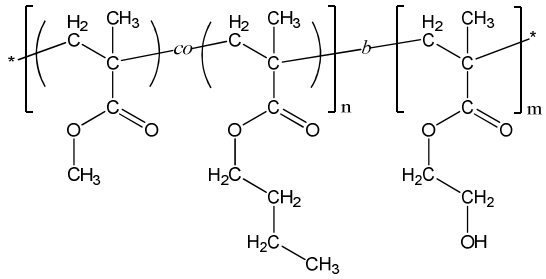
Sample Name:

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

Sample #: **P40471-MMAnBuMAran-b-HEMA-iso**

Structure:



Composition:

$M_n \times 10^3$ (g/mol)	27.0–*b*–11.5
M_w/M_n	1.4

Molar ratio MMA : nBuMA	51 : 49 (mol%)
Weight ratio MMA : nBuMA	42 : 58 (wt%)
Molar ratio MMA : nBuMA : HEMA	24 : 23 : 53 (mol%)

T_g	17°C

Synthesis Procedure:

Poly([methyl methacrylate–*co*–n-butyl methacrylate]–*b*–2-hydroxy ethyl 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.

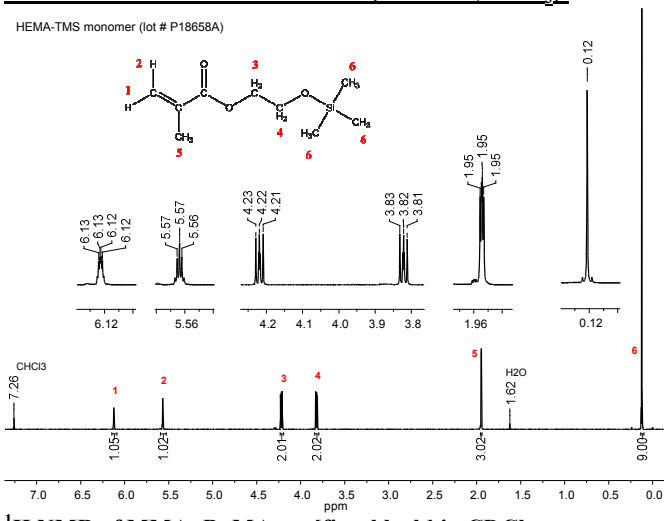
Characterization:

The polymer composition was determined by ^{1}H 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 -*OCH$_2$CH$_2$O*- protons and the peak area of nBuMA -*OCH$_2$*- protons and using SEC data for the first (MMAnBuMA) block.

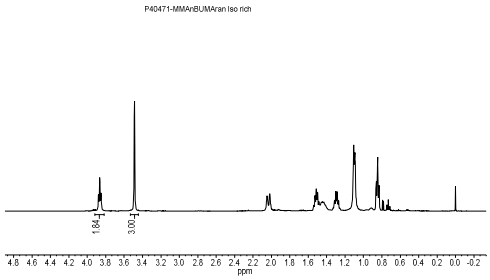
The average molecular weight and polydispersity index of the polymer were determined by size exclusion chromatography (SEC) using DMF (0.023 M LiBr in DMF) as an eluent.

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.

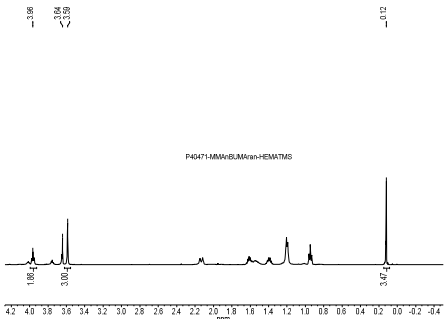
^{1}H NMR of HEMA-TMS monomer (500 MHz, $CDCl_3$):



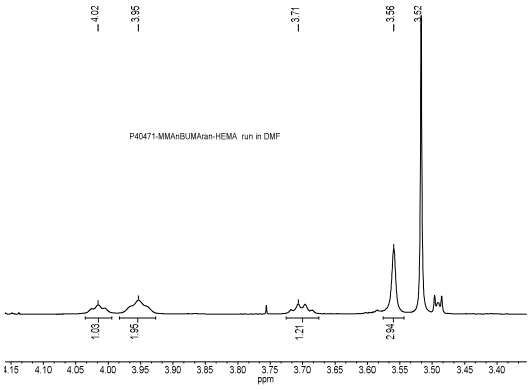
^{1}H NMR of MMAnBuMAran [first block] in $CDCl_3$:



^{1}H NMR of MMAnBuMAran-b-HEMA-TMS



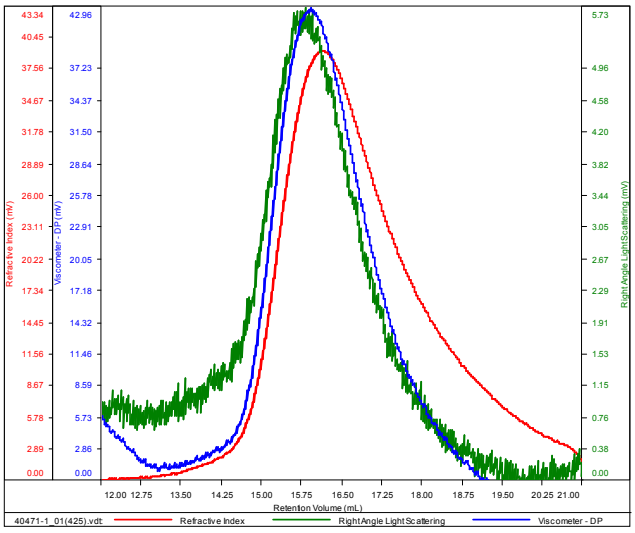
^{1}H NMR of MMAnBuMAran-b-HEMA



SEC elugram of MMAnBuMAran [first block] in THF:

P40471-MMAnBuMAran

Conc (mg/mL)	10.0231
dn/dc (mL/g)	0.0650
Method	PS80k_December-2016-0004.vcm
Solvent	DMF w 0.023M LiBr
Column	PSS

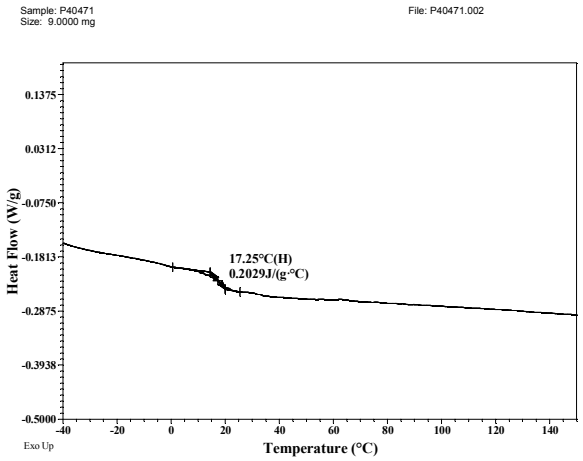


Sample	Mn	Mw	Mp	Mw/Mn	IV
40471-1_01(425).vdt	27,293	41,161	43,640	1.508	0.0979

Dependance 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

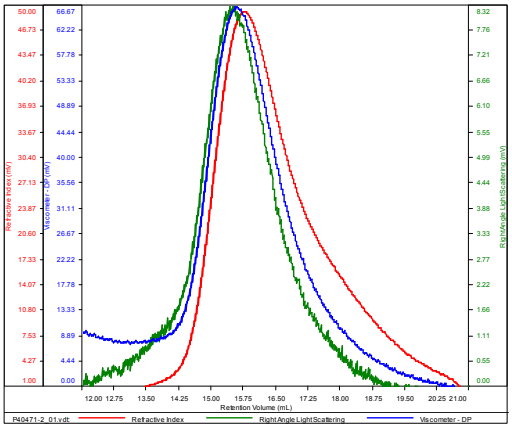
DSC thermogram of isotactic MMAnBuMA-b-HEMA diblock copolymer (2nd heating scan, 10°C/min):



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

P40471-MMAnBuMAran-HEMATMS

Conc (mg/mL)	9.8075
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
P40471-2_01.vdt	45,566	63,815	60,401	1.400	0.1540