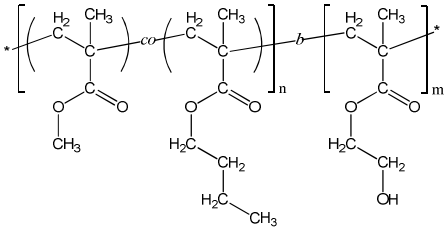
Sample Name:

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

Sample #: **P40381-MMAnBuMAran-b-HEMA**

Structure:



Composition:

M_n x 10^3 (g/mol)	39.0-b-37.0
M_w/M_n	1.11
MMA: nBuMA	50:50 (mol%)
MMA: nBuMA	41:59 (wt %)
T_g (MMAnBuMA)	70 °C
T_g (HEMA)	110 °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 (n-BuMA) were co-polymerized; and then 2-[trimethylsilyloxy]ethyl methacrylate (hydroxyprotected 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.

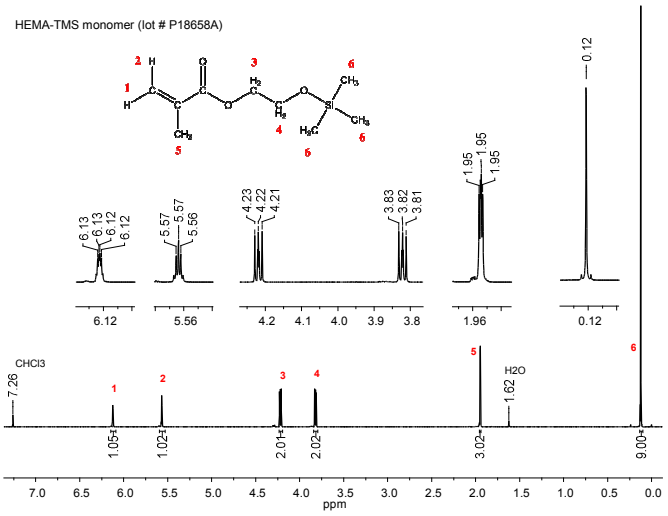
Characterization:

The polymer composition 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_2CH_2O- protons and the peak area of nBuMA -OCH_2- protons and using SEC data for the first (MMAnBuMA) block.

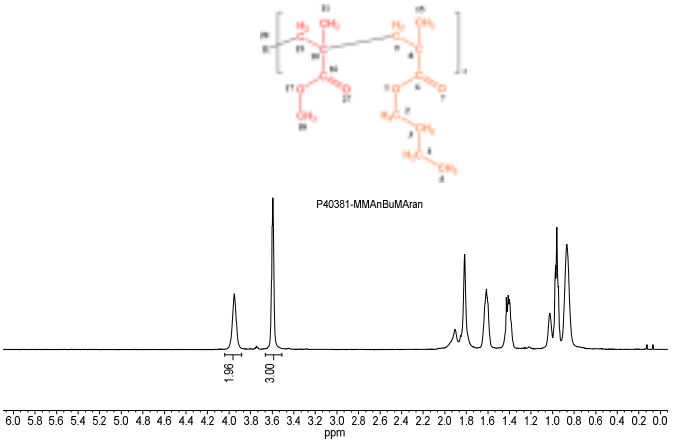
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMAnBuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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.

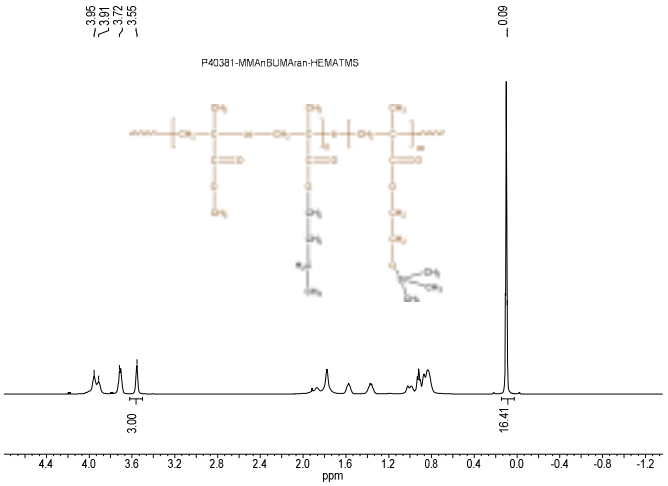
^{1}H NMR of HEMATMS monomer (500 MHz, $CDCl_3$):



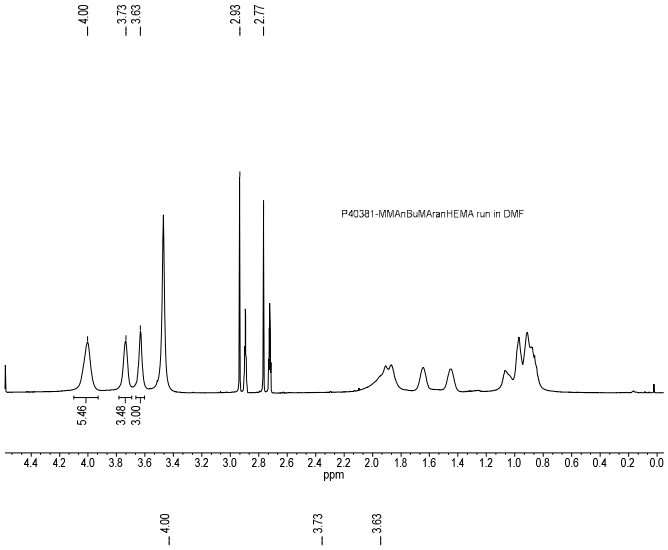
^{1}H NMR of MMAnBuMA [first block] in $CDCl_3$:

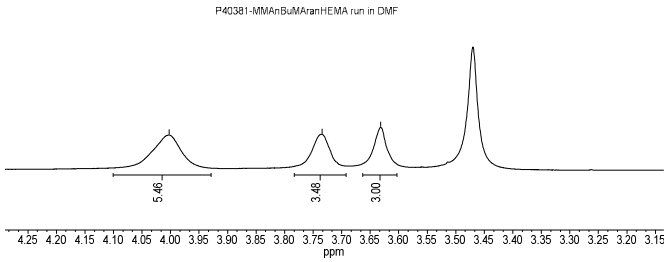


^{1}H NMR of MMAnBuMA-b-HEMATMS in $CDCl_3$:



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

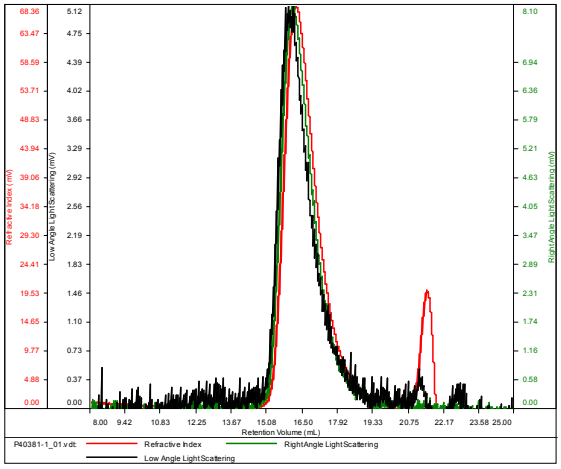




SEC elugram of MMAnBuMA [first block]:

P40381-MMAnBuMAran

Conc (mg/mL)	9.9206
dn/dc (mL/g)	0.0650
Method	PS80k_December-2016-0004.vcm
Solvent	DMF w 0.023M LiBr
Column	PSS

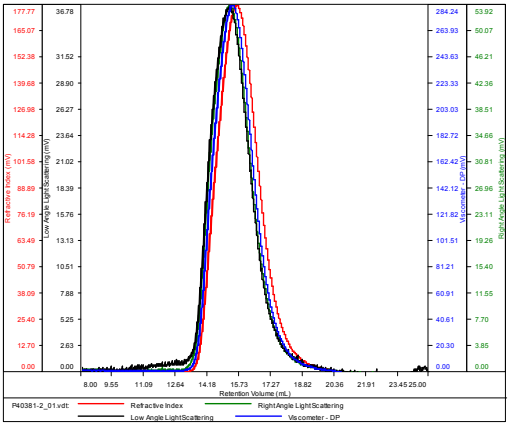


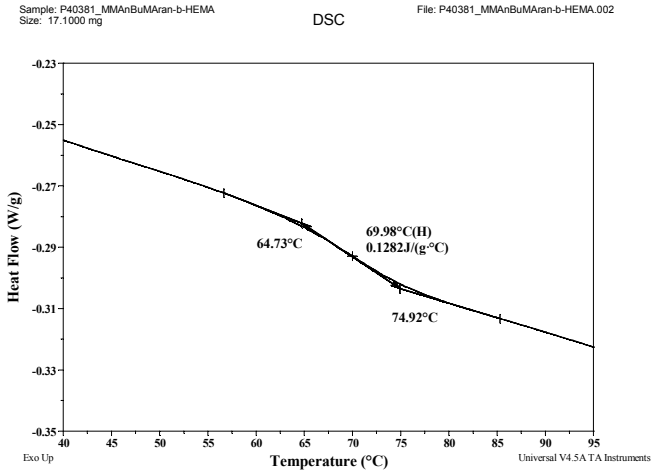
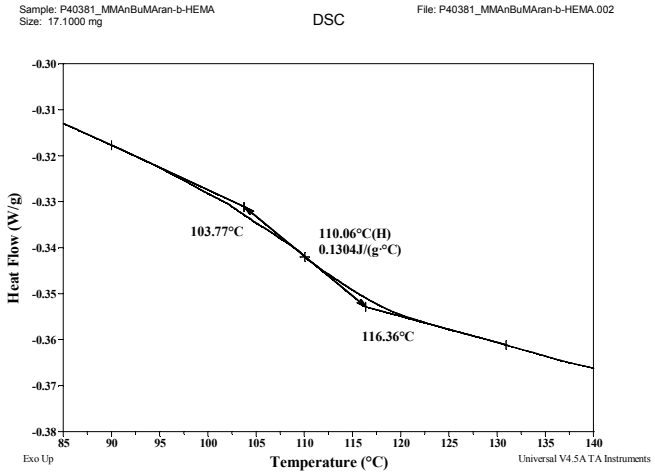
Sample	Mn	Mw	Mp	Mw/Mn	IV
P40381-1_01.vdt	38,979	41,079	39,668	1.054	0.0955

SEC elugram of MMAnBuMA-b-HEMATMS:

P40381-MMAnBuMAran-HEMA

Conc (mg/mL)	39.4902
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
P40381-2_01.vdt	96,620	107,136	102,648	1.109	0.1810

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