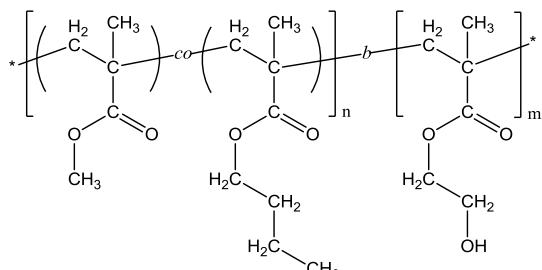


Sample Name:

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

Sample #: P40430-MMAnBuMAran-b-HEMA

Structure:



Composition:

$M_n \times 10^3$ (g/mol)	47.0- <i>b</i> -22.0
M_w/M_n	1.24
Molar ratio MMA : nBuMA	51 : 49 (mol%)
Weight ratio MMA : nBuMA	42 : 58 (wt%)
Molar ratio MMA : nBuMA : HEMA	
T_{g1} (MMAnBuMA)	70 °C
T_{g2} (HEMA)	107 °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 (nBuMA) were co-polymerized; followed by addition of 2-[trimethylsilyloxy]ethyl methacrylate (hydroxyl-protected HEMA monomer). The obtained block copolymer was precipitated in acidic methanol solution to deprotect the hydroxyl group.

Solubility:

The polymer is soluble in THF and DMF.

Characterization:

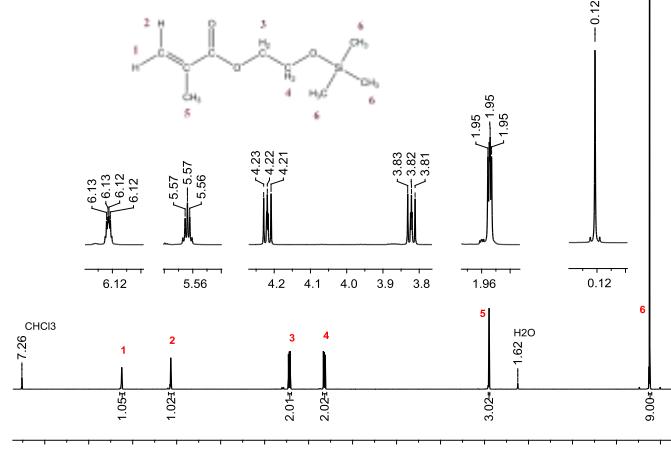
The polymer composition was determined by ^1H NMR. MMA:nBuMA molar ratio was calculated by comparing the peak area of nBuMA $-O\text{CH}_2-$ protons at 3.9 ppm and the peak area of MMA $-O\text{CH}_3$ protons at 3.6 ppm. Molecular weight of the second (HEMA) block was calculated by comparing the peak area of HEMA $-O\text{CH}_2\text{CH}_2\text{O}-$ protons and the peak area of nBuMA $-O\text{CH}_2-$ protons and using SEC data for the first (MMAnBuMA) block.

The average molecular weight and polydispersity index of the polymer were determined by size exclusion chromatography (SEC) using DMF (0.023 M LiBr in DMF) as an eluent.

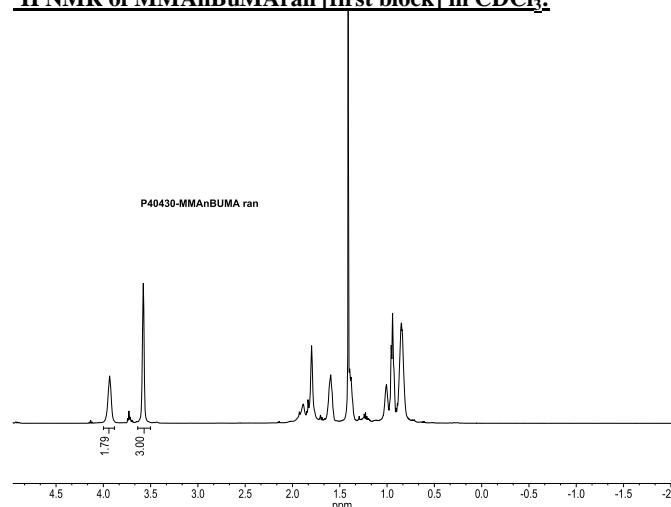
Thermal analysis was performed on TA Instruments Q100 differential scanning calorimeter (DSC) under a nitrogen atmosphere. The glass transition temperature (T_g) of the polymer was measured at a scan rate of 10°C/min shortly after creating thermal history of the sample.

