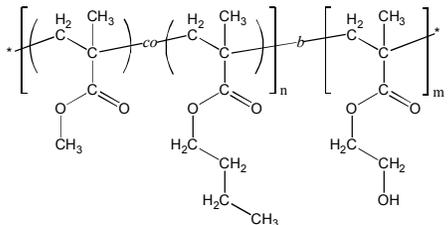


Sample Name:

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

Sample #: P10842p-MMA*n*BuMA*r*an-*b*-HEMA

Structure:



Composition:

$M_n \times 10^3$ (g/mol)	45.0- <i>b</i> -46.0
M_w/M_n	1.3
Molar ratio MMA : <i>n</i> BuMA	50 : 50 (mol/mol)
Weight ratio MMA : <i>n</i> BuMA	20 : 29 : 51 (wt%)
T_g (MMA <i>n</i> BuMA)	65 °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.

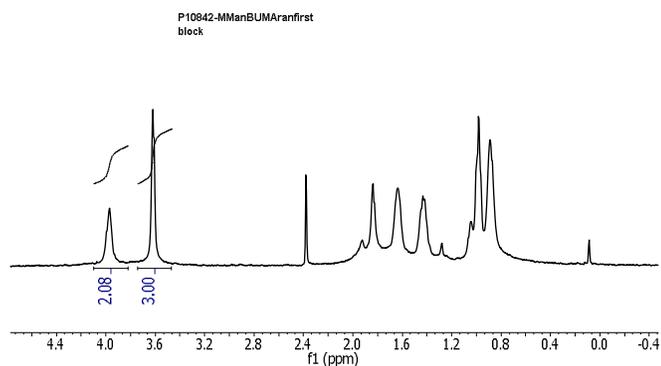
Characterization:

The polymer composition was determined by ^1H NMR. MMA:*n*BuMA molar ratio was calculated by comparing the integration of the $-\text{OCH}_2-$ protons of *n*BuMA (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 $-\text{OCH}_2-$ protons of HEMATMS to the integration of methoxy group of MMA and using SEC data for the first (MMA*n*BuMA) block.

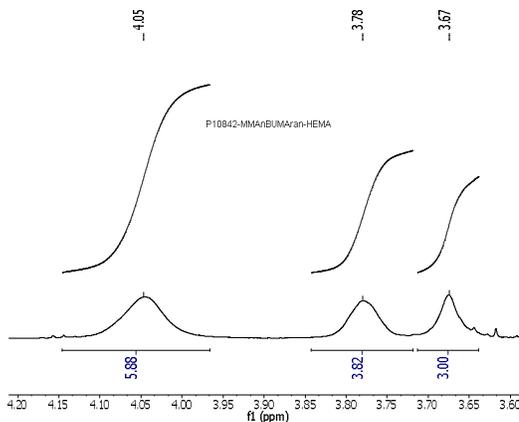
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA*n*BuMA-*b*-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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]:



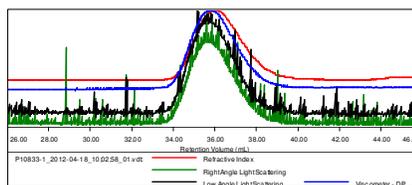
^1H NMR of MMA*n*BuMA*r*an-*b*-HEMA diblock copolymer:



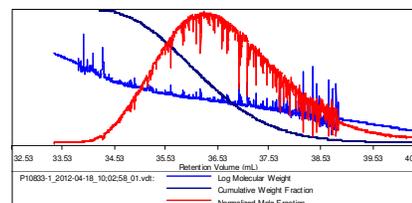
SEC of MMA*n*BuMA*r*an [first block]:

Sample ID: P10842-I-MMA*n*BuMA

Concentration (mg/mL)	9.4867
Sample dn/dc (mL/g)	0.0800
Method File	PS80-APR2012-0000.vcm
Column Set	3x PL 1113-6300
System	System 1

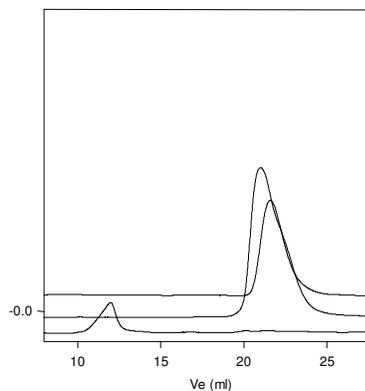


Sample	Mn (Da)	Mw (Da)	Mp (Da)	Mw/Mn	IV (dL/g)
P10833-1_2012-04-18_10:02:58_01.vtl	45,122	50,254	48,215	1.114	0.2719



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

P10842-MMA*n*BuMA*r*an-*b*-HEMA



Size exclusion chromatography of
1. MMA*n*BuMA ran block Mn 45,000 Mw: 55,000 Mw/Mn 1.11
2. MMA*n*BuMA*r*an-*b*-HEMATMS: 45,000-*b*-71,500 Mw/Mn: 1.30
After deprotection Mn 45,000-*b*-46,000 Mw/Mn 1.3
In THF shows micellization