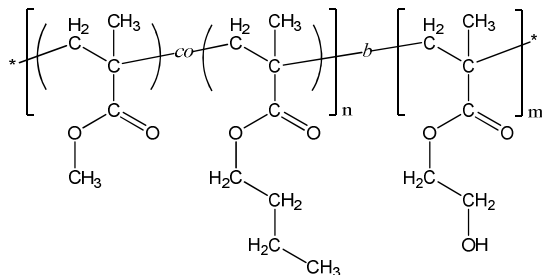


Isotactic Rich **Poly(methyl methacrylate-*co*_(random)-n-butyl methacrylate)-*block*-poly(2-hydroxyethyl methacrylate)**

Sample #: **P40498-MMA_nBuMA_ran-b-HEMA-iso**

Structure:



Composition:

$M_n \times 10^3$ (g/mol)	31.0– <i>b</i> –11.0
M_w/M_n	1.2
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}	3 °C
T_{g2}	24 °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:

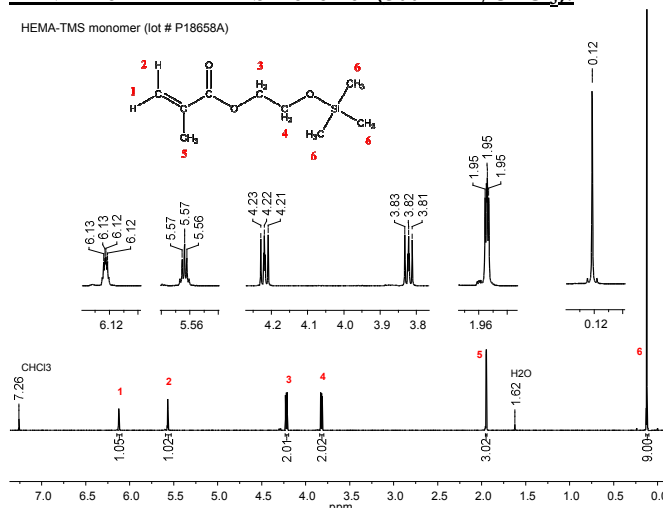
The polymer composition was determined by ^1H NMR. MMA:nBuMA molar ratio was calculated by comparing the peak area of nBuMA $-OCH_2-$ protons at 3.9 ppm and the peak area of MMA $-OCH_3$ protons at 3.6 ppm. Molecular weight of the second (HEMA) block was calculated by comparing the peak area of HEMA $-OCH_2CH_2O-$ protons and the peak area of nBuMA $-OCH_2-$ protons and using SEC data for the first (MMA:nBuMA) 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.

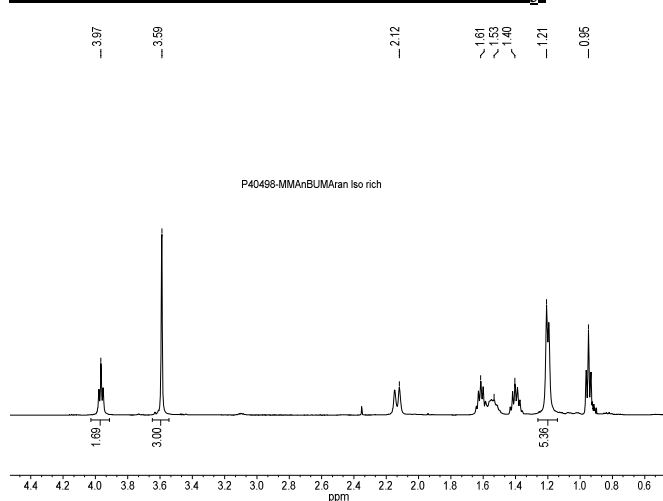
Thermal analysis was performed on TA Instruments Q100 differential scanning calorimeter (DSC) under a nitrogen atmosphere. The glass transition temperature (T_g) of the polymer was measured at a scan rate of 10°C/min shortly after creating thermal history of the sample.