^1H NMR of HEMA-TMS monomer (500 MHz, CDCl_3):

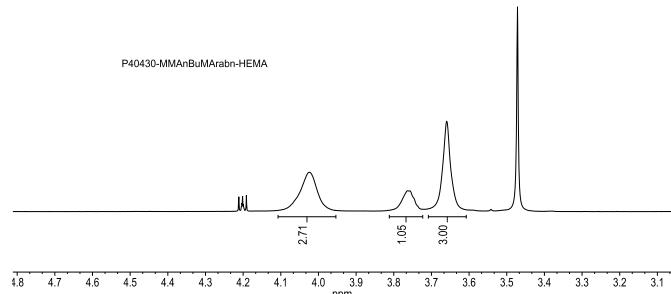
HEMA-TMS monomer (lot # P18658A)



^1H NMR of MMAnBuMAran [first block] in CDCl_3 :



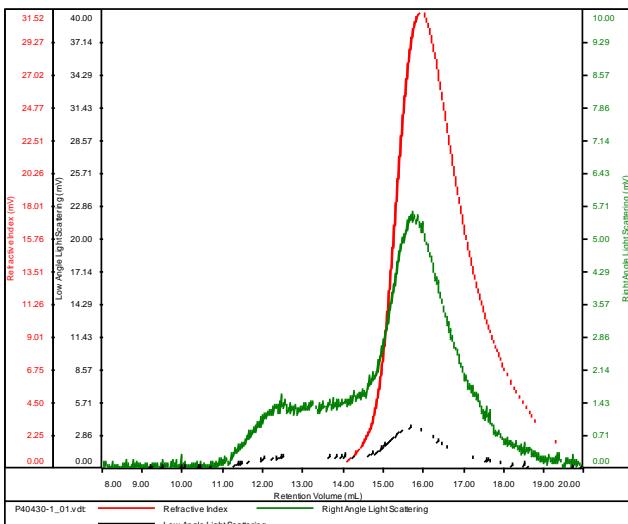
^1H NMR of MMAnBuMAran-b-HEMA [final] in DMF-d_7 :



SEC elugram of MMABuMAran [first block] in DMF:

P40430 MMABuMAran

Conc (mg/mL)	6.1844
dn/dc (mL/g)	0.0650
Method	PS80k_December-2016-0004.vcm
Solvent	DMF w 0.023M LiBr
Column	PSS

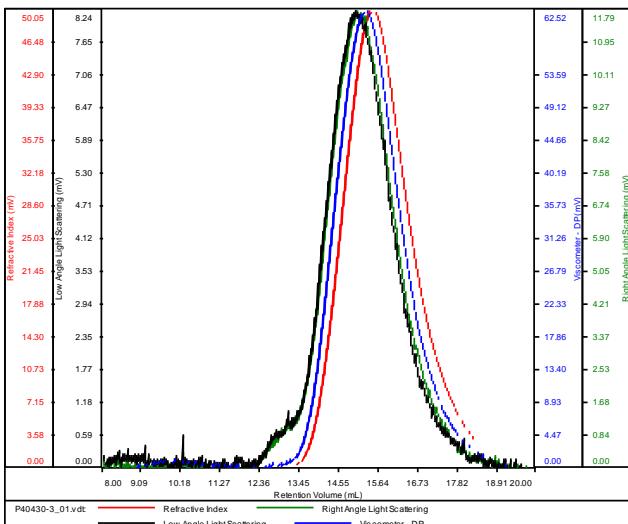


Sample	Mn	Mw	Mp	Mw/Mn	IV
P40430-1_01.vdt	47,240	58,001	56,364	1.228	0.1112

SEC elugram of MMABuMAran-HEMA in DMF:

**P40430
MMABuMAran-HEMA**

Conc (mg/mL)	10.3216
dn/dc (mL/g)	0.0650
Method	PS80k_December-2016-0004.vcm
Solvent	DMF w 0.023M LiBr



Sample	Mn	Mw	Mp	Mw/Mn	IV
P40430-3_01.vdt	69,611	86,393	79,039	1.241	0.1447

DSC thermogram of MMABuMA-b-HEMA diblock copolymer (2nd heating scan, 10°C/min):

