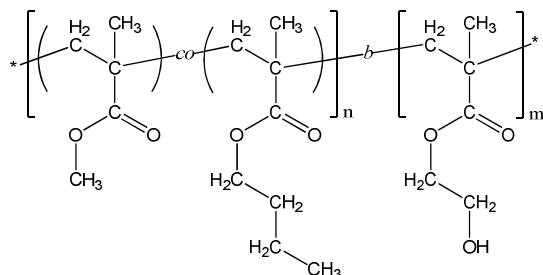


Sample Name:

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

Sample #: P40507-MMA_nBuMA_ran-b-HEMA-iso

Structure:



Composition:

$M_n \times 10^3$ (g/mol)	23.5–b–18.5
M_w/M_n	1.3
Molar ratio MMA : nBuMA	55 : 45 (mol%)
Weight ratio MMA : nBuMA	48 : 52 (wt%)
T_{g1}	17 °C
T_{g2}	38 °C
T_{g3}	88 °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.

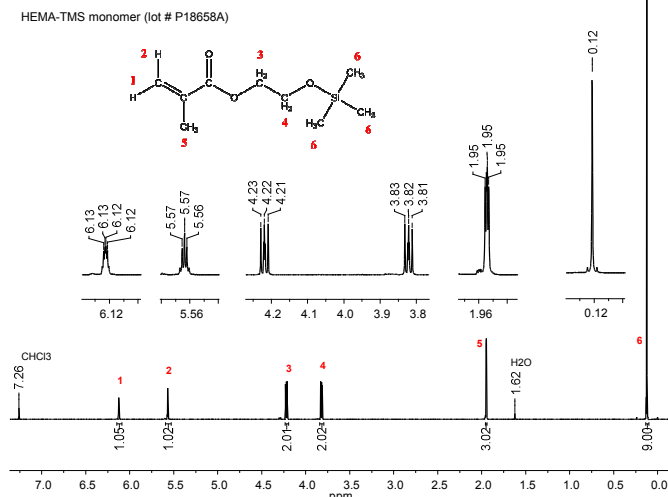
Solubility:

The polymer is soluble in THF and DMF.

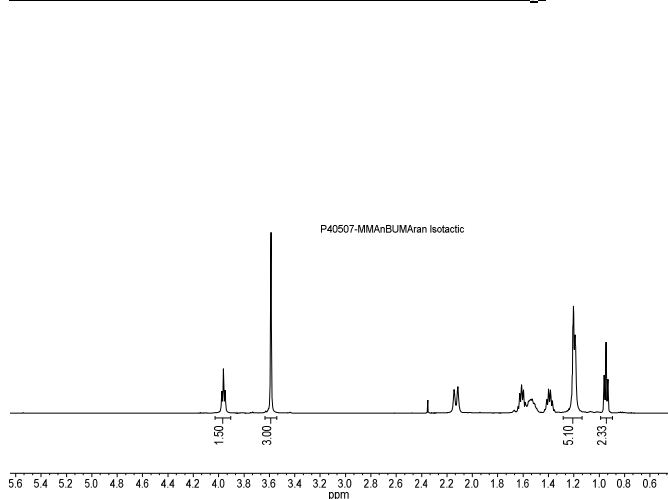
Characterization:

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

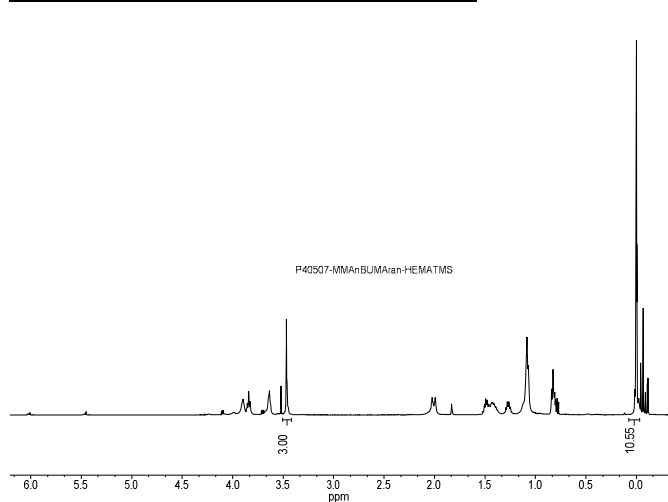
^1H NMR of HEMA-TMS monomer (500 MHz, CDCl₃):



