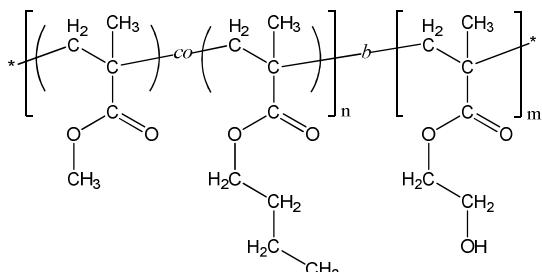


**Sample Name:**

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

**Sample #:** P40417-MMAnBuMArAn-b-HEMA

**Structure:**



**Composition:**

$M_n \times 10^3$ (g/mol)	21.0- <i>b</i> -26.0
$M_w/M_n$	1.16
Molar ratio MMA : nBuMA	51 : 49 (mol%)
Weight ratio MMA : nBuMA	42 : 58 (wt%)
Molar ratio MMA : nBuMA : HEMA	24 : 23 : 53 (mol%)
$T_{g1}$ (MMAnBuMA)	75 °C
$T_{g2}$ (HEMA)	114 °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:**

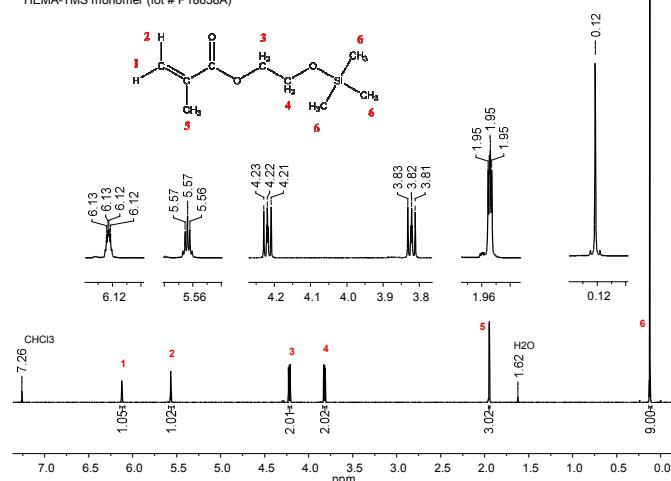
The polymer composition was determined by  $^1\text{H}$  NMR. MMA:nBuMA molar ratio was calculated by comparing the peak area of nBuMA  $-\text{OCH}_2-$  protons at 3.9 ppm and the peak area of MMA  $-\text{OCH}_3$  protons at 3.6 ppm. Molecular weight of the second (HEMA) block was calculated by comparing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

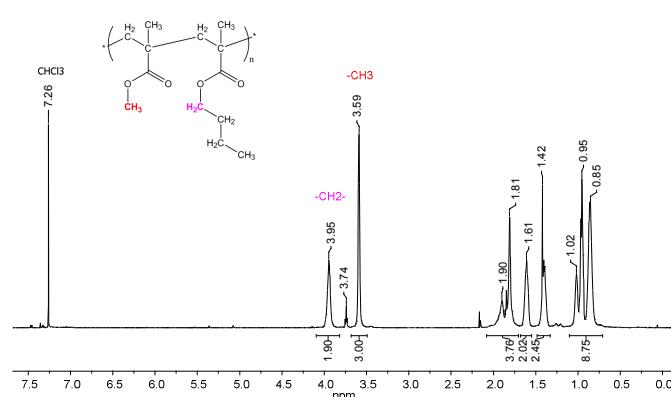
**$^1\text{H}$  NMR of HEMA-TMS monomer (500 MHz,  $\text{CDCl}_3$ ):**

HEMA-TMS monomer (lot # P18658A)



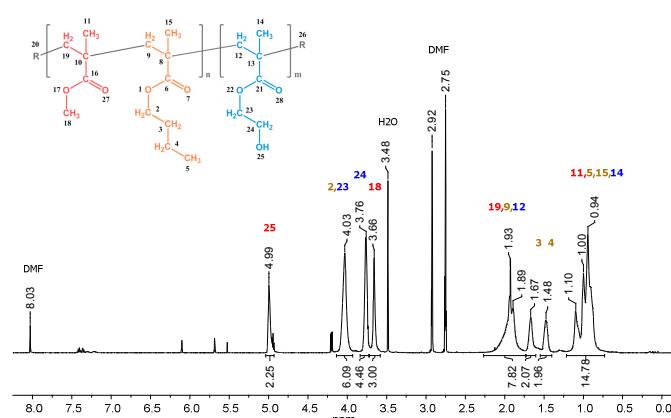
**$^1\text{H}$  NMR of MMAnBuMArAn [first block] in  $\text{CDCl}_3$ :**

