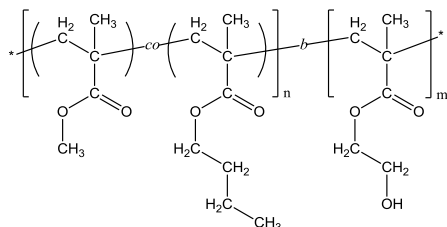


Sample Name:

**Poly(methyl methacrylate-*co*<sub>(random)</sub>-n-butyl methacrylate)  
-*block*-poly(2-hydroxyethyl methacrylate)**

Sample #: P40370-MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA

**Structure:**



**Composition:**

$M_n \times 10^3$ (g/mol)	48.5.0-b-40.0
$M_w/M_n$	1.38
MMA: nBuMA	51.0:49.0 (mol/mol)
MMA: nBuMA	42.0-58.0 (wt %)
$T_g$ (MMA <sub>n</sub> BuMA)	61 °C
$T_g$ (HEMA)	97 °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 and DMF.

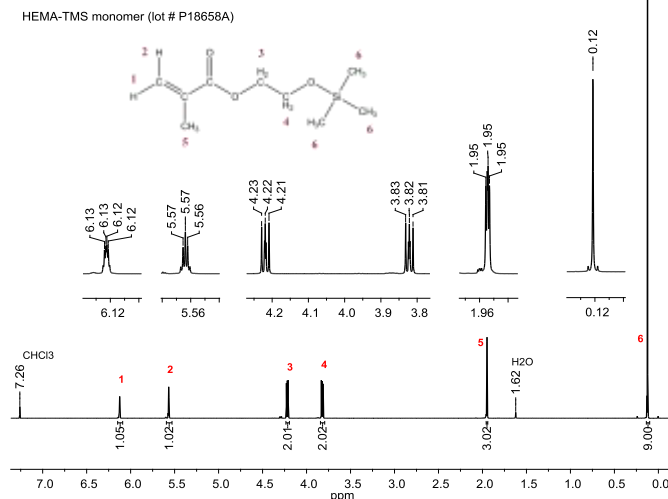
**Characterization:**

The polymer composition was determined by  $^1\text{H}$  NMR. MMA:nBuMA molar ratio was calculated by comparing the peak area of nBuMA -OCH<sub>2</sub>- protons at 3.9 ppm and the peak area of MMA -OCH<sub>3</sub> protons at 3.6 ppm. Molecular weight of the second (HEMA) block was calculated by comparing the peak area of HEMA -OCH<sub>2</sub>CH<sub>2</sub>O- protons and the peak area of nBuMA -OCH<sub>2</sub>- protons and using SEC data for the first (MMA<sub>n</sub>BuMA) block.

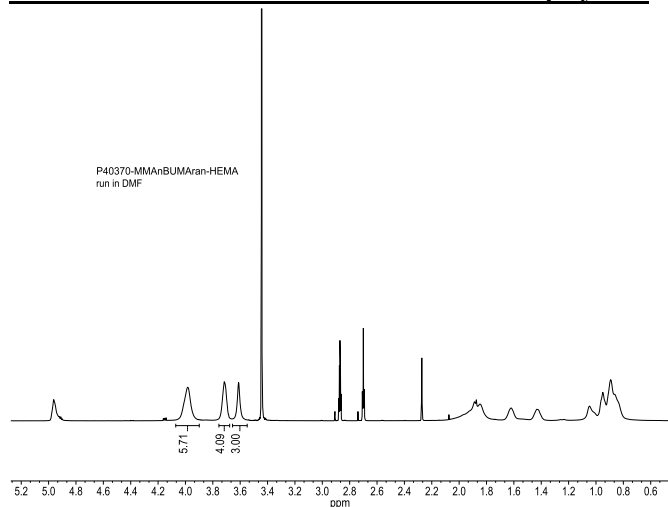
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA<sub>n</sub>BuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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.

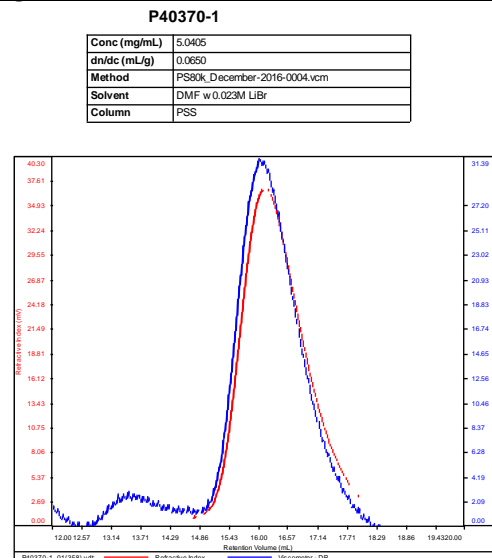
### $^1\text{H}$ NMR of HEMATMS monomer (500 MHz, CDCl<sub>3</sub>):



### $^1\text{H}$ NMR of MMA<sub>n</sub>BuMA-b-HEMA diblock copolymer:



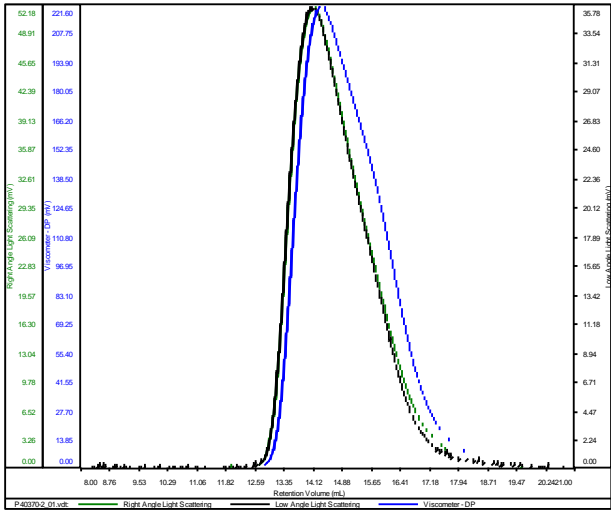
### SEC elugram of MMA<sub>n</sub>BuMA [first block] in DMF:



Sample	Mn	Mw	Mp	Mw/Mn	IV
P40370-1_01(358).vdt	48,509	57,953	44,637	1.193	0.0956

SEC elugram of [MMA-nBuMA]-b-[HEMA] in DMF:  
P40370-MMAAnBUMAran-HEMA

Conc	18.0515
dn/dc	0.0650
Solvent	DMF w 0.023M LiBr
Flow Rate	0.7000
Method	PS80K_2017-July-05-0000.vcm



Sample	Mn	Mw	Mp	Mw/Mn	IV
P40370-2_01.vdt	87,821	120,796	82,278	1.375	0.3158

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