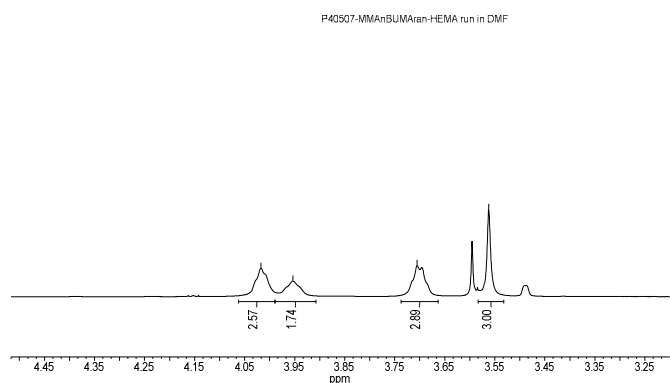
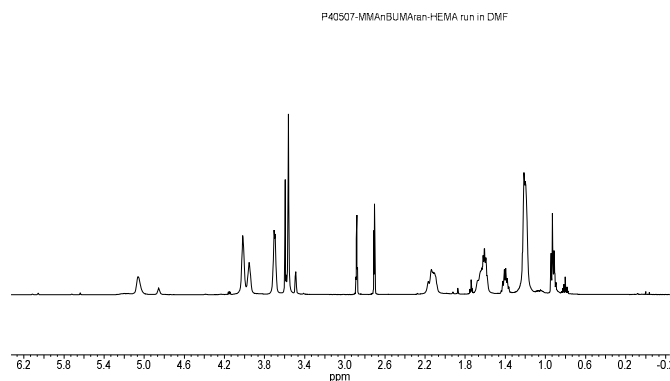
^1H NMR of MMA_nBuMA_ran [first block] in CDCl₃:



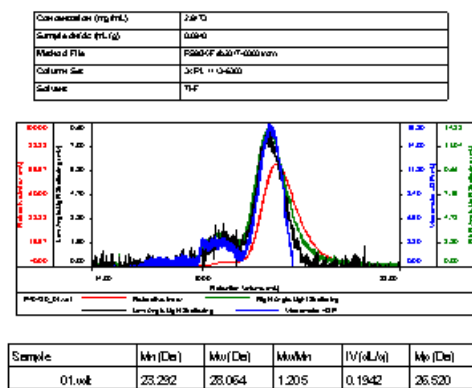
^1H NMR of MMA_nBuMA_ran-b-HEMA-TMS



¹H NMR of the product in DMF:



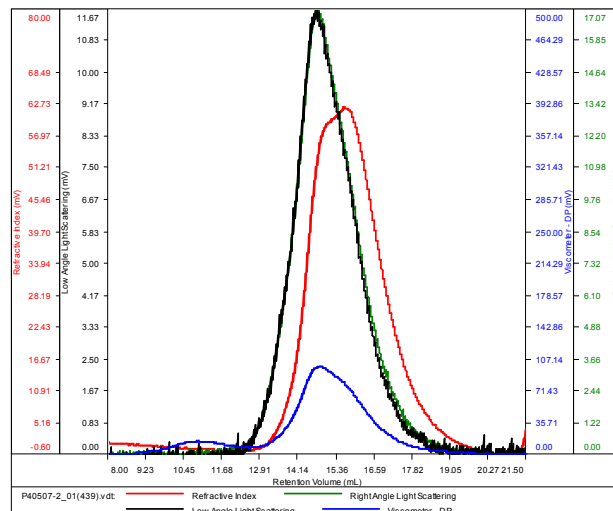
SEC elugram of MMAAnBuMAran [first block] in DMF:



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

P40507-MMAAnBuMAran-HEMATMS

Conc	16.0199
dn/dc	0.0650
Solvent	DMF w 0.023M LiBr
Flow Rate	0.7000
Method	PS80k-March2017-0002.vcm



Dependence of T_g on molecular weight for the first block:

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

Sample: P40507_MMAAnBuMAran-b-HEMA_iso
Size: 13.2000 mg

