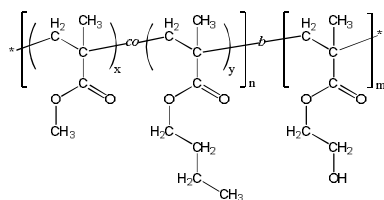


**Sample Name:** Poly(methyl methacrylate-*co* (random)-n-butyl methacrylate)-*block*-poly(2-hydroxyethyl methacrylate)

**Sample #** P40210-MMAAnBuMAran-b-HEMA

**Structure:**



**Composition:**

$M_n \times 10^3$ (g/mol)	25.5–b–26.0
$M_w/M_n$	1.19

Molar ratio MMA : nBuMA	50:50 (mol%)
Molar ratio MMA : HEMA	1 : 1.9
Molar ratio MMAAnBuMA : HEMA	51:49 (mol%)
Weight ratio MMA : nBuMA : HEMA	21:29:50 (wt %)

$T_g$ (MMA-nBuMA block)	77 °C
$T_g$ (HEMA block)	118 °C

### Synthesis Procedure:

Poly (methyl methacrylate-*co*-n-butyl methacrylate)-*b*-poly(2-hydroxyethyl methacrylate) block copolymer was synthesized by living anionic polymerization. First, methyl methacrylate (MMA) and n-butyl methacrylate (n-BuMA) were co-polymerized; and then 2-[trimethylsilyloxy]ethyl methacrylate (hydroxyl-protected HEMA monomer) was added. The obtained block copolymer was precipitated in acidic methanol solution to deprotect the hydroxyl group.

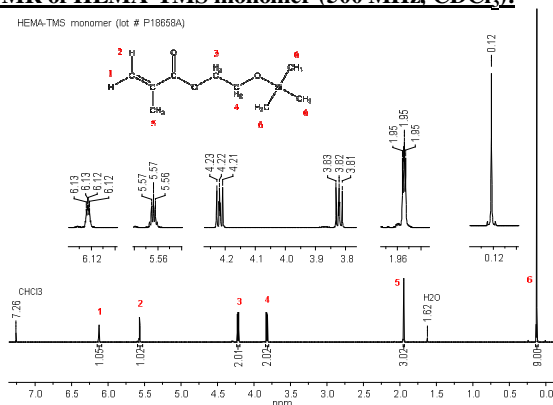
**Solubility:** The polymer is soluble in THF, DMF.

### Characterization:

The polymer composition (molar ratio) was calculated by  $^1\text{H}$  NMR. The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC) using DMF (0.023 M LiBr in DMF) as an eluent. Thermal analysis of the sample was done on a TA Q100 differential scanning calorimeter (DSC) at a heating rate of 10°C/min. The glass transition temperature ( $T_g$ ) was determined as a midpoint of step change in heat flow curve for the second heating scan.

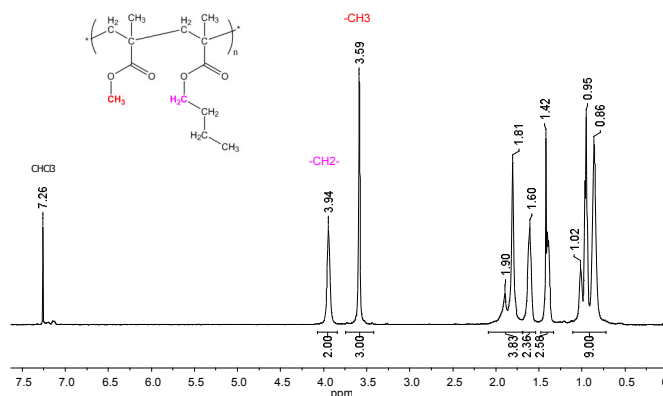
### $^1\text{H}$ NMR of HEMA-TMS monomer (500 MHz, $\text{CDCl}_3$ ):

HEMA-TMS monomer (lot # P18658A)



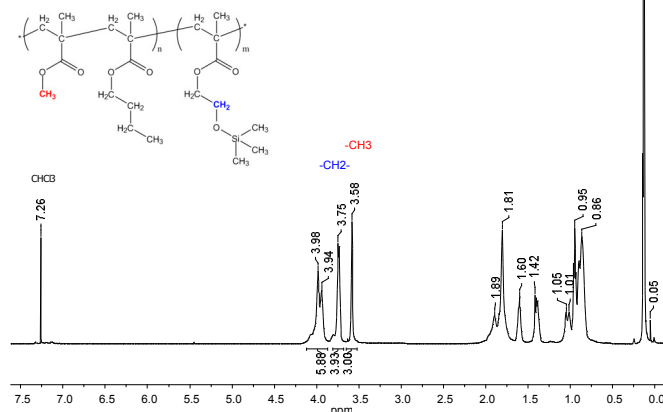
### $^1\text{H}$ NMR of MMA-nBuMA [first block] in $\text{CDCl}_3$ :

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 40210-1\_MMAAnBuMAran



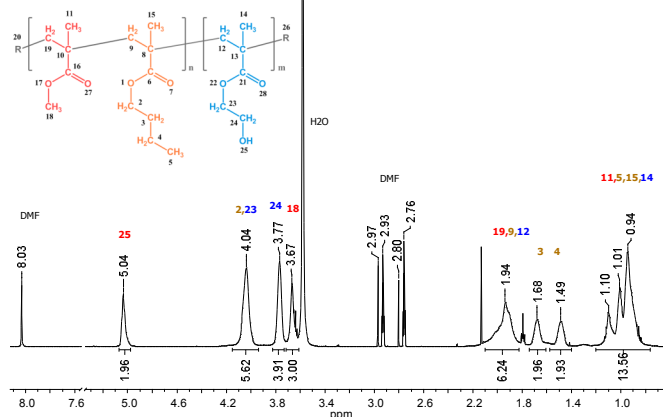
### $^1\text{H}$ NMR of MMAAnBuMA-b-HEMATMS [protected] in $\text{CDCl}_3$ :

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 40210-2\_MMAAnBuMA-b-HEMATMS



### $^1\text{H}$ NMR of MMAAnBuMA-b-HEMA [final] in $\text{DMF-d}_7$ :

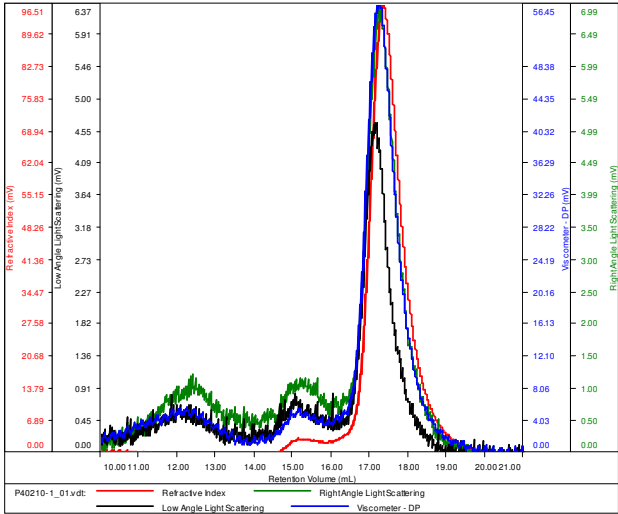
$^1\text{H}$  NMR (500 MHz,  $\text{DMF-d}_7$ ): 40210-3\_MMAAnBuMA-b-HEMA



SEC elugram of MMA-nBuMA [first block]:

P40210-1-MMAAnBuMAran

Conc (mg/mL)	3.8014
dn/dc (mL/g)	0.0650
Method	PS80k-October2016-0000.vcm
Solvent	DMF w 0.023M LiBr
Column	PSS

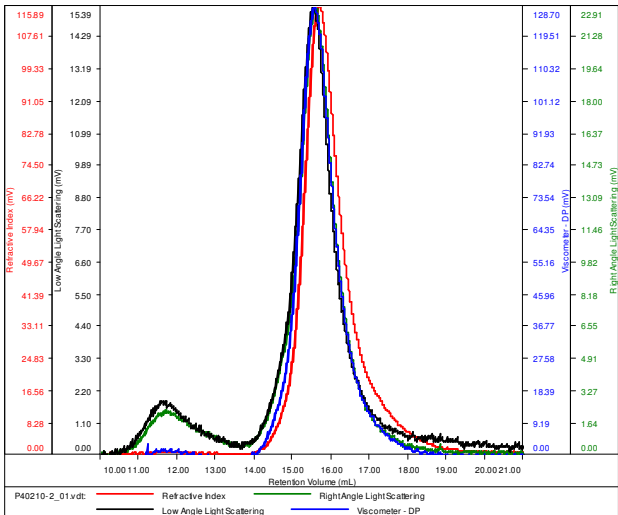


Sample	Mn	Mw	Mp	Mw/Mn	IV
P40210-1_01.vdt	25,691	27,806	26,162	1.082	0.1636

SEC of MMAAnBuMA-b-HEMATMS [protected diblock]:

P40210-2-MMAAnBuMAranHEMATMS

Conc (mg/mL)	5.8562
dn/dc (mL/g)	0.0650
Method	PS80k-October2016-0000.vcm
Solvent	DMF w 0.023M LiBr
Column	PSS



Sample	Mn	Mw	Mp	Mw/Mn	IV
P40210-2_01.vdt	66,301	79,047	74,542	1.192	0.2826

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