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 40417-1\_MMAnBuMA



**$^1\text{H}$  NMR of MMAnBuMArAn-b-HEMA [final] in  $\text{DMF-d}_7$ :**

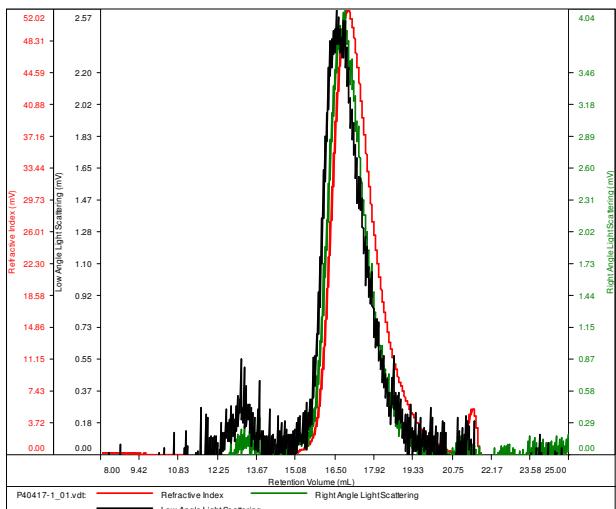
$^1\text{H}$  NMR (500 MHz,  $\text{DMF-d}_7$ ): 40417-3\_MMAnBuMA-b-HEMA



**SEC elugram of MMABuMAran [first block] in DMF:**

**P40417-MMABuMAran**

Conc (mL/mL)	8.5952
d <sub>n</sub> /d <sub>c</sub> (mL/g)	0.0650
Method	PS80k_December-2016-0004.vcm
Solvent	DMF w 0.023M LiBr
Column	PSS

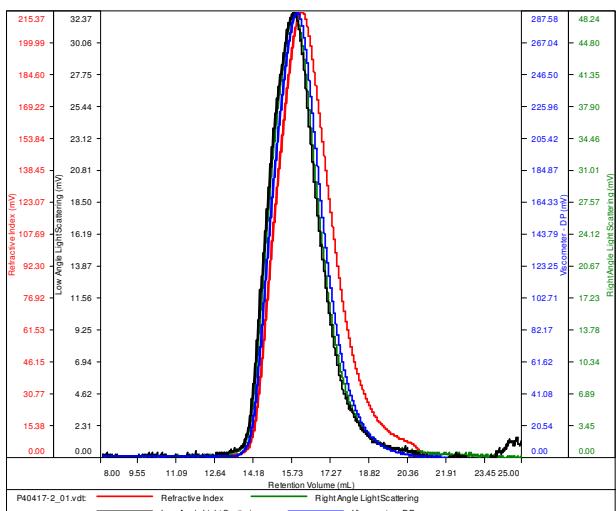


Sample	Mn	Mw	Mp	Mw/Mn	IV
P40417-1_01.vdt	20,953	23,249	24,656	1.110	0.0709

**SEC elugram of MMABuMA-b-HEMATMS [protected diblock copolymer] in DMF:**

**P40417-2  
MMABuMAran-HEMATM**

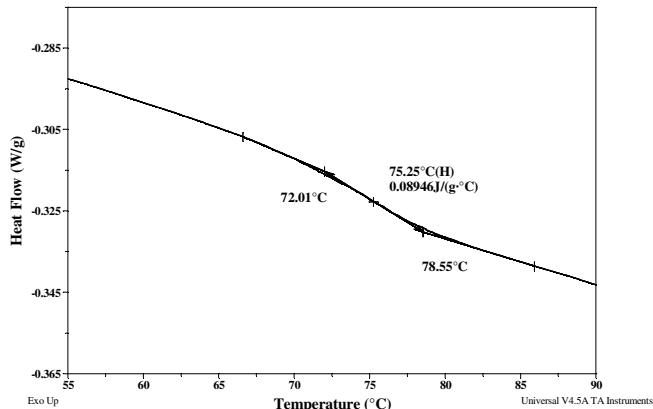
Conc (mL/mL)	53.1827
d <sub>n</sub> /d <sub>c</sub> (mL/g)	0.0650
Method	PS80k_December-2016-0004.vcm
Solvent	DMF w 0.023M LiBr
Column	PSS



Sample	Mn	Mw	Mp	Mw/Mn	IV
P40417-2_01.vdt	61,910	72,054	75,168	1.164	0.1401

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

Sample: P40417\_MMABuMAran-b-HEMA  
Size: 15.0000 mg DSC File: P40417\_MMABuMAran-b-HEMA.001



Sample: P40417\_MMABuMAran-b-HEMA  
Size: 15.0000 mg DSC File: P40417\_MMABuMAran-b-HEMA.001

