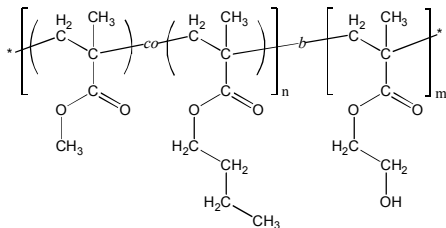


Sample Name:

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

Sample #: P10543-MMAAnBuMAran-b-HEMA

Structure:



Composition:

$M_n \times 10^3$ (g/mol)	18.5- <i>b</i> -21.0
M_w/M_n	1.15
Molar ratio MMA : nBuMA	50 : 50 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	19 : 28 : 53 (wt%)
T_g (MMAAnBuMA)	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.

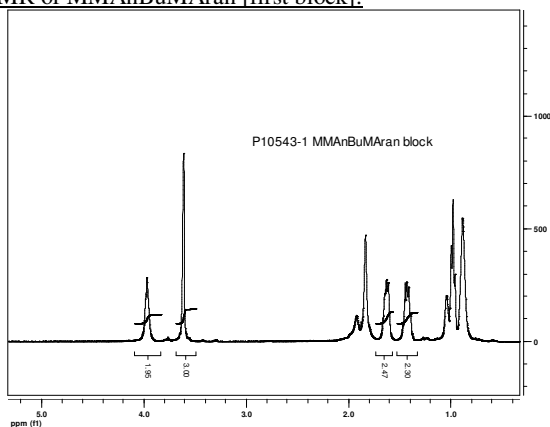
Characterization:

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 (MMAAnBuMA) block.

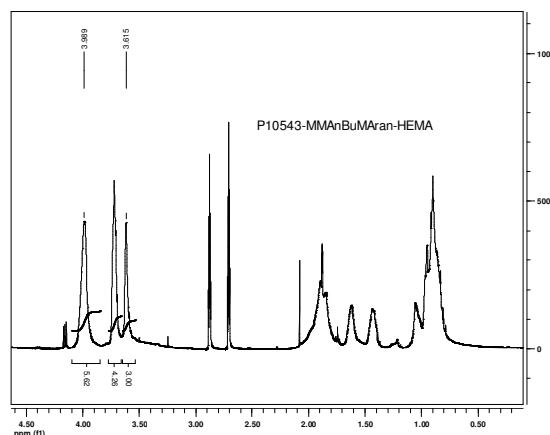
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMAAnBuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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 MMAAnBuMAran [first block]:



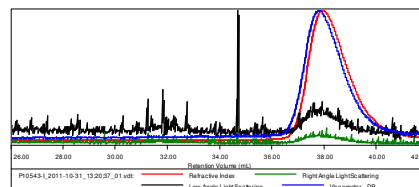
¹H NMR of MMAAnBuMAran-b-HEMA in DMF-d₇:



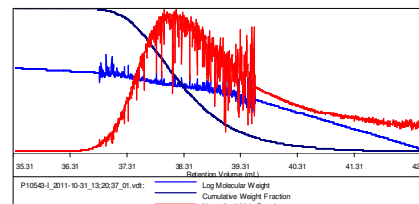
SEC of MMAAnBuMAran [first block]:

Sample ID: P10543-1-MMAAnBuMA

Concentration (mg/mL)	6.8006
Sample dn/dc (mL/g)	0.0800
Method File	PS80K-Oct-0000.vcm
Column Set	3x PL 1113-6300
System	System 1

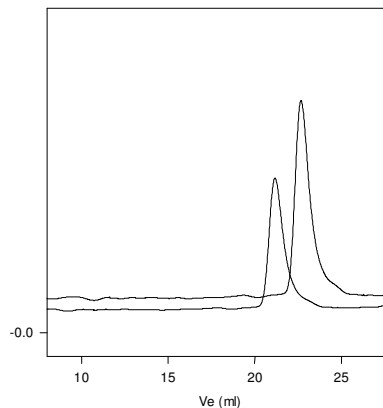


Sample	Mn (Da)	Mw (Da)	Mp (Da)	Mw/Mn	IV (dL/g)
P10543-1_2011-10-31_13:20:37_01.vdt	18,554	25,810	26,303	1.391	0.2146



SEC of MMAAnBuMAran and MMAAnBuMA-b-HEMATMS:

P10543-MMAAnBuMAranHEMA



Size exclusion chromatography of
1. Random copolymer of MMA and nBuMA: Mn 18,500 Mw: 21,200 Mw/Mn 1.15
Poly(MMA-nBuMAran)-b- Poly 2-Hydroxy ethyl methacrylate (Protected with TMS)
Mn 21,500-b-32,600 Mw/Mn 1.15
After Deprotection of HEMA TMS : Mn 18,500-b-21,000 Mw/Mn 1.15
In THF After deprotection , the SEC profile shows no micellization