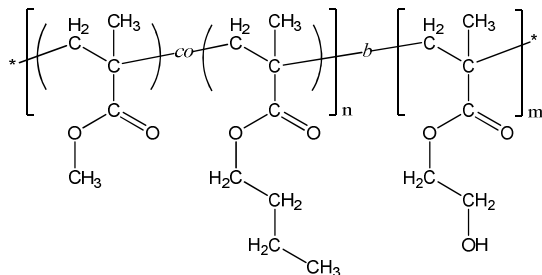


Sample Name:

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

Sample #: P40362-MMA_nBuMA_ran-b-HEMA-iso

Structure:



Composition:

$M_n \times 10^3$ (g/mol)	27.0–b–14.0
M_w/M_n	1.26
Molar ratio MMA : nBuMA	51 : 49 (mol%)
Weight ratio MMA : nBuMA	42 : 58 (wt%)
Molar ratio MMA : nBuMA : HEMA	24 : 23 : 53 (mol%)
T_{g2}	59.0 °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.

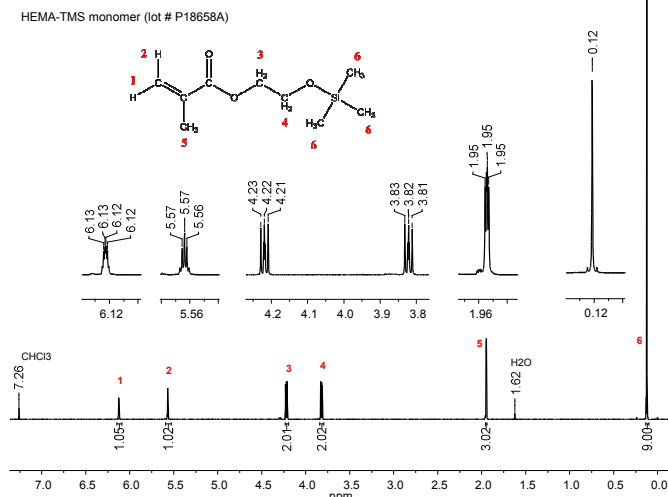
Characterization:

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.

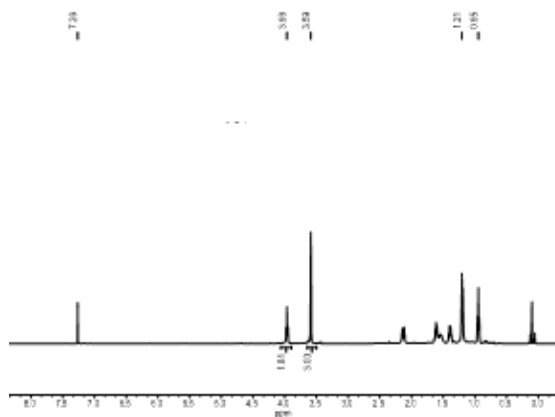
The average molecular weight and polydispersity index of the polymer were determined by size exclusion chromatography (SEC) using DMF (0.023 M LiBr in DMF) as an eluent.

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.

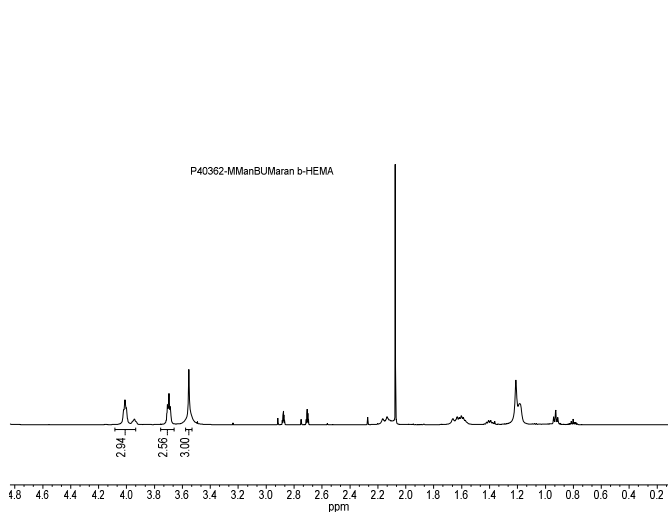
^1H NMR of HEMA-TMS monomer (500 MHz, CDCl₃):



