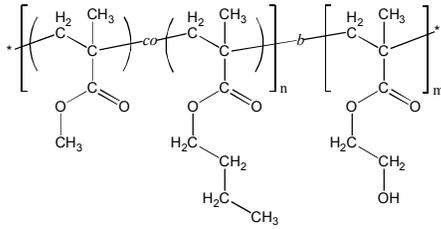


Sample Name:

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

Sample #: P18773-MMA_nBuMA_ran-b-HEMA

Structure:



Composition:

$M_n \times 10^3$ (g/mol)	24.5- <i>b</i> -29.0
M_w/M_n	1.3
Molar ratio MMA : nBuMA	52 : 48 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	20 : 26 : 54 (wt%)
T_g (MMA _n BuMA)	81 °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.

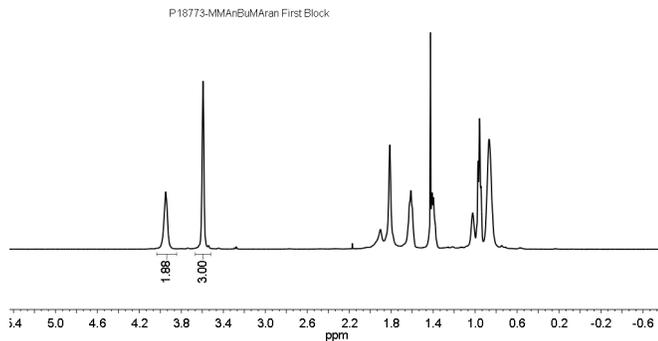
Characterization:

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

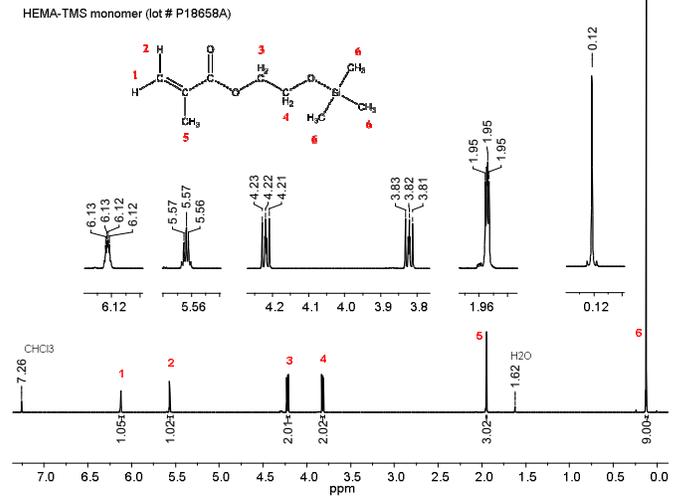
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA_nBuMA-*b*-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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.

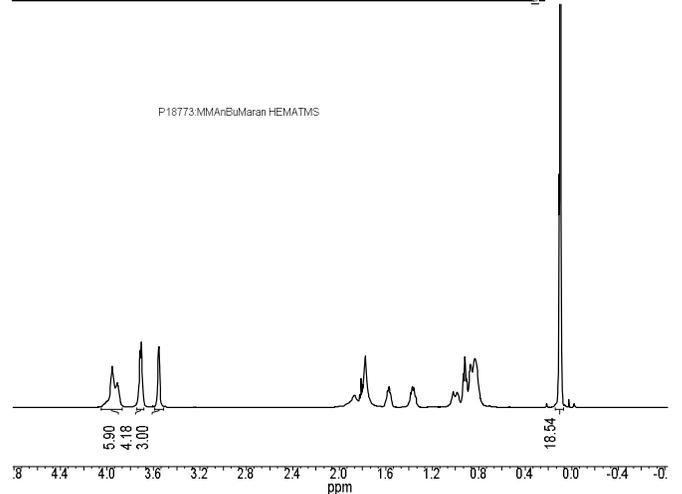
¹H NMR of MMA_nBuMA_ran [first block]:



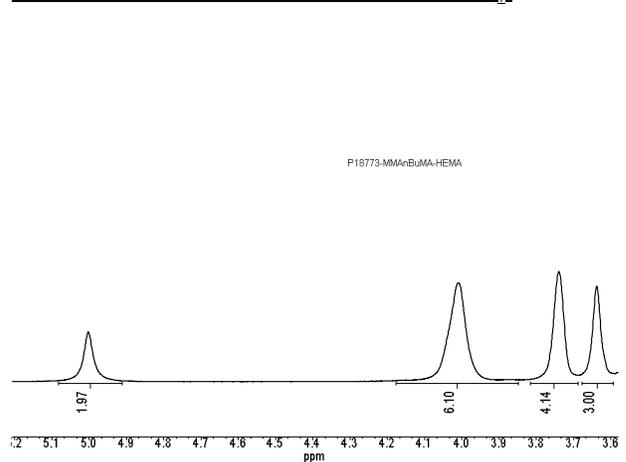
¹H NMR of HEMATMS monomer (500 MHz, CDCl₃):



¹H NMR of MMA_nBuMA_ran-b-HEMATMS in CDCl₃:



