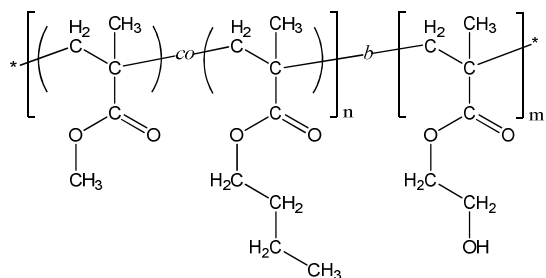


Sample Name:

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

Sample #: **P40445-MMA_nBuMA_ran-b-HEMA**

Structure:



Composition:

$M_n \times 10^3$ (g/mol)	24.0–b–24.0
M_w/M_n	1.5
Molar ratio MMA: nBuMA	51: 49 (mol %)
Weight ratio MMA: nBuMA	42: 58 (wt %)
Molar ratio MMA: nBuMA : HEMA	24: 23: 53 (mol %)
T_{g1} (MMA _n BuMA)	64 °C
T_{g2} (HEMA)	104 °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 (nBuMA) were co-polymerized; followed by addition of 2-[trimethylsilyloxy]ethyl methacrylate (hydroxy-protected HEMA monomer). The obtained block copolymer was precipitated in acidic methanol solution to deprotect the hydroxyl group.

Characterization:

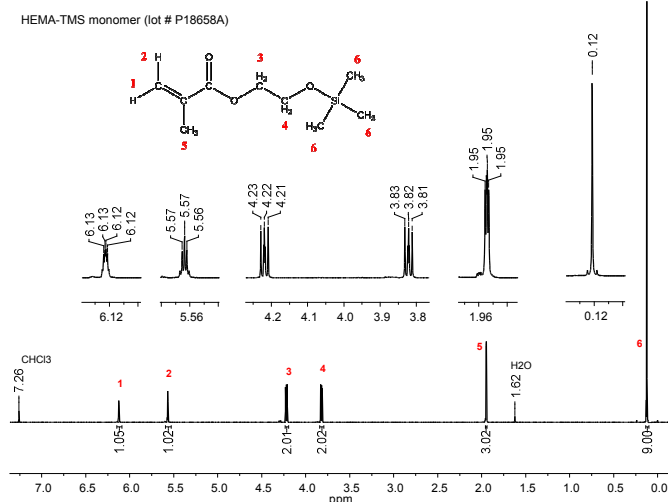
The polymer composition was determined by ^1H NMR. MMA:nBuMA molar ratio was calculated by comparing the peak area of nBuMA $-\text{OCH}_2-$ protons at 3.9 ppm and the peak area of MMA $-\text{OCH}_3$ protons at 3.6 ppm. Molecular weight of the second (HEMA) block was calculated by comparing the peak area of HEMA $-\text{OCH}_2\text{CH}_2\text{O}-$ protons and the peak area of nBuMA $-\text{OCH}_2-$ protons and using SEC data for the first (MMA_nBuMA) block. The average molecular weight and polydispersity index of the polymer were determined by size exclusion chromatography (SEC) using DMF (0.023 M LiBr in DMF) as an eluent.

Thermal analysis was performed on TA Instruments Q100 differential scanning calorimeter (DSC) under a nitrogen atmosphere. The glass transition temperature (T_g) of the polymer was measured at a scan rate of 10°C/min shortly after creating thermal history of the sample.

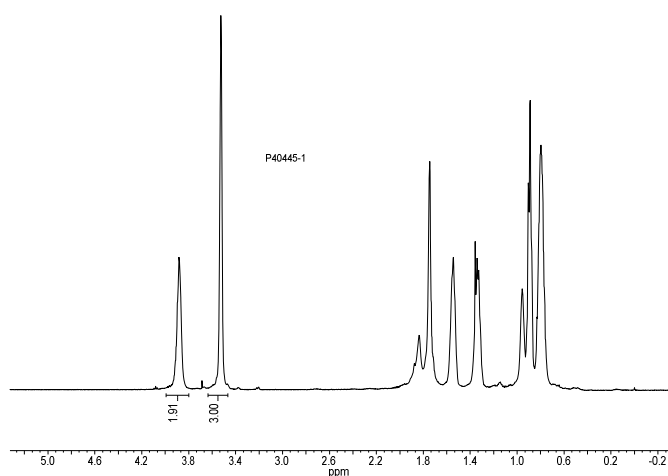
Solubility:

The polymer is soluble in THF and DMF.

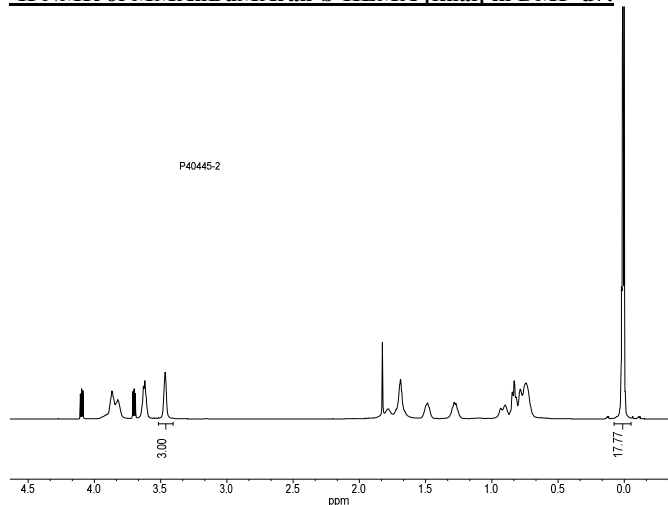
^1H NMR of HEMA-TMS monomer (500 MHz, CDCl_3):



^1H NMR of MMA_nBuMA_ran [first block] in CDCl_3 :



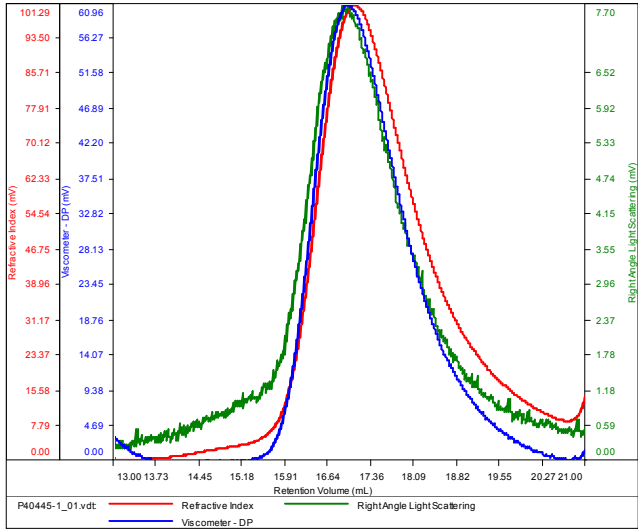
^1H NMR of MMA_nBuMA_ran-b-HEMA [final] in DMF-d_7 :



SEC elugram of MManBuMAran [first block] in DMF:

P40445-1

Conc (mg/mL)	20.3673
dn/dc (mL/g)	0.0650
Method	PS80k_December-2016-0004.vcm
Solvent	DMF w 0.023M LiBr
Column	PSS

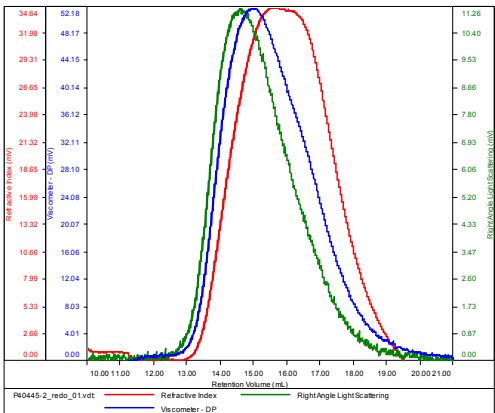


Sample	Mn	Mw	Mp	Mw/Mn	IV
P40445-1_01.vdt	23,466	25,884	24,887	1.103	0.0600

SEC elugram of MManBuMA-b-HEMA diblock copolymer in DMF:

P40445-2-MManBuMAran-HEMATMS

Conc (mg/mL)	11.0457
dn/dc (mL/g)	0.0650
Method	PS80k_December-2016-0004.vcm
Solvent	DMF w 0.023M LiBr
Column	PSS



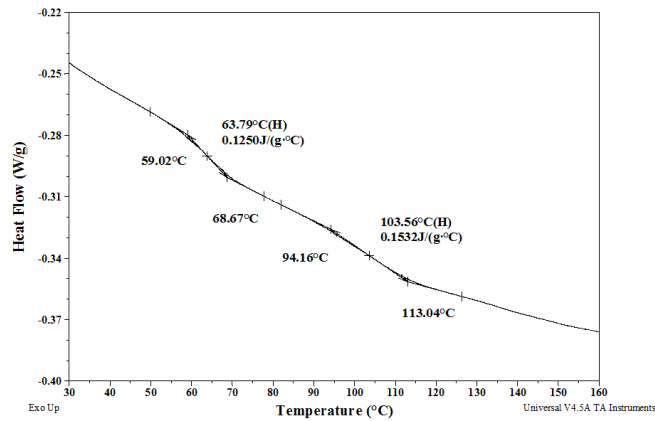
Sample	Mn	Mw	Mp	Mw/Mn	IV
P40445-2_redo_01.vdt	61,690	94,377	85,345	1.530	0.1576

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

Sample: P40445_MManBuMA-HEMA
Size: 17.2000 mg

DSC

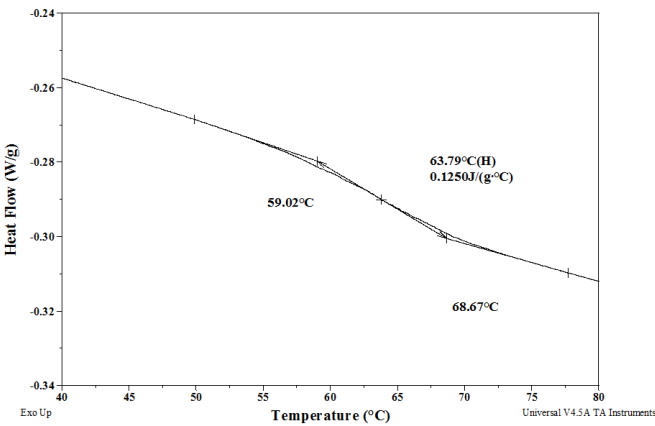
File: P40445_MManBuMA-HEMA.001



Sample: P40445_MManBuMA-HEMA
Size: 17.2000 mg

DSC

File: P40445_MManBuMA-HEMA.001



Sample: P40445_MManBuMA-HEMA
Size: 17.2000 mg

DSC

File: P40445_MManBuMA-HEMA.001

