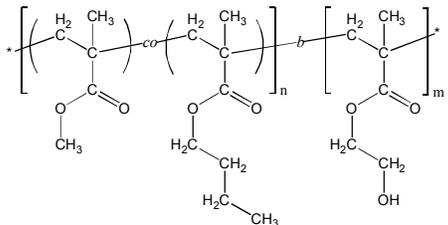


Sample Name:

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

Sample #: P11491-MMA*n*BuMA*r*an-*b*-HEMA

Structure:



Composition:

$M_n \times 10^3$ (g/mol)	24.5- <i>b</i> -27.0
M_w/M_n	1.15
Molar ratio MMA : nBuMA	75 : 25 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	32 : 15 : 53 (wt%)

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.

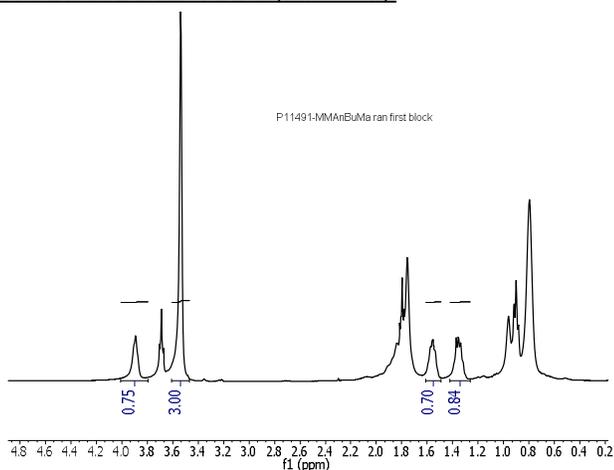
Characterization:

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 $\delta = 3.9$ ppm) to the integration of methoxy group of MMA (at $\delta = 3.6$ 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*n*BuMA) block.

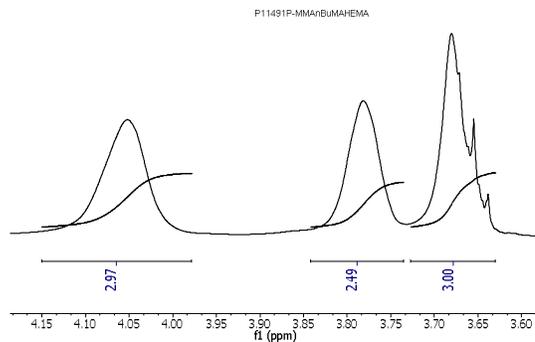
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA*n*BuMA-*b*-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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.

^1H NMR of MMA*n*BuMA*r*an [first block]:



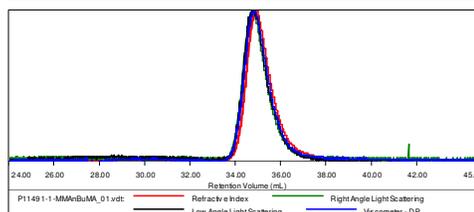
^1H NMR of MMA*n*BuMA*r*an-*b*-HEMA diblock copolymer:



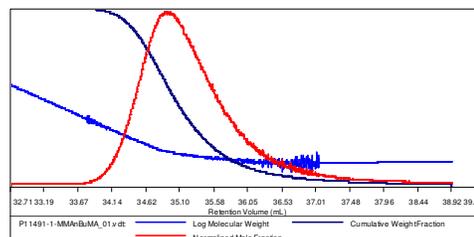
SEC of MMA*n*BuMA*r*an [first block]:

Sample ID: P11491-1-MMA*n*BuMA

Concentration (mg/mL)	5.4675
Sample dn/dc (mL/g)	0.0800
Method File	PS80K-Mby-2013-0000.vcm
Column Set	3x PL 1113-6300
System	System 1

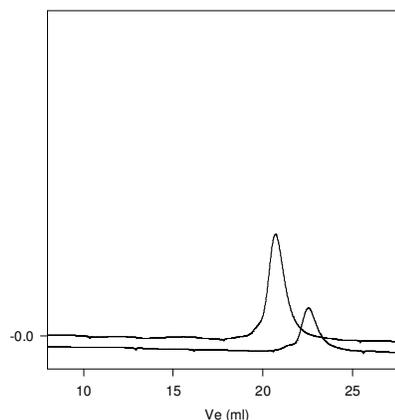


Sample	Mn	Mw	Mp	Mw/Mn	IV
P11491-1-MMA <i>n</i> BuMA_01.vdt	24,339	25,754	25,407	1.058	0.2933



SEC of MMA*n*BuMA*r*an and MMA*n*BuMA*r*an-*b*-HEMATMS:

P11491-MMA*n*BuMA*r*an-*b*-HEMA



Size exclusion chromatography of
1. MMA*n*BuMA ran block Mn 24,500 Mw/Mn 1.05
2. MMA*n*BuMA*r*an-*b*-HEMATMS: 24,500-42,000 MW/Mn : 1.15
After deprotection Mn 24,500-*b*-27,000 Mw/Mn 1.15