^1H NMR of MMA_nBuMA_ran (first block) in CDCl₃:



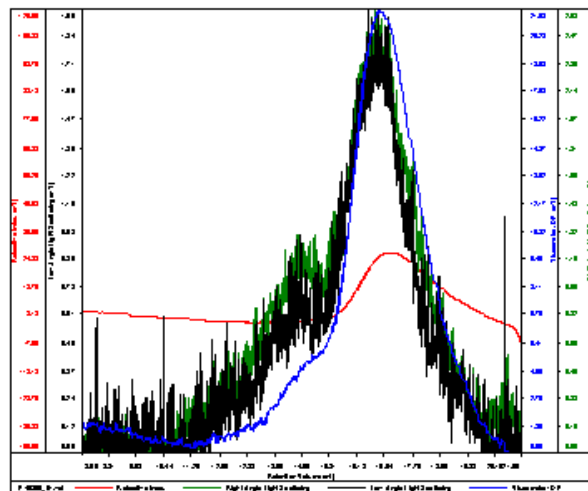
^1H NMR of MMA_nBuMA_ran-b-HEMA



SEC elugram of MManBuMAran [first block] in THF:

P4036 -MManBUMAran

Conc (mg/mL)	6.2331
dn/dc (mL/g)	0.0650
Method	PS80k_December-2016-0004.vcm
Solvent	DMF w 0.023M LiBr
Column	PSS



Sample	Mn	Mw	Mp	Mw/Mn	IV
P4036_01.vdt	26,812	34,602	26,068	1.291	0.0962

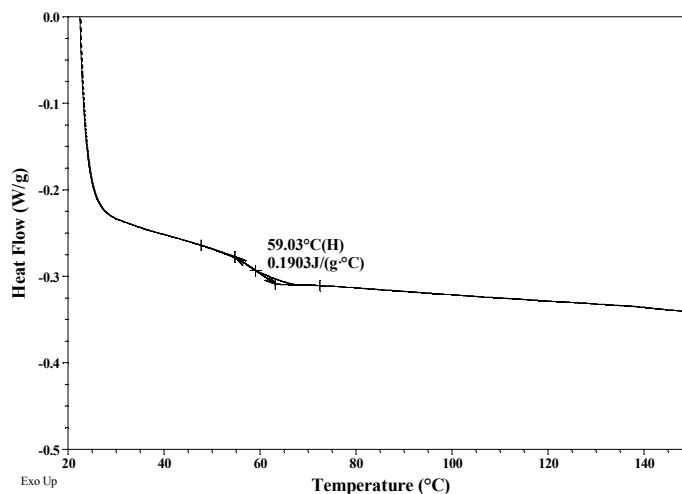
Dependence of T_g on molecular weight for the first block:

isotactic MManBuMAran	
$M_n \times 10^3$ (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: P40362
Size: 9.0000 mg

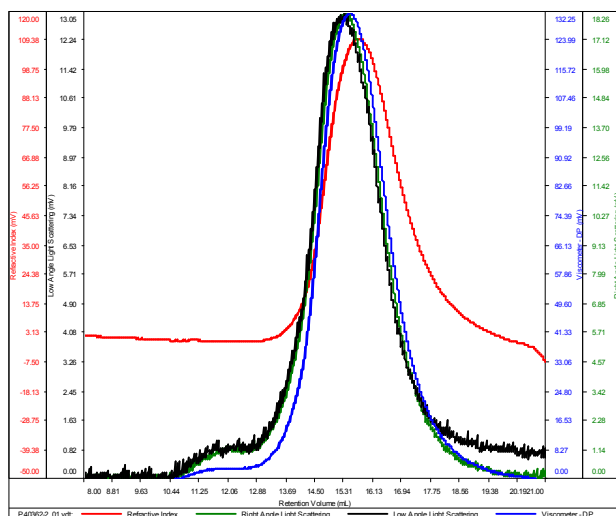
File: P40362.001



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

P40362-MManBUMAran-HEMAiso

Conc (mg/mL)	25.1190
dn/dc (mL/g)	0.0650
Method	PS80k_December-2016-0004.vcm
Solvent	DMF w 0.023M LiBr
Column	PSS



Sample	Mn	Mw	Mp	Mw/Mn	IV
P40362-2_01.vdt	49,017	61,303	57,942	1.251	0.1357