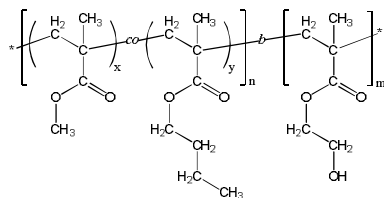


Sample Name: Poly(methyl methacrylate-*co* (random)-n-butyl methacrylate)-*block*-poly(2-hydroxyethyl methacrylate)

Sample # P40212-MMAAnBuMAran-b-HEMA

Structure:



Composition:

$M_n \times 10^{-3}$ (g/mol)	25.5–b–30.0
M_w/M_n	1.17

Molar ratio MMA : nBuMA	50:50 (mol%)
Molar ratio MMA : HEMA	1 : 2
Molar ratio MMAAnBuMA : HEMA	48:52 (mol%)
Weight ratio MMA : nBuMA : HEMA	19:27:54 (wt %)

T_g (MMA-nBuMA block)	77 °C
T_g (HEMA block)	116 °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.

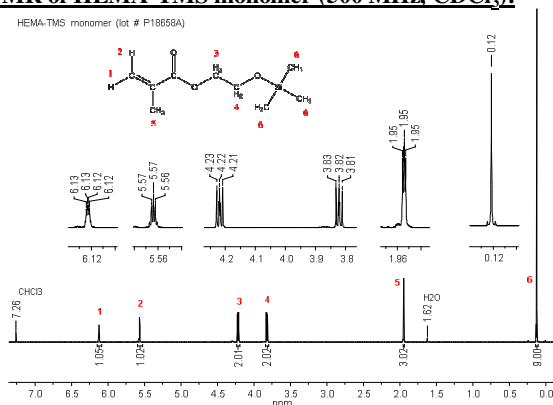
Characterization:

The polymer composition (molar ratio) was calculated by ^1H 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.

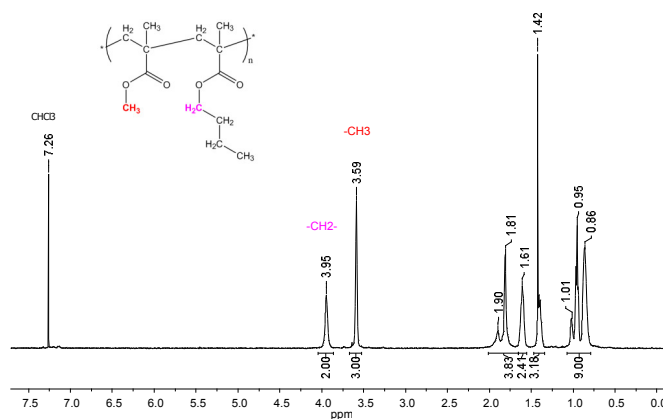
^1H NMR of HEMA-TMS monomer (500 MHz, CDCl_3):

HEMA-TMS monomer (lot # P18658A)



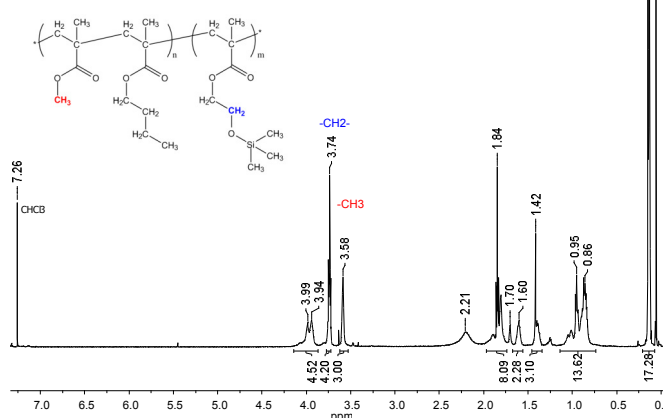
^1H NMR of MMA-nBuMA [first block] in CDCl_3 :

^1H NMR (500 MHz, CDCl_3): 40212-1_MMAAnBuMAran



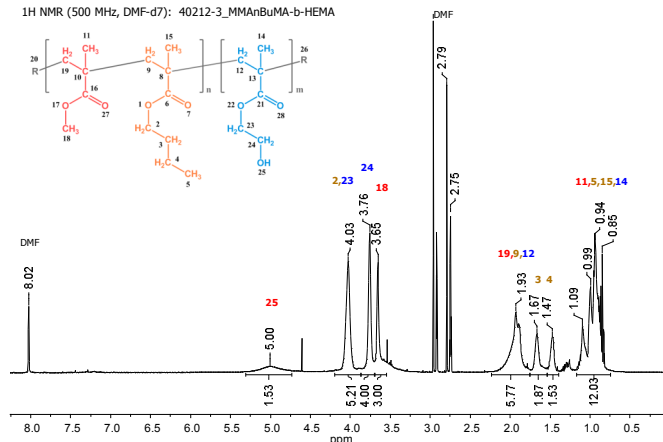
^1H NMR of MMAAnBuMA-b-HEMATMS [protected] in CDCl_3 :

^1H NMR (500 MHz, CDCl_3): 40212-2_MMAAnBuMA-b-HEMATMS



^1H NMR of MMAAnBuMA-b-HEMA [final] in DMF-d_7 :

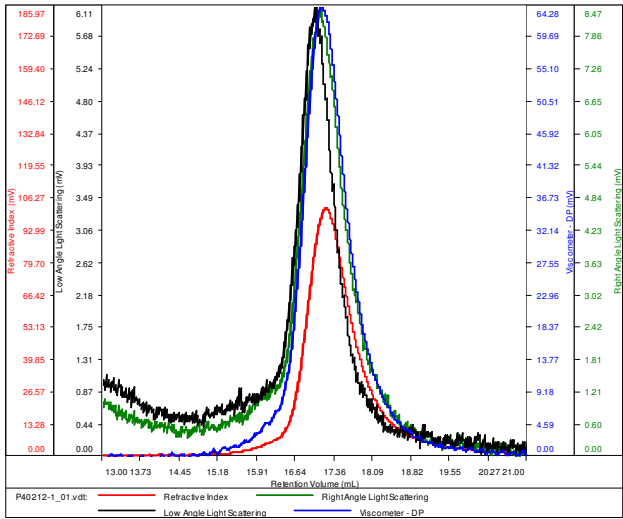
^1H NMR (500 MHz, DMF-d_7): 40212-3_MMAAnBuMA-b-HEMA



SEC elugram of MMA-nBuMA [first block]:

P40212-1-MMAAnBuMAran

Conc (mg/mL)	11.0153
dn/dc (mL/g)	0.0650
Method	PS80k-Nov2016-0000.vcm
Solvent	DMF w 0.023M LiBr
Column	PSS

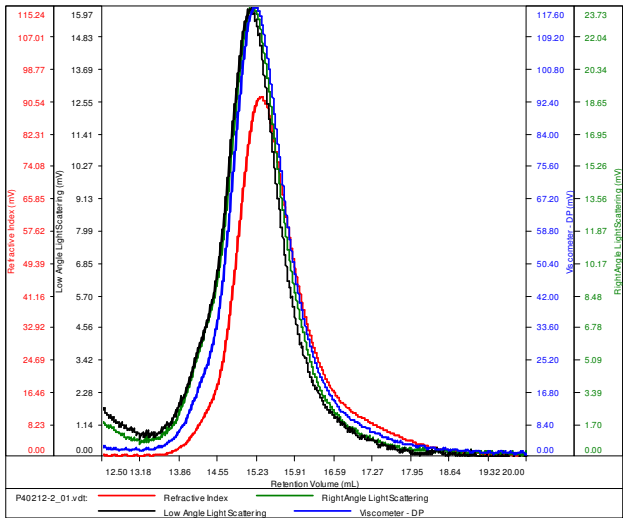


Sample	Mn	Mw	Mp	Mw/Mn	IV
P40212-1_01.vdt	25,494	27,714	25,561	1.087	0.0695

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

P40212-2-MMAAnBuMAranHEMATMS

Conc (mg/mL)	12.2590
dn/dc (mL/g)	0.0650
Method	PS80k-Nov2016-0000.vcm
Solvent	DMF w 0.023M LiBr
Column	PSS



Sample	Mn	Mw	Mp	Mw/Mn	IV
P40212-2_01.vdt	72,664	85,387	80,782	1.175	0.1399

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

