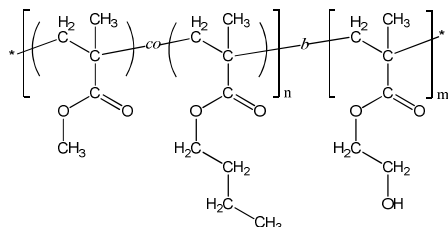


Sample Name:

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

Sample #: P40369-MMA_nBuMA_ran-b-HEMA

Structure:



Composition:

$M_n \times 10^3$ (g/mol)	35.0-b-24.0
M_w/M_n	1.13
MMA: nBuMA	51.0:49.0 (mol/mol)
MMA: nBuMA	42.0-58.0 (wt %)
T_g (MMA _n 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.

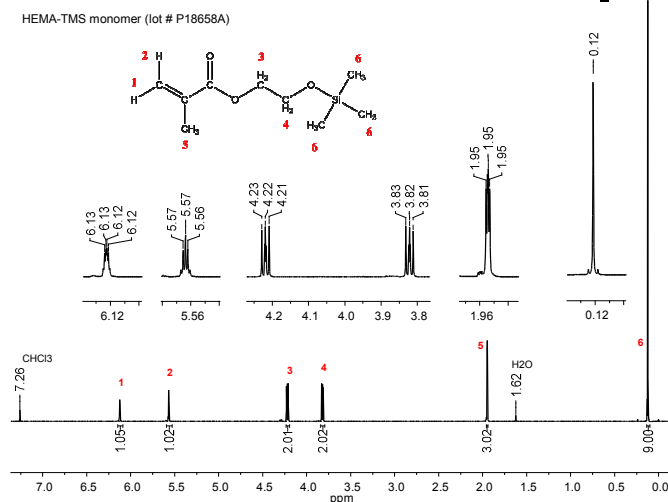
Characterization:

The polymer composition was determined by ^1H NMR. MMA:nBuMA molar ratio was calculated by comparing the peak area of nBuMA -OCH₂- protons at 3.9 ppm and the peak area of MMA -OCH₃ protons at 3.6 ppm. Molecular weight of the second (HEMA) block was calculated by comparing the peak area of HEMA -OCH₂CH₂O- protons and the peak area of nBuMA -OCH₂- protons and using SEC data for the first (MMA_nBuMA) block.

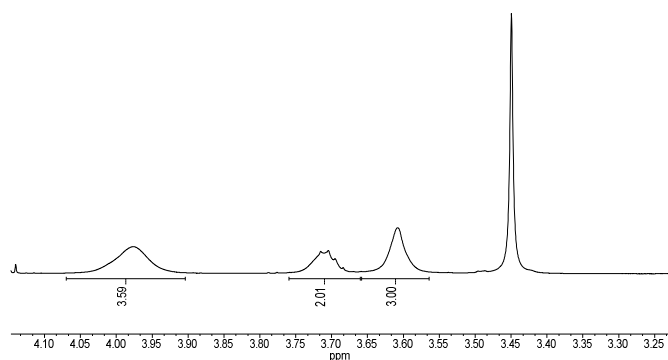
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA_nBuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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 HEMATMS monomer (500 MHz, CDCl₃):



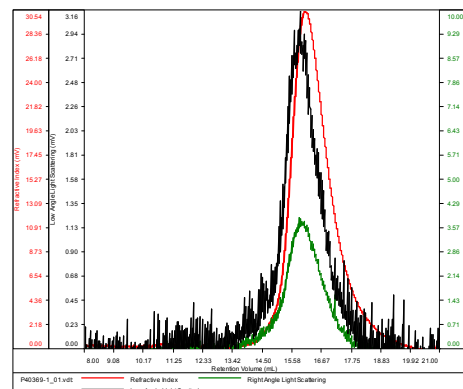
^1H NMR of MMA_nBuMA-b-HEMA diblock copolymer:



SEC elugram of MMA_nBuMA [first block] in DMF:

P40369-MMA_nBuMA_ran

Conc (mg/mL)	4.7873
dn/dc (mL/g)	0.0650
Method	PSS04_December-2016-0004.vcm
Solvent	DMF w 0.023M LiBr
Column	PSS

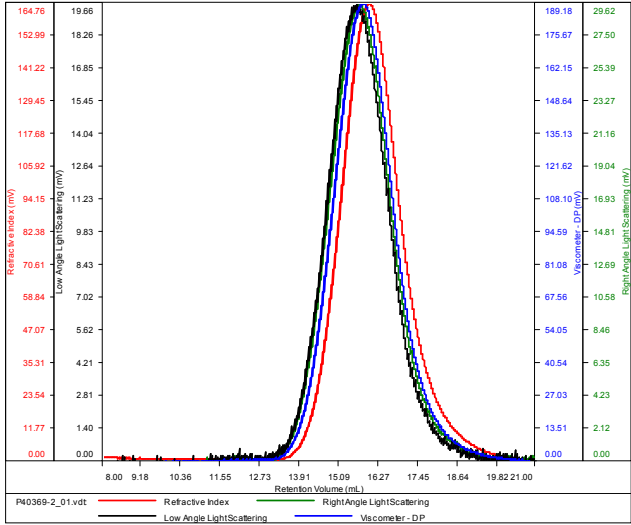


Sample	Mn	Mw	Mp	Mw/Mn	IV
P40369-1_01.vcl	35,211	43,078	40,661	1.223	0.0864

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

P40369-MMA_nBuMA_ran-HEMA

Conc (mg/mL)	33.2877
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
P40369-2_01.vdt	57,786	65,203	58,242	1.128	0.1360

DSC thermogram of MMA_nBuMA_ran-b-HEMA

(2nd heating scan, 10°C/min):