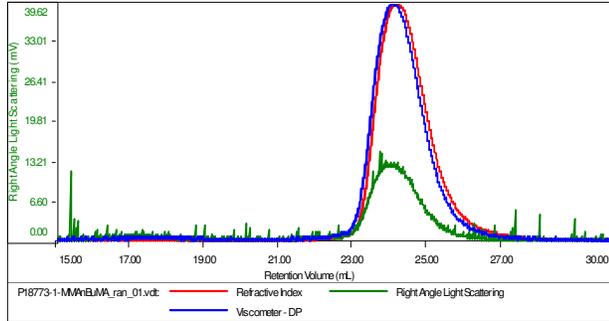
¹H NMR of MMA_nBuMA_ran-b-HEMA in DMF-*d*₇:



SEC of MManBuMAran [first block] in THF:

Sample ID: P18773-MManBuMAran

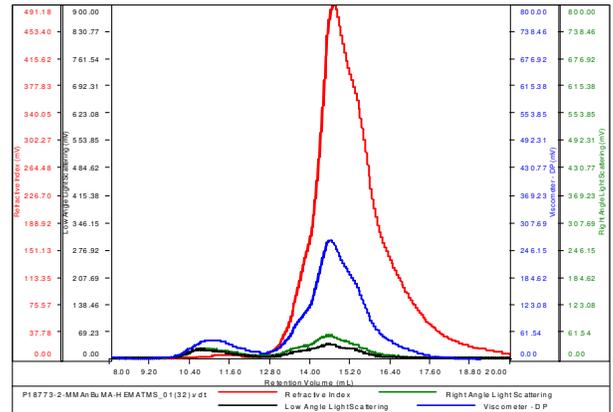
Concentration (mg/mL)	1.0058
Sample dn/dc (mL/g)	0.0840
Method File	PS80KJuly11-2014-0000.vcm
Column Set	3x PL 1113-6300
Solvent	THF



Sample	Mn	Mw	Mp	Mw/Mn	IV
P18773-1-MManBuMA_ran_01.vct	24,503	27,177	26,956	1.109	0.9963

SAMPLE ID: P18773-2-MManBuMA-HEMATMS

Conc (mg/mL)	20.1412
dn/dc (mL/g)	0.0700
Method	ps80kJune2014-0000.vcm
Solvent	DMF w 0.03M LiBr
Column	PSS

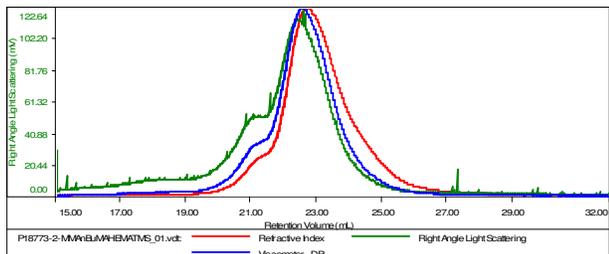


Sample	Mn	Mw	Mp	Mw/Mn	IV
P18773-2-MManBuMA-HEMATMS_01(32).vct	71,183	89,680	84,105	1.260	0.2581

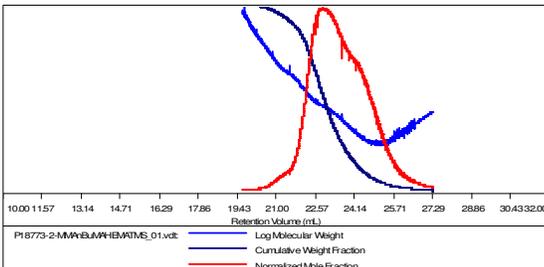
SEC of MManBuMAran-b-HEMATMS in THF and DMF:

Sample ID: P18773-2-MManBuMA-HEMATMS

Concentration (mg/mL)	4.3071
Sample dn/dc (mL/g)	0.0820
Method File	PS80KJuly11-2014-0000.vcm
Column Set	3x PL 1113-6300
Solvent	THF

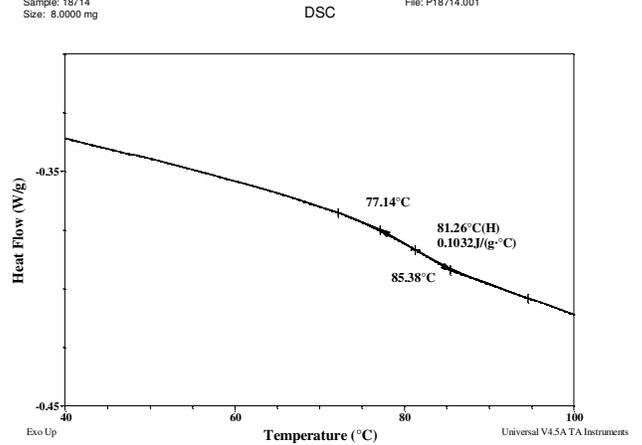


Sample	Mn	Mw	Mp	Mw/Mn	IV
P18773-2-MManBuMA-HEMATMS_01.vct	73,059	99,625	89,495	1.364	1.7489



DSC of MManBuMAran-b-HEMA:

Sample: 18714 Size: 8.0000 mg File: P18714.001



Sample: 18714 Size: 8.0000 mg File: P18714.001

