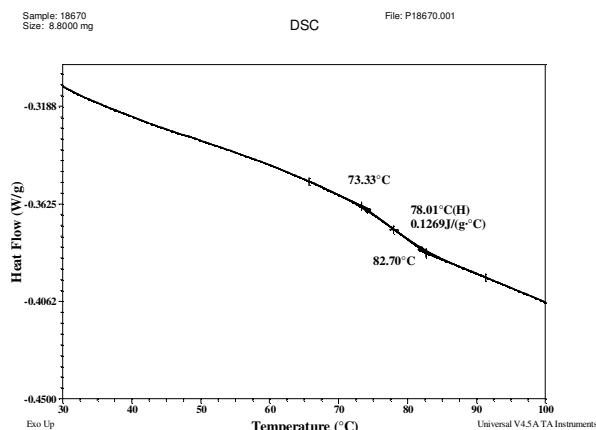
(d) SAMPLE ID: P18670-MManBuMA-HEMATMS

Conc (mg/mL)	60.4873
dn/dc (mL/g)	0.0580
Method	ps80k042014-0000.vcm
Solvent	DMF w 0.03M LiBr
Column	PSS



Sample	Mn	Mw	Mp	Mw/Mn	IV
P18670-2-MManBuMA-HEMATMS_01.vdt	57,524	60,860	55,953	1.058	0.1977

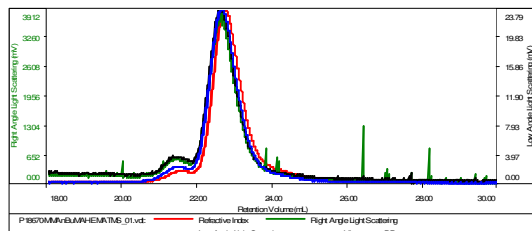
DSC of MManBuMAran-b-HEMA:



SEC of MManBuMAran-b-HEMATMS in (a) THF and (b) DMF:

(c) Sample ID: P18670-2-MManBuMA-HEMATMS

Concentration (mg/mL)	11.6772
Sample dn/dc (mL/g)	0.0800
Method File	PS80K-Apr15-2014-0000.vcm
Column Set	3x PL 1113-6300
Solvent	THF



Sample	Mn	Mw	Mp	Mw/Mn	IV
P18670-MManBuMA-HEMATMS_01.vdt	58,619	62,631	64,940	1.051	0.1034