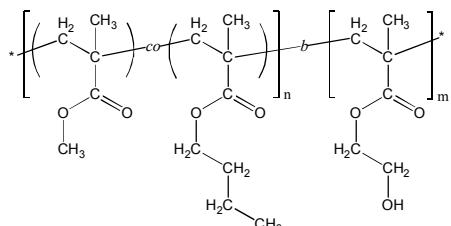


Sample Name:

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

Sample #: P19424-MMAnBuMArAn-b-HEMA

Structure:



Composition:

M _n x 10 ³ (g/mol)	21.0- <i>b</i> -27.5
M _w /M _n	1.16
Molar ratio MMA : nBuMA	51 : 49 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	18 : 25 : 57 (wt%)
T _g (MMAnBuMA)	79 °C
T _g (HEMA)	117 °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 (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:

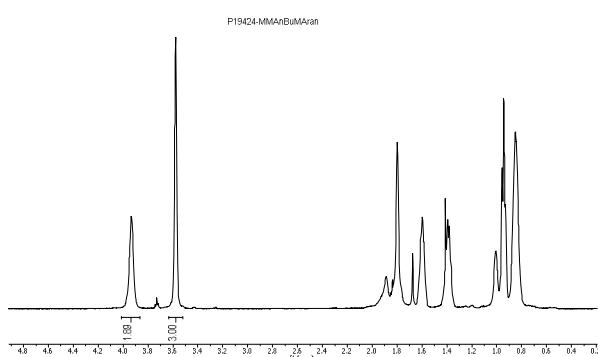
The polymer composition was determined by ¹H NMR. MMA:nBuMA molar ratio was calculated by comparing the integration of the -OCH₂- protons of nBuMA (at δ = 3.9 ppm) to the integration of methoxy group of MMA (at δ = 3.6 ppm). Molecular weight of the second (HEMA) block was calculated by comparing the integration of -OCH₂- protons of HEMATMS to the integration of methoxy group of MMA 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 MMAnBuMArAn-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.

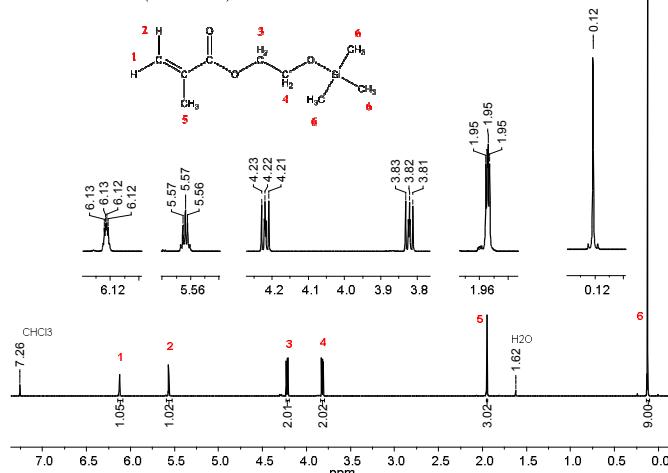
¹H NMR of MMAnBuMArAn [first block]:

P19424-I
Company: Polymer Source
1H_proton_13C_13C_01(Polymer_Source) PSource 8



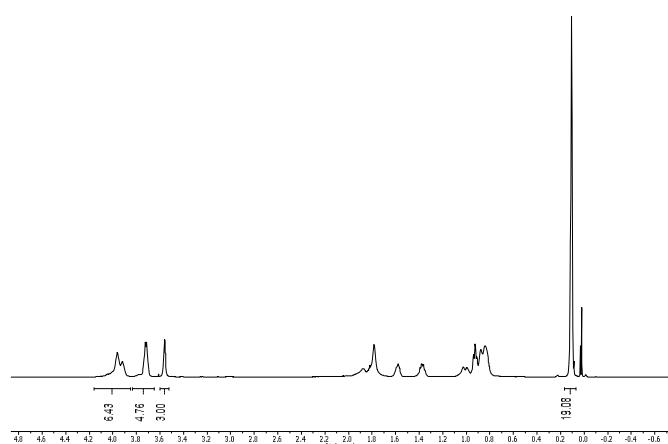
¹H NMR of HEMATMS monomer (500 MHz, CDCl₃):

HEMA-TMS monomer (lot # P18658A)



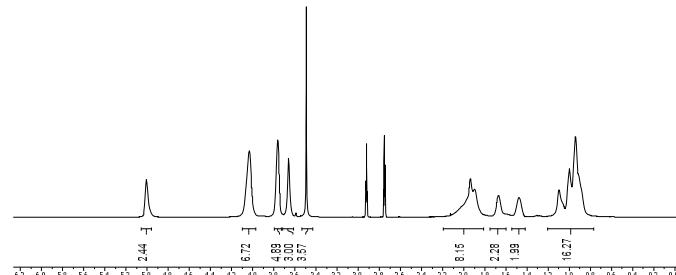
¹H NMR of MMAnBuMArAn-b-HEMA in CDCl₃:

P19424-MMAnBuMArAn-b-HEMATMS



¹H NMR of MMAnBuMArAn-b-HEMA in DMF-d₇:

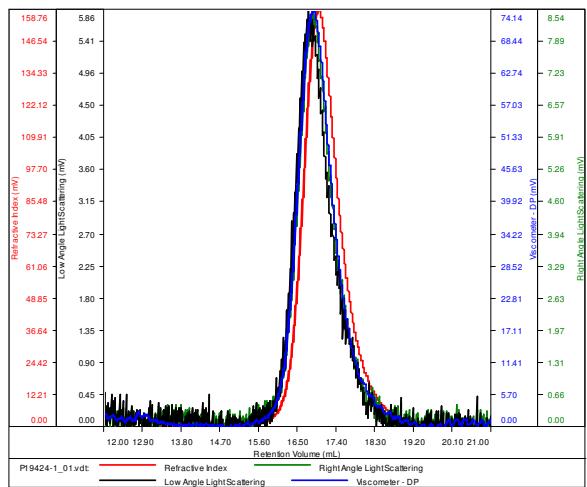
P19424-MMAnBuMArAn-b-HEMA



SEC of MMAAnBuMAran [first block]:

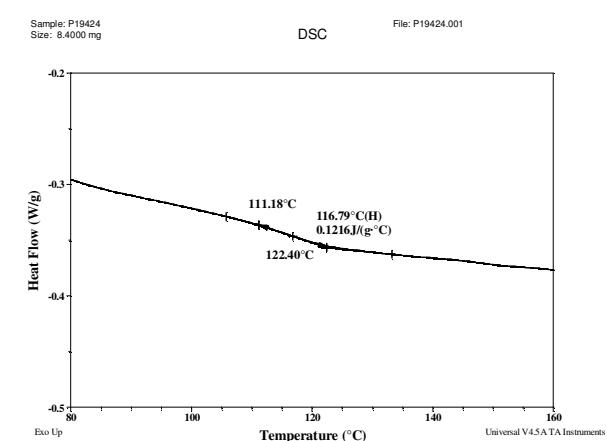
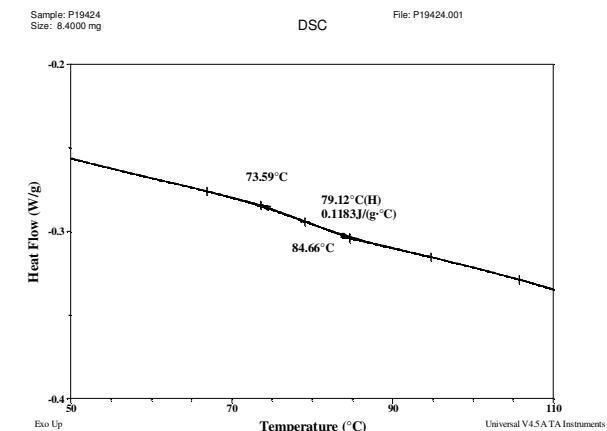
SAMPLE ID: P19424-1-MMAAnBuMAran

Conc (mg/mL)	7.2154
d _n /d _c (mL/g)	0.0650
Method	ps80kJuly292015-0000.vcm
Solvent	DMF w 0.03M LiBr
Column	PSS



Sample	Mn	Mw	Mp	Mw/Mn	IV
P19424-1_01.vdt	21,135	22,645	21,829	1.071	0.1173

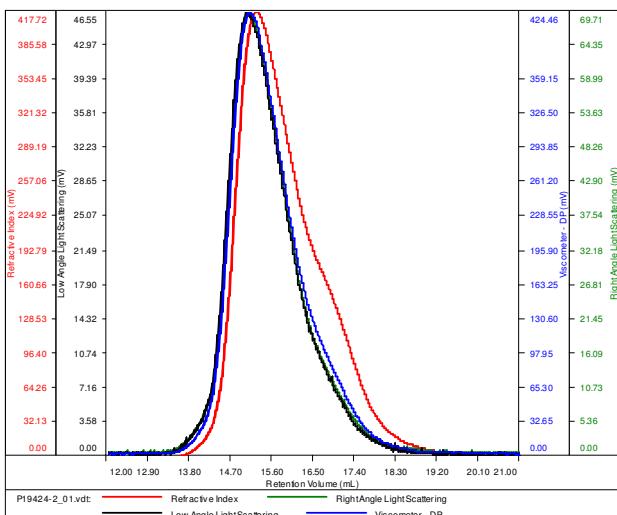
DSC of MMAAnBuMAran-b-HEMA:



SEC of MMAAnBuMAran-b-HEMATMS:

SAMPLE ID:
P19424-MMAAnBuMAranHEMATMS

Conc (mg/mL)	39.7693
d _n /d _c (mL/g)	0.0560
Method	ps80kJuly292015-0000.vcm
Solvent	DMF w 0.03M LiBr
Column	PSS



Sample	Mn	Mw	Mp	Mw/Mn	IV
P19424-2_01.vdt	63,956	74,278	82,261	1.161	0.1927