¹H NMR of HEMA-TMS monomer (500 MHz, CDCl₃):

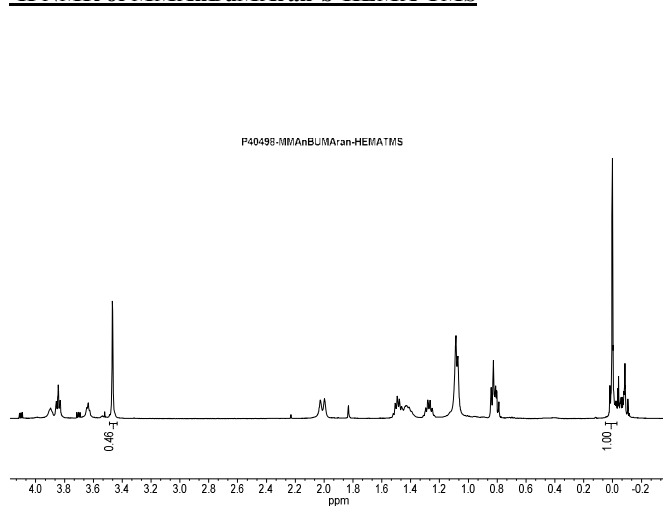
HEMA-TMS monomer (lot # P18658A)



¹H NMR of MManBuMAran [first block] in CDCl₃:



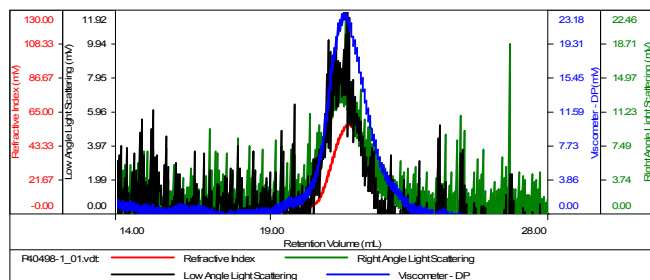
¹H NMR of MMA_nBuMA_ran-b-HEMA-TMS



SEC elugram of MManBuMAran [first block] in THF:

P40498-MManBuMAran

Concentration (mg/mL)	1.9724
Sample dn/dc (mL/g)	0.0840
Method File	PS80K-Feb2017-0000.vcm
Column Set	3x PL 1113-6300
Solvent	THF

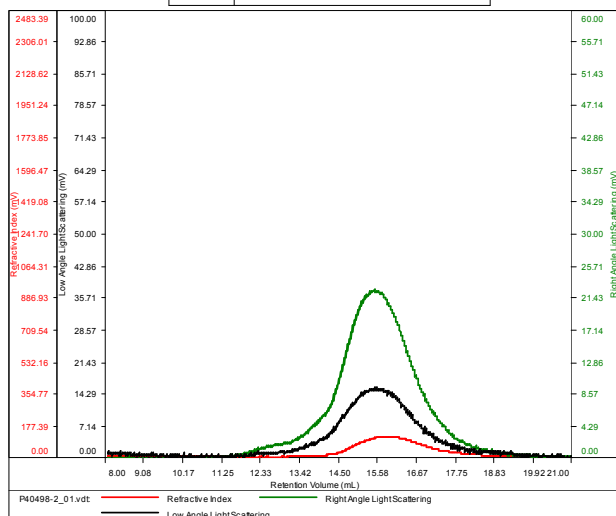


Sample	Mn (Da)	Mw (Da)	Mw/Mn	IV (dL/g)	Mp (Da)
P40498-1_01.vdt	30,817	37,507	1.217	0.4654	33,214

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

P40498-MManBuMAran-HEMA

ID	P40498-2
Conc	24.6828
Recovery	2468.2847
dn/dc	0.0650
Method	PS80K-March2017-0002.vcm



Sample	Mn	Mw	Mp	Mw/Mn	IV
P40498-2_01.vdt	50,643	60,918	54,540	1.203	0.1635

Dependence of T_g on molecular weight for the first block:

isotactic MManBuMAran	
M _n × 10 ³ (g/mol)	Glass transition temperature (T _g)
70.0	-4 °C
105.5	11 °C
109.0	14 °C

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

Sample: P40498_iso-MManBuMAran-b-HEMA
Size: 17.0000 mg

