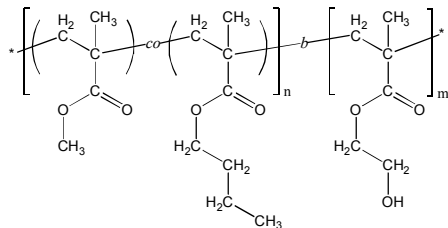


Sample Name:

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

Sample #: P10542-MMA_nBuMA_ran-b-HEMA

Structure:



Composition:

$M_n \times 10^3$ (g/mol)	31.5- <i>b</i> -31.0
M_w/M_n	1.15
Molar ratio MMA : nBuMA	50 : 50 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	21 : 29 : 50 (wt%)
T_g (MMA _n 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.

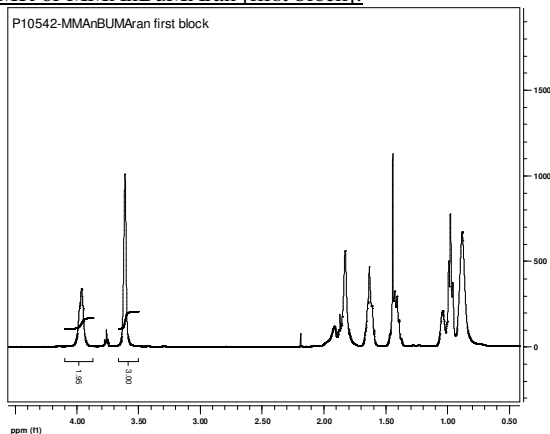
Characterization:

The polymer composition was determined by ¹H NMR. MMA: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.

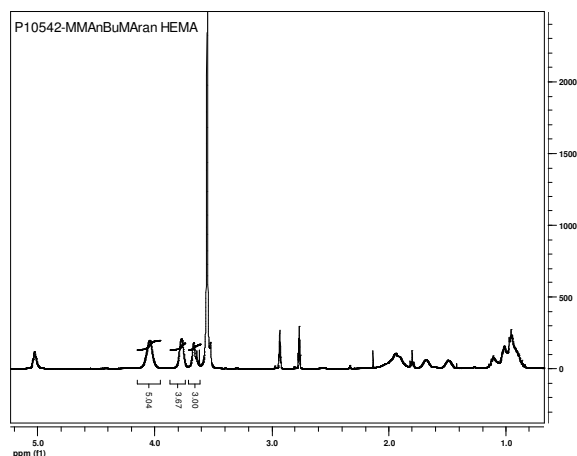
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA_nBuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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]:

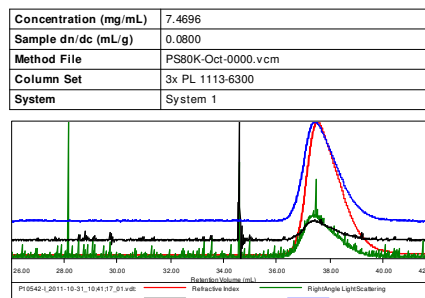


¹H NMR of MMA_nBuMA_ran-b-HEMA in DMF-d₇:

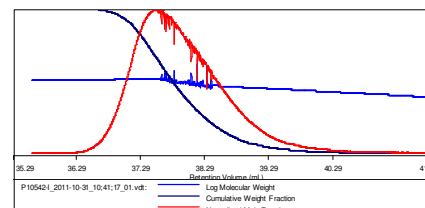


SEC of MMA_nBuMA_ran [first block]:

Sample ID: P10542-I-MMA_nBuMA

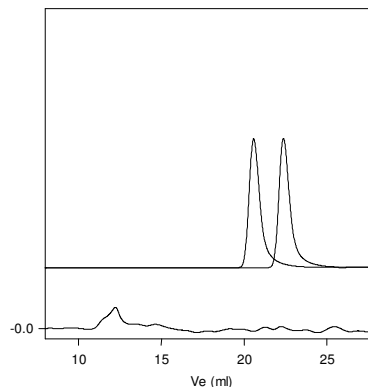


Sample	Mn (Da)	Mw (Da)	Mp (Da)	Mw/Mn	IV (dL/g)
P10542-I_2011-10-31_10:41:17_01.vdt	31,375	31,482	32,951	1.003	0.2571



SEC of MMA_nBuMA_ran-b-HEMATMS:

P10542-MMA_nBuMA_ranHEMA



Size exclusion chromatography of
1. Random copolymer of MMA and nBuMA: Mn 31,500 Mw: 33,000 Mw/Mn 1.05
Poly(MMA-nBuMA_ran)-b- Poly 2-Hydroxy ethyl methacrylate (Protected with TMS)
Mn 31,500-b-48,200 Mw/Mn 1.15
After Deprotection of HEMA TMS : Mn 31,500-b-31,000 Mw/Mn 1.15
In THF after deprotection, the SEC profile shows micellization