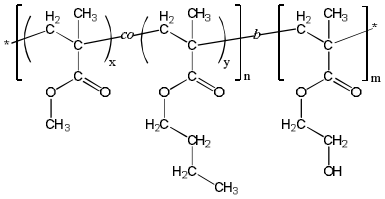
Sample Name: **Poly(methyl methacrylate–*co* *(random)*–n-butyl methacrylate)–*block*–poly(2-hydroxyethyl methacrylate)**

Sample # **P40202-MMAnBuMAran-b-HEMA**

Structure:



Composition:

M_n x 10^3 (g/mol)	28.0–*b*–38.5
M_w/M_n	1.13

Molar ratio MMA : nBuMA	50:50 (mol%)
Molar ratio MMA : HEMA	1 : 2.5
Molar ratio MMAnBuMA : HEMA	44:56 (mol%)
Weight ratio MMA : nBuMA : HEMA	17:25:58 (wt %)

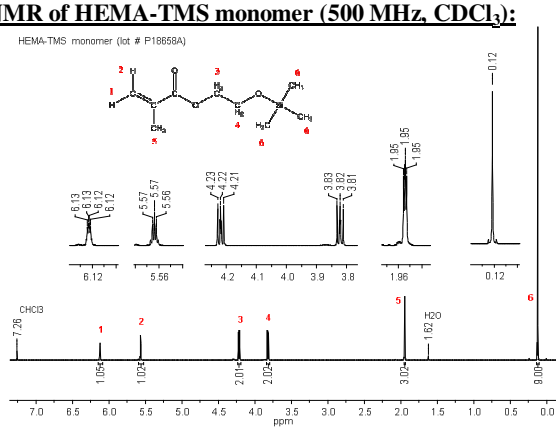
T_g (MMA-nBuMA block)	77 °C
T_g (HEMA block)	116 °C

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.

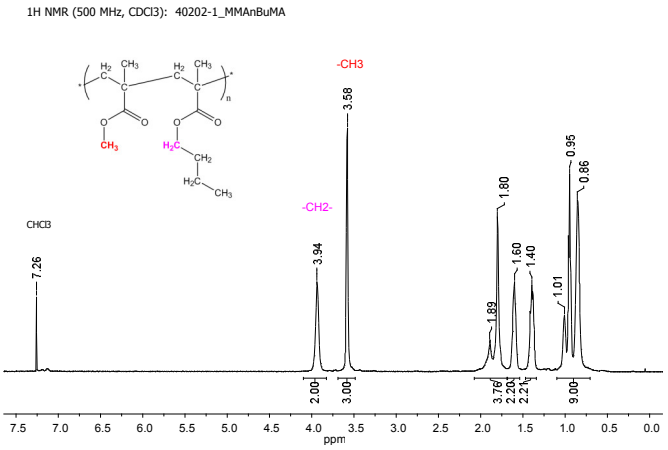
Solubility: The polymer is soluble in THF, DMF.

Characterization:
The polymer composition (molar ratio) was calculated by ^{1}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.

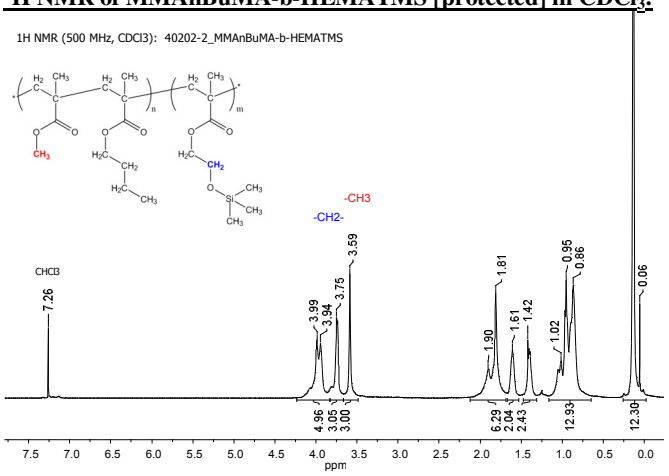
^{1}H NMR of HEMA-TMS monomer (500 MHz, $CDCl_3$):



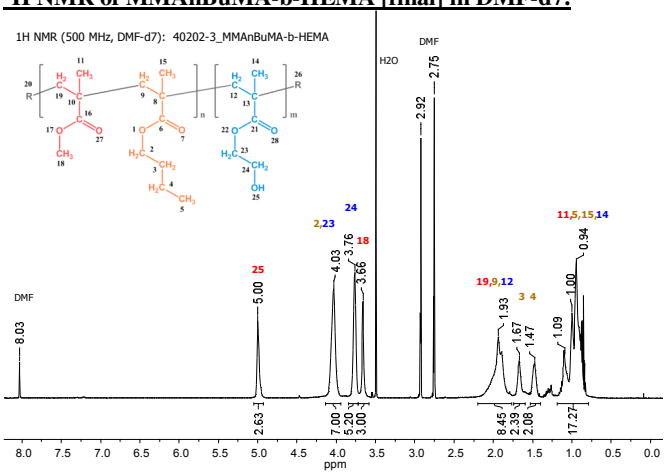
^{1}H NMR of MMA-nBuMA [first block] in $CDCl_3$:



^{1}H NMR of MMAnBuMA-b-HEMATMS [protected] in $CDCl_3$:



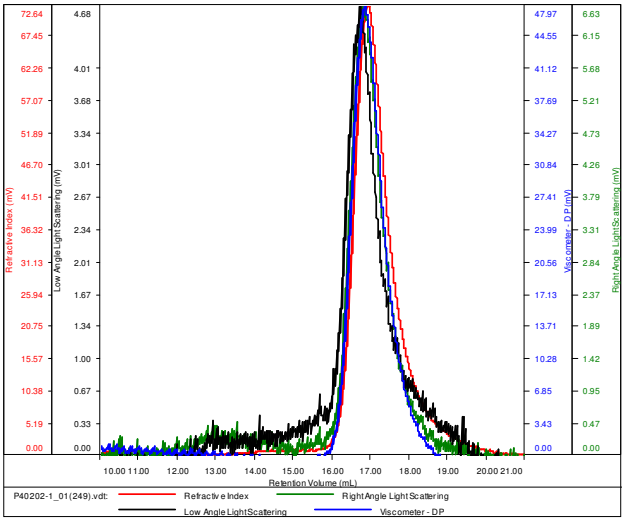
^{1}H NMR of MMAnBuMA-b-HEMA [final] in DMF-d7:



SEC elugram of MMA-nBuMA [first block]:

P40202-1-MMAnBuMAran

Conc (mg/mL)	4.8793
dn/dc (mL/g)	0.0650
Method	PS80k-October292016-0001.vcm
Solvent	DMF w 0.023M LiBr
Column	PSS

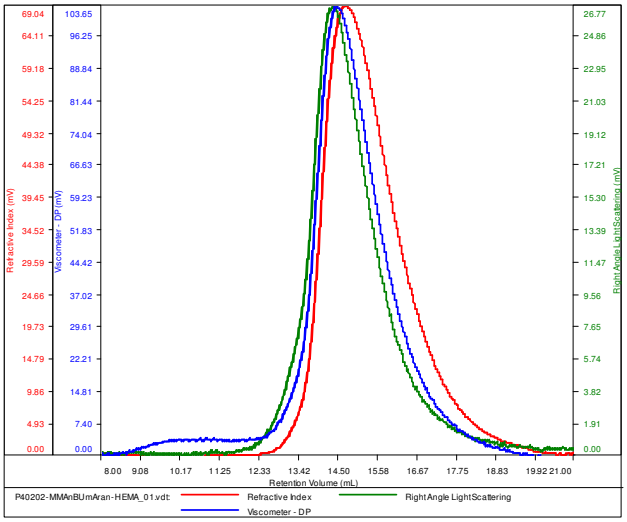


Sample	Mn	Mw	Mp	Mw/Mn	IV
P40202-1_01(249).vdt	28,250	32,784	31,066	1.160	0.1076

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

P40202-MMAnBuMA-HEMATMS

Conc (mg/mL)	13.8414
dn/dc (mL/g)	0.0690
Method	PS80k_December-2016-0004.vcm
Solvent	DMF w 0.023M LiBr
Column	PSS



Sample	Mn	Mw	Mp	Mw/Mn	IV
P40202-MMAnBUmAran-HEMA_01.vdt	88,080	99,446	116,050	1.129	0.1593

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