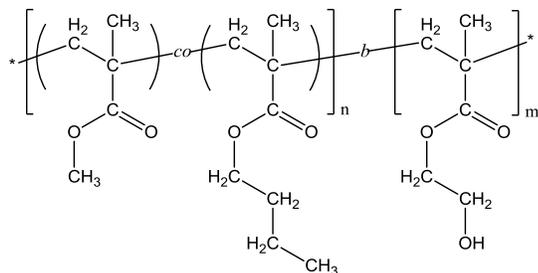


Sample Name:

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

Sample #: P40511-MMA_nBuMA_ran-b-HEMA

Structure:**Composition:**

$M_n \times 10^3$ (g/mol)	23.5–26.5
M_w/M_n	1.4
Molar ratio MMA : nBuMA	53 : 47 (mol%)
Weight ratio MMA : nBuMA	45 : 55 (wt%)
Molar ratio MMA : nBuMA : HEMA	
Iso-contents :	
>96%	
T_{g1}	10 °C
T_{g2}	48 °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:

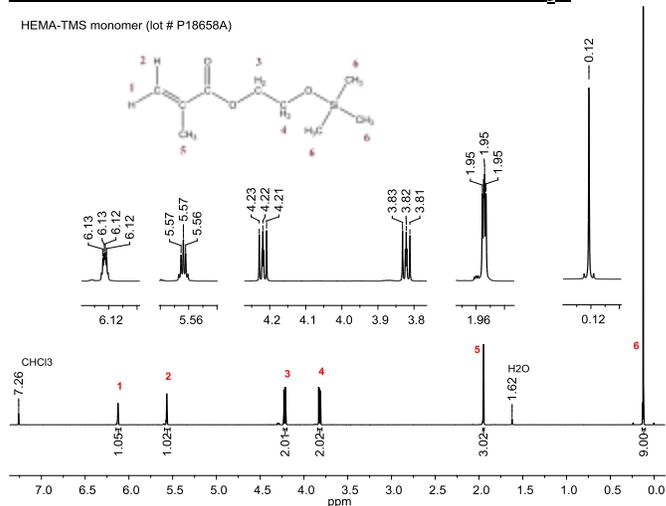
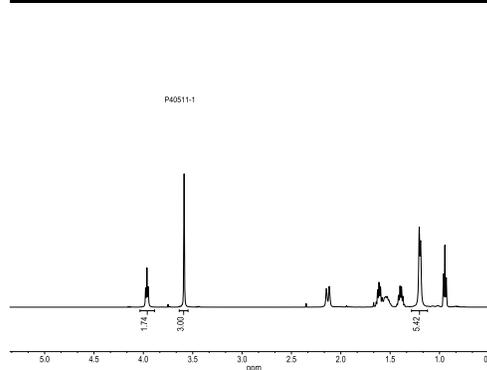
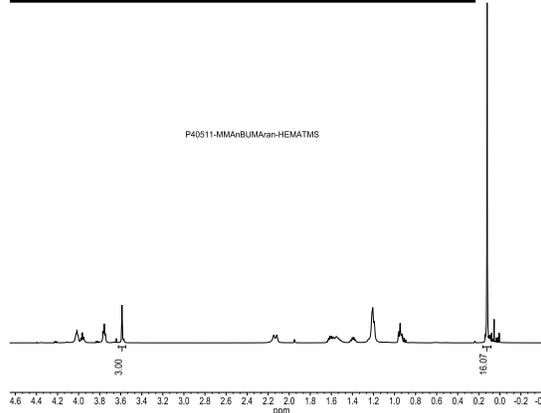
The polymer is soluble in THF and DMF.

Characterization:

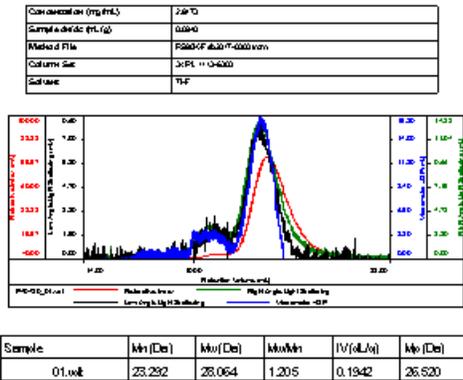
The polymer composition was determined by ^1H NMR. MMA:nBuMA molar ratio was calculated by comparing the peak area of nBuMA - OCH_2 - protons at 3.9 ppm and the peak area of MMA - OCH_3 protons at 3.6 ppm. Molecular weight of the second (HEMA) block was calculated by comparing the peak area of HEMA - $\text{OCH}_2\text{CH}_2\text{O}$ - 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.

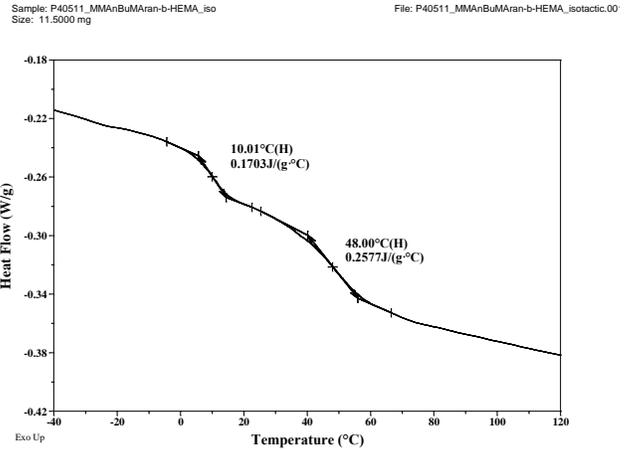
Thermal analysis was performed on TA Instruments Q100 differential scanning calorimeter (DSC) under a nitrogen atmosphere. The glass transition temperature (T_g) of the polymer was measured at a scan rate of 10°C/min shortly after creating thermal history of the sample.

 ^1H NMR of HEMA-TMS monomer (500 MHz, CDCl_3): **^1H NMR of MMA_nBuMA_ran [first block] in CDCl_3 :** **^1H NMR of MMA_nBuMA_ran-b-HEMA-TMS**

SEC elugram of MManBuMAran [first block] in DMF:



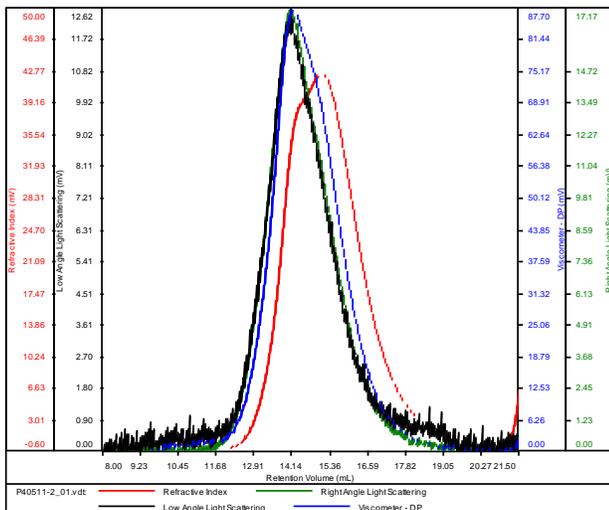
DSC thermogram of MManBuMA-b-HEMA diblock copolymer (2nd heating scan, 10°C/min):



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

P40511-MManBUMAran-HEMATMS
Isotactic rich

Conc	10.9799
dn/dc	0.0680
Solvent	DMF w 0.023M LiBr
Flow Rate	0.7000
Method	PS80k-March2017-0002.vcm



Dependance 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