

## Sample Name:

**Poly(methyl methacrylate-co<sub>(random)</sub>-n-butyl methacrylate)-block-poly(2-hydroxyethyl methacrylate)**

## Sample #: P10354-MMA<sub>n</sub>BuMA<sub>r</sub>an-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 <sub>n</sub> 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:

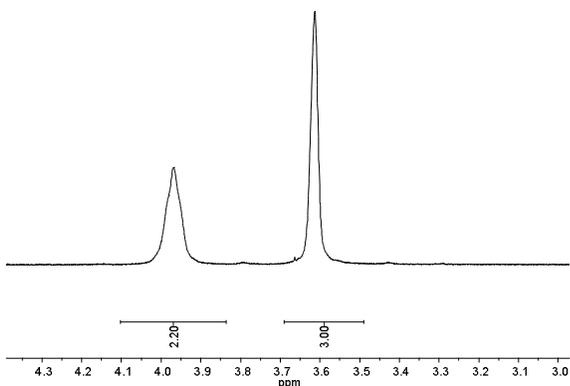
The polymer composition was determined by <sup>1</sup>H NMR. MMA:nBuMA molar ratio was calculated by comparing the integration of the -OCH<sub>2</sub>- protons of nBuMA (at δ = 3.9 ppm) to the integration of methoxy group of MMA (at δ = 3.6 ppm). Molecular weight of the second (HEMA) block was calculated by comparing the integration of -OCH<sub>2</sub>- protons of HEMATMS to the integration of methoxy group of MMA and using SEC data for the first (MMA<sub>n</sub>BuMA) block.

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

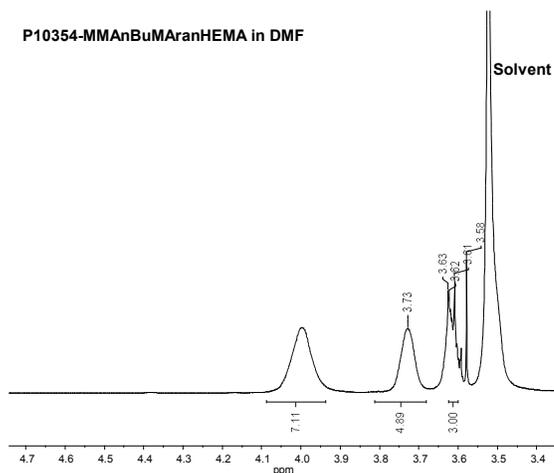
Thermal analysis of the sample was done on a TA Q100 differential scanning calorimeter (DSC) at a heating rate of 10°C/min. The glass transition temperature ( $T_g$ ) was determined as a midpoint of step change in heat flow curve for the second heating scan.

### <sup>1</sup>H NMR of MMA<sub>n</sub>BuMA<sub>r</sub>an [first block]:

P10354-1 MMA<sub>n</sub>BuMA<sub>r</sub>an first block MMA:nBuMA 48:52 ratio



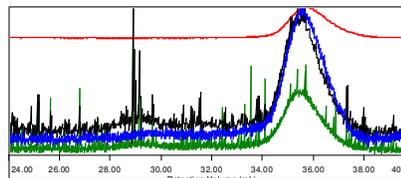
### <sup>1</sup>H NMR of MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA in DMF-d<sub>7</sub>:



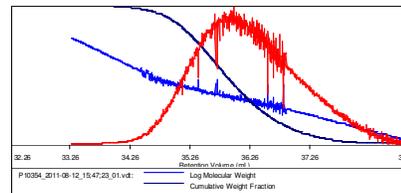
### SEC of MMA<sub>n</sub>BuMA<sub>r</sub>an [first block]:

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

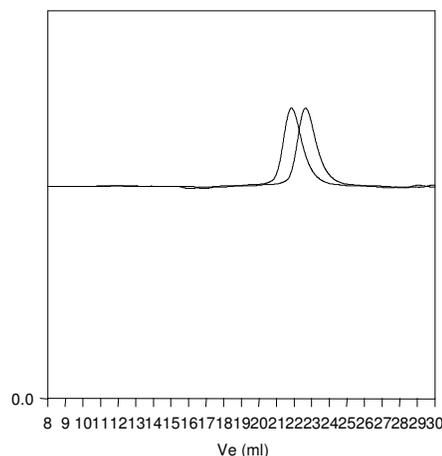


Sample	Mn (Da)	Mw (Da)	Mp (Da)	Mw/Mn	IV (dL/g)
P10354_2011-08-12_15:47:23_01.vdt	46,361	54,854	53,449	1.183	0.2813



### SEC of MMA<sub>n</sub>BuMA<sub>r</sub>an and MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMATMS:

P10354 MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMA



Size exclusion chromatography of

- MMA<sub>n</sub>BuMA<sub>r</sub>an block Mn 46,500 Mw: 53,500 Mw/Mn 1.15
- MMA<sub>n</sub>BuMA<sub>r</sub>an-b-HEMATMS: 46,500-90,000 MW/Mn : 1.18  
After deprotection : Mn 46500-b-58,000

DSC of MManBuMAran:

