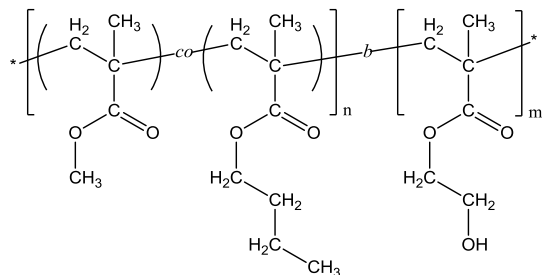


Sample Name:

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

Sample #: P40512-MMA_nBuMA_ran-b-HEMA

Structure:**Composition:**

$M_n \times 10^3$ (g/mol)	9.5–17.0
M_w/M_n	1.4
Molar ratio MMA : nBuMA	53 : 47 (mol%)
Weight ratio MMA : nBuMA	45 : 55 (wt%)
Iso-contents :	>96%
T_{g1}	10 °C
T_{g2}	40 °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:

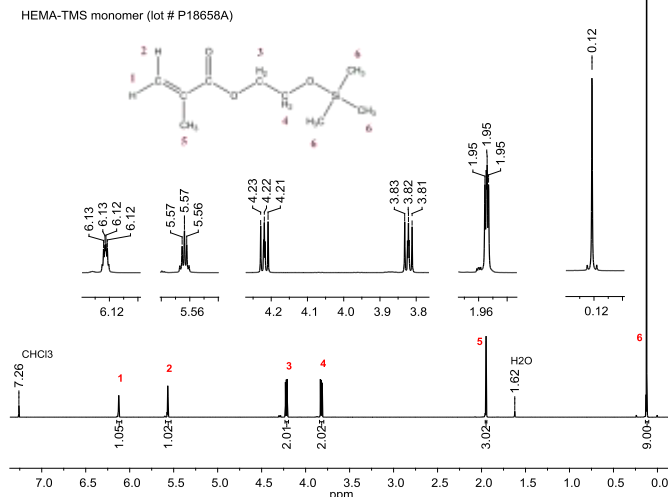
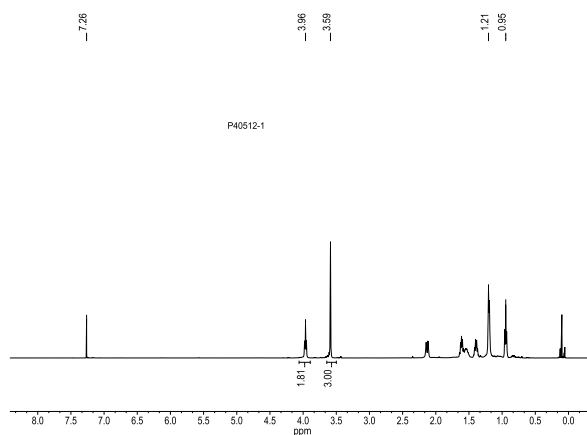
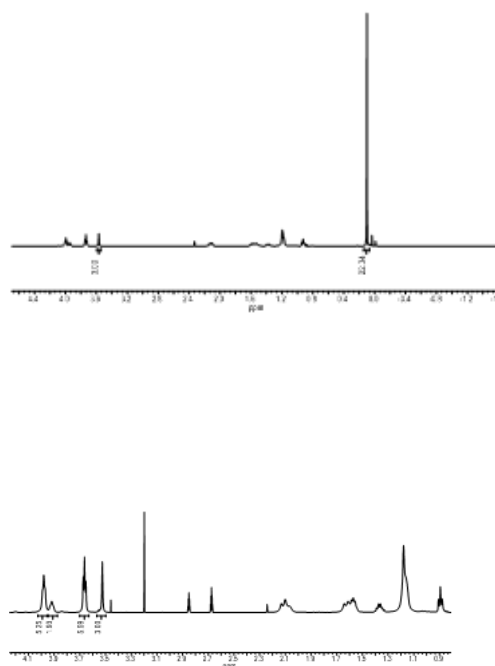
The polymer is soluble in THF and DMF.

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.

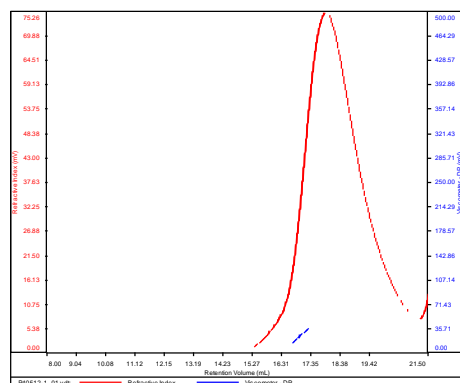
Thermal analysis was performed on TA Instruments Q100 differential scanning calorimeter (DSC) under a nitrogen atmosphere. The glass transition temperature (T_g) of the polymer was measured at a scan rate of 10°C/min shortly after creating thermal history of the sample.

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

P40512-MManBUMAran

Conc	17.0824
dn/dc	0.0650
Solvent	DMF w 0.023M LiBr
Flow Rate	0.7000
Method	PS80k-March2017-0002.vcm

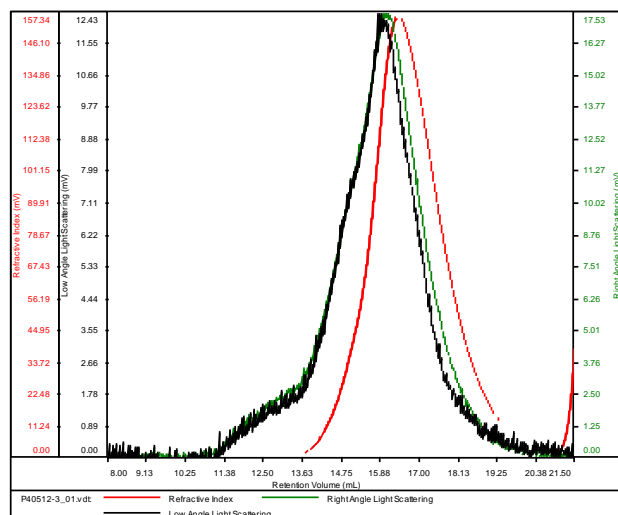


Sample	Mn	Mw	Mp	Mw/Mn	IV
P40512-1_01.vdt	9,150	11,724	11,216	1.281	0.0583

SEC elugram of MManBuMA-b-HEMA in DMF:

P40512-MManBUMAran-HEMA

Conc	36.3797
dn/dc	0.0640
Solvent	DMF w 0.023M LiBr
Flow Rate	0.7000
Method	PS80k-March2017-0002.vcm

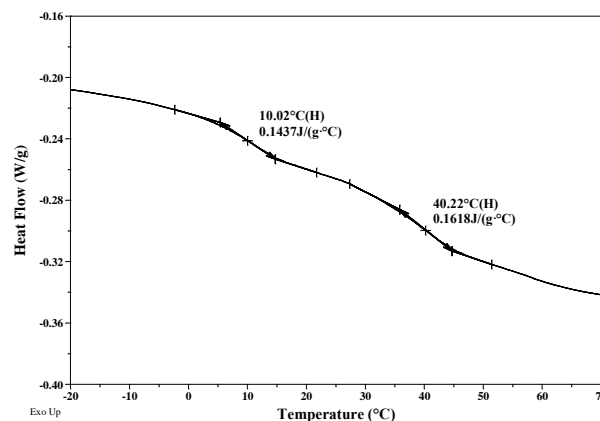


Sample	Mn	Mw	Mp	Mw/Mn	IV
P40512-3_01.vdt	26,616	37,730	30,770	1.418	0.0916

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

Sample: P401512_MManBuMAran-HEMA_isotac
Size: 13.9000 mg

File: P40512_MManBuMAran-b-HEMA_isotactic.00



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