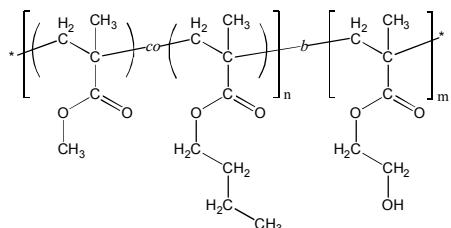


Sample Name:

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

Sample #: P18714-MMAnBuMArAn-b-HEMA

Structure:



Composition:

$M_n \times 10^3$ (g/mol)	19.5- <i>b</i> -24.0
M_w/M_n	1.14
Molar ratio MMA : nBuMA	55 : 45 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	21 : 24 : 55 (wt%)
T_g (MMAnBuMA)	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 (hydroxyl-protected 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.

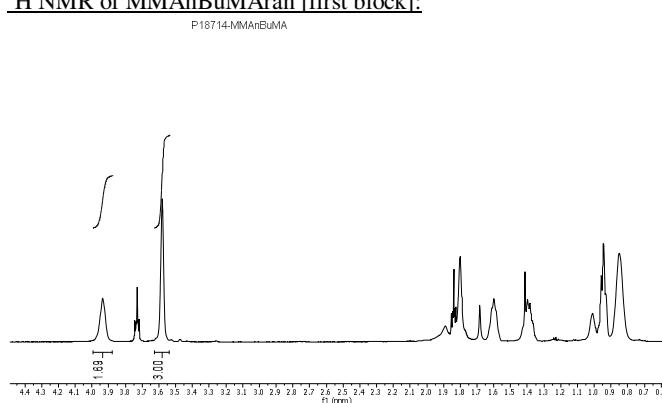
Characterization:

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 (MMAnBuMA) block.

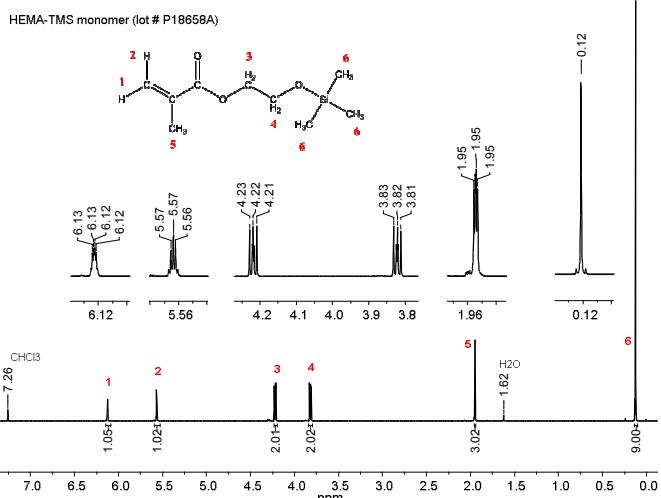
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMAnBuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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.

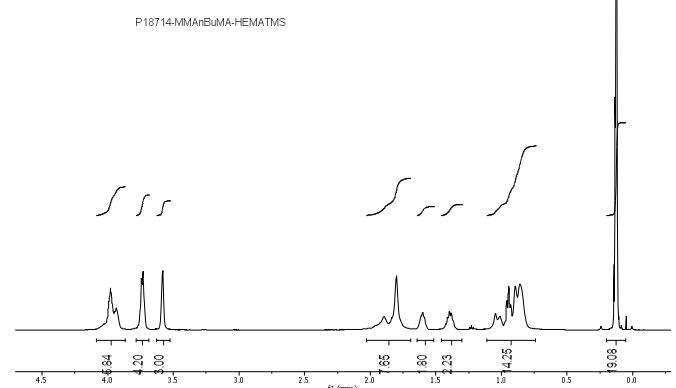
^1H NMR of MMAnBuMArAn [first block]:



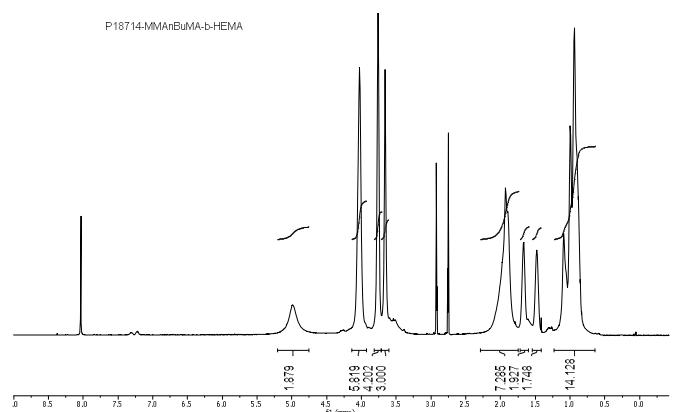
^1H NMR of HEMATMS monomer (500 MHz, CDCl_3):



^1H NMR of MMAnBuMArAn-b-HEMA:



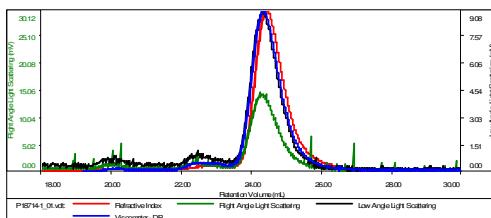
^1H NMR of MMAnBuMArAn-b-HEMA (500MHz, DMF-d_7):



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

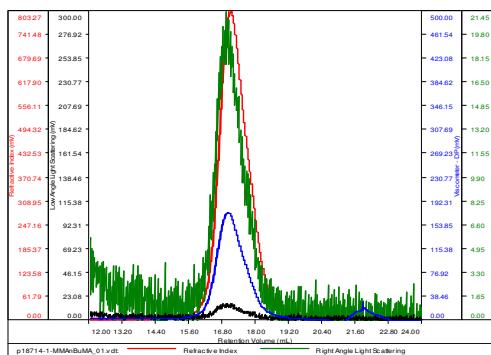
(a) **Sample ID: P18714-1-MMAAnBuMA**

Concentration (mg/mL)	12.5512
Sample dn/dc (mL/g)	0.0840
Method File	PS80K-Apr152014-0000.vcm
Column Set	3x PL 1113-6300
Solvent	THF



(b) **Sample ID: P18714-1-MMAAnBuMA**

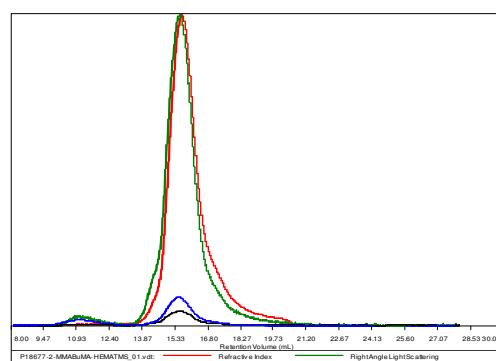
Conc (mg/mL)	22.4976
dn/dc (mL/g)	0.0650
Method	ps80kJune2014-0000.vcm
Solvent	DMF w 0.03M LiBr
Column	PSS



Sample | Mn | Mw | Mp | Mw/Mn | IV
P18714-1-MMAAnBuMA_01.vdt | 19,892 | 21,508 | 19,883 | 1.081 | 0.1031

(d) **SAMPLE ID: P18677-MMAAnBUMAran HEMATMS
dn/dc in DMF:0.059 mL/g**

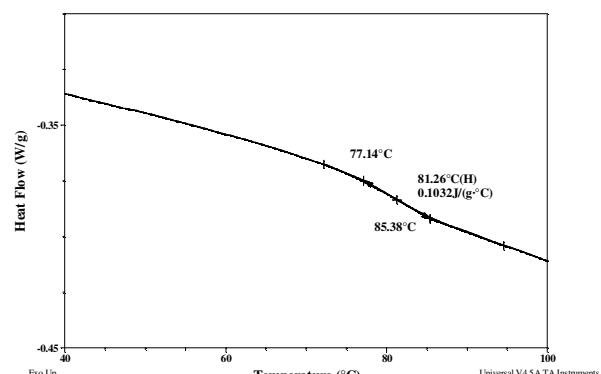
Conc (mg/mL)	44.8507
dn/dc (mL/g)	0.0590
Method	ps89k-May2014-0003.vcm
Solvent	DMF w 0.03M LiBr
Column	PSS



Sample	Mn	Mw	Mp	Mw/Mn	IV
P18677-2-MMAAnBUMAran HEMATMS_01.vdt	65,194	68,967	69,186	1.058	0.1597

DSC of MMAAnBuMAran-b-HEMA:

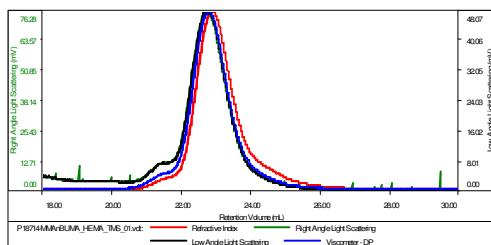
Sample: 18714
Size: 8.0000 mg DSC File: P18714.001



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

(c) **Sample ID: P18714-2-MMAAnBuMA-HEMATMS**

Concentration (mg/mL)	34.5564
Sample dn/dc (mL/g)	0.0800
Method File	PS80K-Apr152014-0000.vcm
Column Set	3x PL 1113-6300
Solvent	THF



Sample | Mn | Mw | Mp | Mw/Mn | IV
P18714-MMAAnBuMA-HEMA-TMS_01.vdt | 57,232 | 65,012 | 65,563 | 1.136 | 0.1095

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

