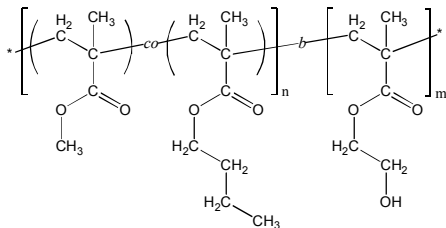


Sample Name:

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

Sample #: P10354-MMA_nBuMA_ran-b-HEMA

Structure:



Composition:

$M_n \times 10^3$ (g/mol)	46.5-b-58.0
M_w/M_n	1.18
Molar ratio MMA:nBuMA	48 : 52 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	17 : 27 : 56 (wt%)
T_g (MMA _n BuMA)	51 °C
T_g (HEMA)	112 °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:

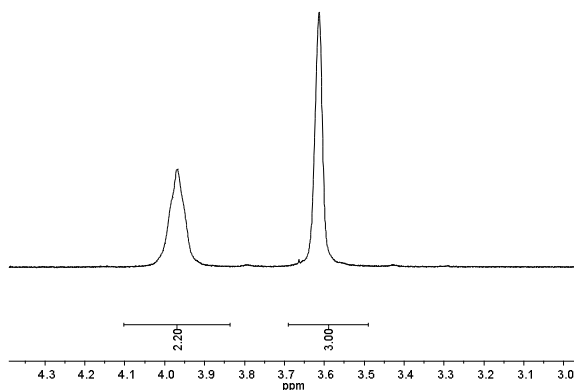
The polymer composition was determined by ¹H NMR. MMA:nBuMA molar ratio was calculated by comparing the integration of the -OCH₂- protons of nBuMA (at δ = 3.9 ppm) to the integration of methoxy group of MMA (at δ = 3.6 ppm). Molecular weight of the second (HEMA) block was calculated by comparing the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

The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA_nBuMA-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.

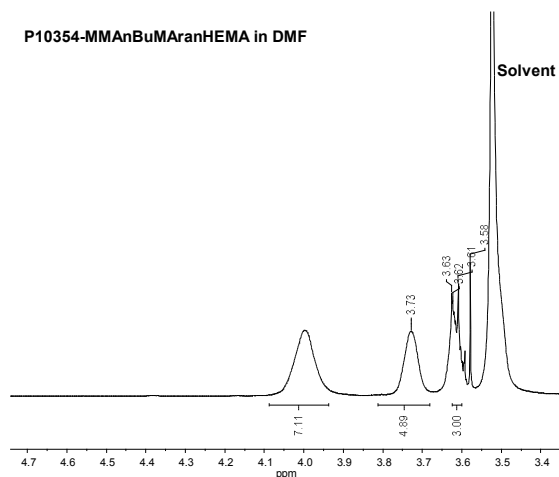
¹H NMR of MMA_nBuMA_ran [first block]:

P10354-1 MMA_nBuMA_ran first block MMA:nBuMA 48:52 ratio



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

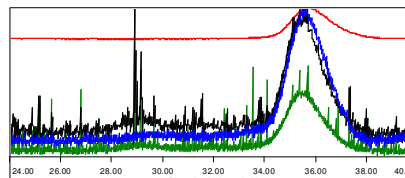
P10354-MMA_nBuMA_ranHEMA in DMF



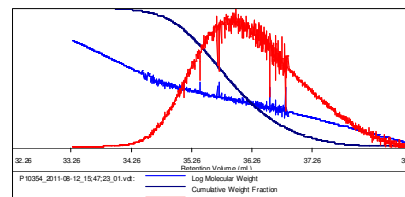
SEC of MMA_nBuMA_ran [first block]:

Sample ID: P10354

Concentration (mg/mL)	1.2450
Sample dn/dc (mL/g)	0.0679
Method File	PS80K-July-0000.vcm
Column Set	3x PL 1113-6300
System	System 1

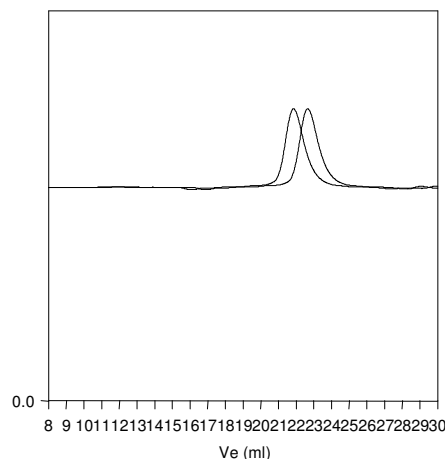


Sample	Mn (Da)	Mw (Da)	Mp (Da)	Mw/Mn	IV (dL/g)
P10354_2011-08-12_15:47:23_01.vdt	46,361	54,854	53,449	1.183	0.2813



SEC of MMA_nBuMA_ran and MMA_nBuMA_ran-b-HEMATMS:

P10354 MMA_nBuMA_ran-b-HEMA



Size exclusion chromatography of

- MMA_nBuMA_ran block Mn 46,500 Mw: 53,500 Mw/Mn 1.15
- MMA_nBuMA_ran-b-HEMATMS: 46,500-90,000 MW/Mn : 1.18 After deprotection : Mn 46500-b-58,000

DSC of MManBuMAran:

