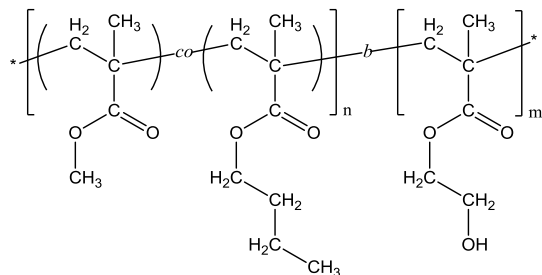


Isotactic Rich **Poly(methyl methacrylate-*co*_(random)-n-butyl methacrylate)-*block*-poly(2-hydroxyethyl methacrylate)**

Sample #: **P40504-MMAnBuMAran-b-HEMA-iso**

Structure:

**Composition:**

$M_n \times 10^3$ (g/mol)	19.0–4.5
M_w/M_n	1.27
Molar ratio MMA : nBuMA	55 : 45 (mol%)
Weight ratio MMA : nBuMA	48 : 52 (wt%)
T_{g1}	11 °C
T_{g2}	44 °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:

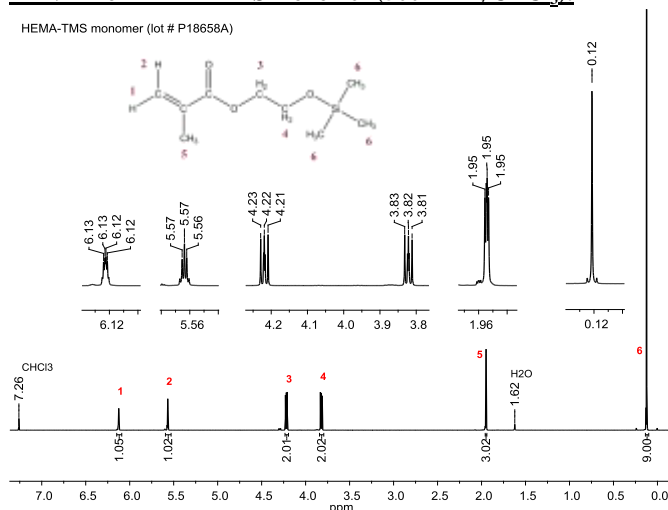
The polymer composition was determined by ^1H NMR. MMA:nBuMA molar ratio was calculated by comparing the peak area of nBuMA $-\text{OCH}_2-$ protons at 3.9 ppm and the peak area of MMA $-\text{OCH}_3$ protons at 3.6 ppm. Molecular weight of the second (HEMA) block was calculated by comparing the peak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

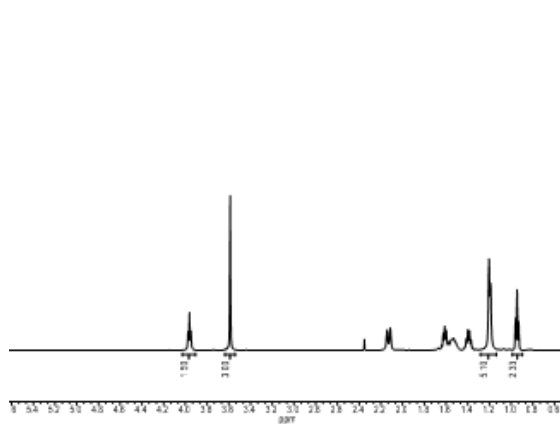
Thermal analysis was performed on TA Instruments Q100 differential scanning calorimeter (DSC) under a nitrogen atmosphere. The glass transition temperature (T_g) of the polymer was measured at a scan rate of 10°C/min shortly after creating thermal history of the sample.

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

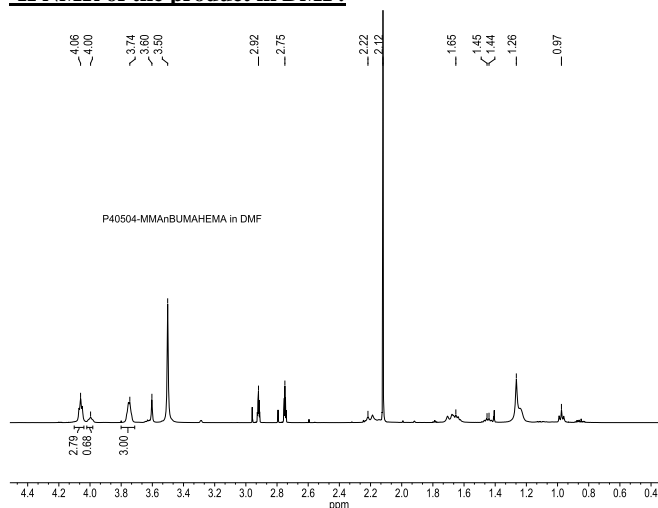
HEMA-TMS monomer (lot # P18658A)



¹H NMR of MMAnRuMA cop [first block] in CDCl₃.



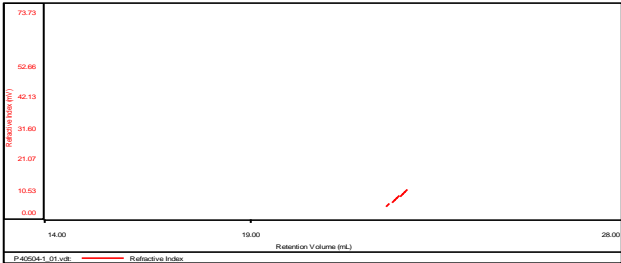
¹H NMR of the product in DMF:



SEC elugram of MManBuMAran [first block] in DMF:

P40504-1

Concentration (mg/mL)	0.6588
Sample dn/dc (mL/g)	0.0840
Method File	PS80K-Feb2017-0000.vcm
Column Set	3x PL 1113-6300
Solvent	THF

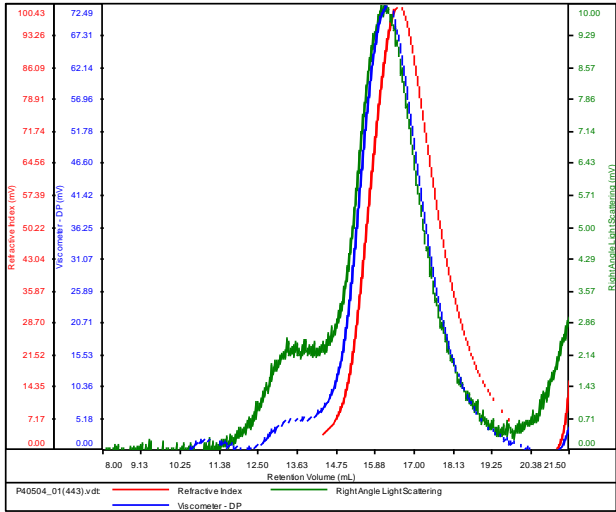


Sample	Mn (Da)	Mw (Da)	Mw/Mn	IV (dL/g)	Mp (Da)
P40504-1_01.vdt	18,889	23,253	1.231	1.0000	17,885

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

P40504-2

Conc	22.4332
dn/dc	0.0650
Solvent	DMF w 0.023M LiBr
Flow Rate	0.7000
Method	PS80K-March2017-0002.vcm



Sample	Mn	Mw	Mp	Mw/Mn	IV
P40504_01(443).vdt	23,736	30,232	26,350	1.274	0.0801

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

Sample: P40504_MManBuMAran-b-HEMA
Size: 19.6000 mg

File: P40504_MManBuMAran-b-HEMA_isotactic.00:

