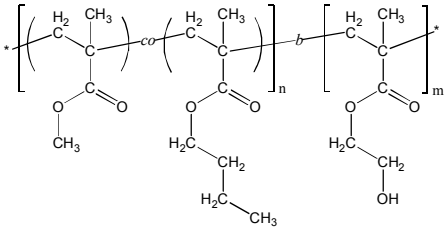
Sample Name:

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

Sample #: P10535-MMAnBuMAran-b-HEMA

Structure:



Composition:

M_n x 10^3 (g/mol)	11.5-*b*-15.0
M_w/M_n	1.15
Molar ratio MMA : nBuMA	50 : 50 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	18 : 25 : 57 (wt%)
T_g (MMAnBuMA)	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.

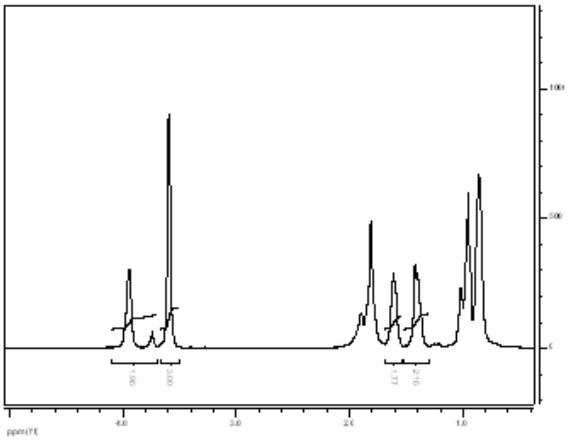
Characterization:

The polymer composition was calculated by ^{1}H NMR. MMA:nBuMA molar ratio was calculated by comparing the peak area of nBuMA -OCH_2- protons at 3.9 ppm and the peak area of MMA -OCH_3 protons at 3.6 ppm. Molecular weight of the second (HEMA) block was calculated by comparing the peak area of HEMA -OCH_2CH_2O- protons and the peak area of nBuMA -OCH_2- protons and using SEC data for the first (MMAnBuMA) block.

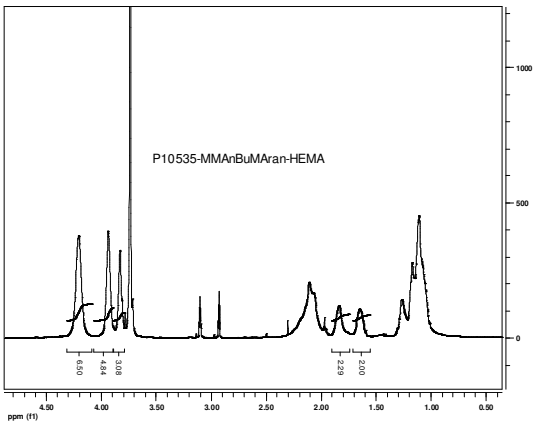
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMAnBuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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.

^{1}H NMR of MMAnBuMAran [first block]:



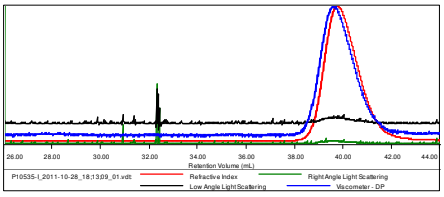
^{1}H NMR of MMAnBuMAran-b-HEMA diblock copolymer:



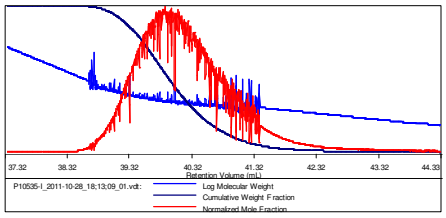
SEC of MMAnBuMAran [first block]:

Sample ID: P10535-MMAnBuMA

Concentration (mg/mL)	9.1218
Sample dn/dc (mL/g)	0.0800
Method File	PS80K-Oct-0000.vcm
Column Set	3x PL 1113-6300
System	System 1

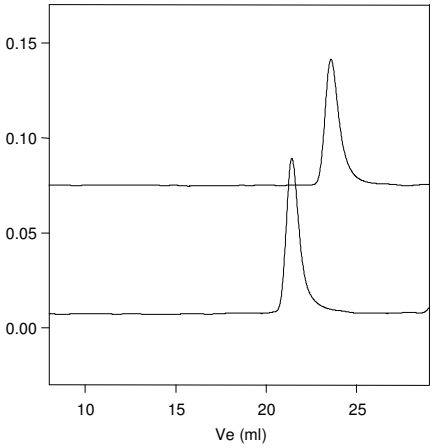


Sample	Mn (Da)	Mw (Da)	Mp (Da)	Mw/Mn	IV (dL/g)
P10535-I_2011-10-28_18;13;09_01.vdt	11,593	12,777	11,543	1.102	0.1298



SEC of MMAnBuMAran and MMAnBuMAran-b-HEMATMS:

P10535-MMAnBuMAran-HEMA



Size exclusion chromatography of
1. Poly nBuMA: Mn 11,500 Mw: 12,600 Mw/Mn 1.10
Poly(nBuMA)-b- Poly 2-Hydroxy ethyl methacrylate (Protected with TMS)
Mn 11,500-b-23,300 Mw/Mn 1.15
After Deprotection of HEMA TMS : Mn 11,500-b-15,000 Mw/Mn 1.15
The deprotected polymer does not elute in THF.