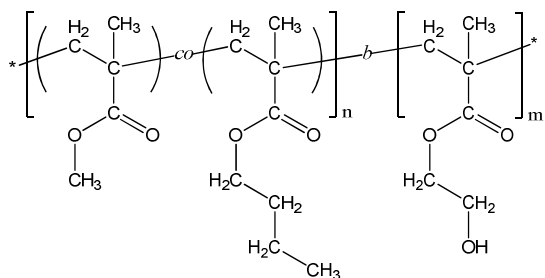


Sample Name:

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

Sample #: **P40446-MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA**

Structure:



Composition:

$M_n \times 10^3$ (g/mol)	24.0–29.0
$M_w/M_n$	1.3
Molar ratio MMA : nBuMA	51 : 49 (mol%)
Weight ratio MMA : nBuMA	42 : 58 (wt%)
Molar ratio MMA : nBuMA : HEMA	24 : 23 : 53 (mol%)
$T_{g1}$ (MMA <sub>n</sub> BuMA)	68 °C
$T_{g2}$ (HEMA)	110 °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 (hydroxy-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.

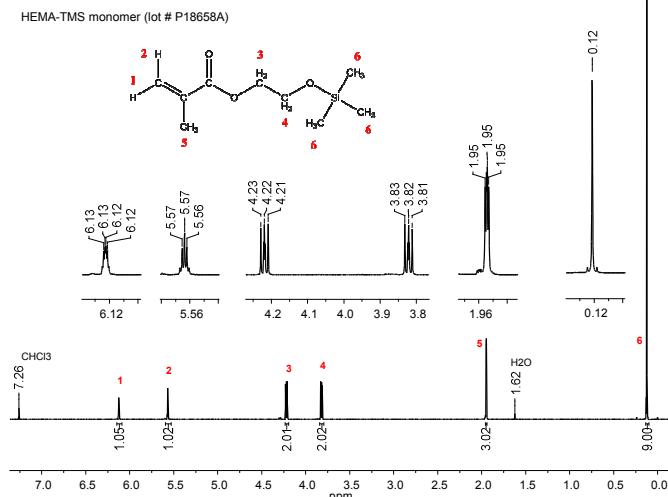
#### Characterization:

The polymer composition was determined by  $^1\text{H}$  NMR. MMA:nBuMA molar ratio was calculated by comparing the peak area of nBuMA -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.

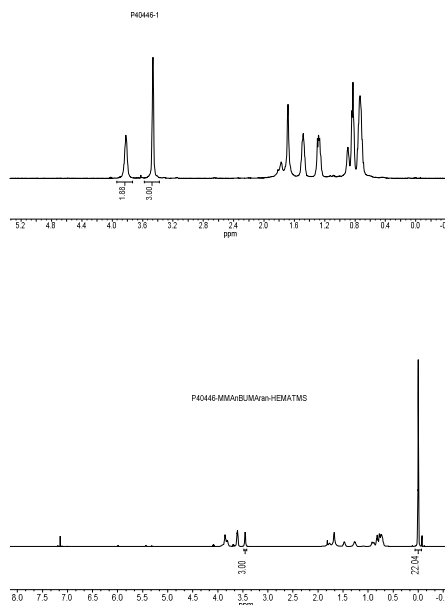
The average molecular weight and polydispersity index of the polymer were determined by size exclusion chromatography (SEC) using DMF (0.023 M LiBr in DMF) as an eluent.

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.

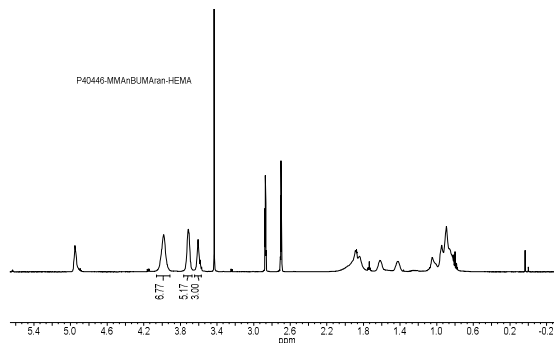
#### $^1\text{H}$ NMR of HEMA-TMS monomer (500 MHz, CDCl<sub>3</sub>):



#### $^1\text{H}$ NMR of MMA<sub>n</sub>BuMA<sub>r</sub>an [first block] in CDCl<sub>3</sub>:



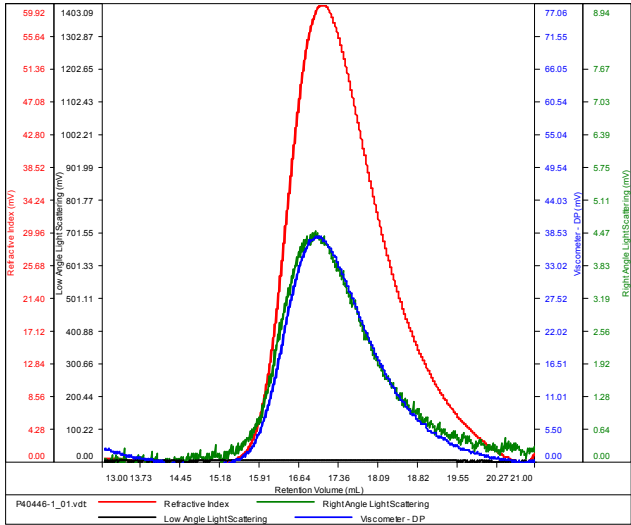
#### $^1\text{H}$ NMR of MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA [final] in DMF-d<sub>7</sub>:



SEC elugram of MManBuMAran [first block] in DMF:

P40446-MManBuMAran

Conc (mg/mL)	11.0962
dn/dc (mL/g)	0.0650
Method	PS80k_December-2016-0004.vcm
Solvent	DMF w 0.023M LiBr
Column	PSS

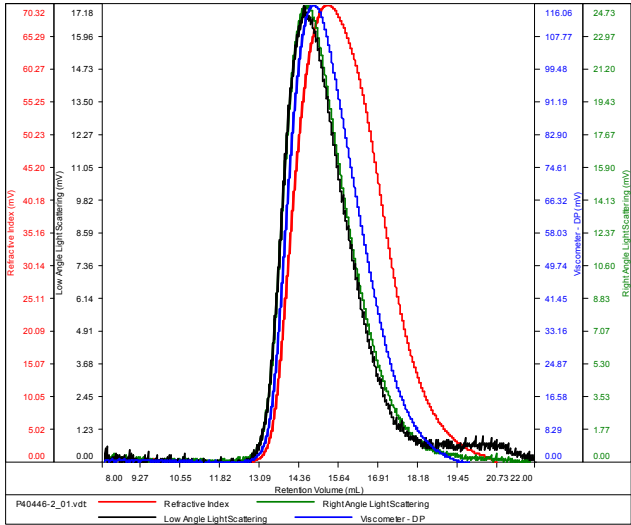


Sample	Mn	Mw	Mp	Mw/Mn	IV
P40446-1_01.vdt	24,185	25,228	24,466	1.043	0.0706

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

P40446-2

Conc (mg/mL)	20.6507
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
P40446-2_01.vdt	69,750	96,942	104,366	1.390	0.1607

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

