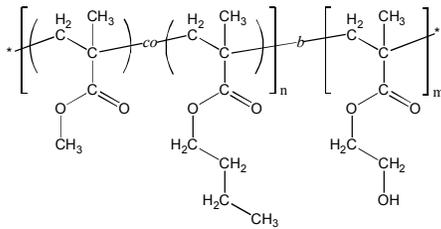


Sample Name:

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

Sample #: P15010-MMAAnBuMAran-b-HEMA

Structure:



Composition:

$M_n \times 10^3$ (g/mol)	26.5-b-21.0
M_w/M_n	1.10
Molar ratio MMA : nBuMA	65 : 35 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	32 : 24 : 44 (wt%)
T_g (MMAAnBuMA)	80 °C
T_g (HEMA)	112 °C

Synthesis Procedure:

Poly([methyl methacrylate-co-n-butyl methacrylate]-b-2-hydroxyethyl methacrylate) block copolymer was synthesized by GTP process polymerization with sequential addition of a mixture of MMA and n-BuMA followed by adding HEMA with protected hydroxyl (trimethyl siloxy ethyl methacrylate monomer). The obtained polymer was precipitated in methanol/acidic to deprotect the hydroxyl group.

Solubility: The polymer is soluble in THF, DMF.

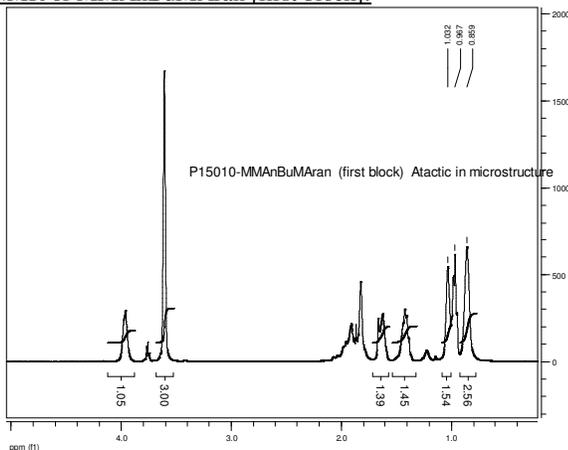
Characterization:

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 (MMAAnBuMA) block.

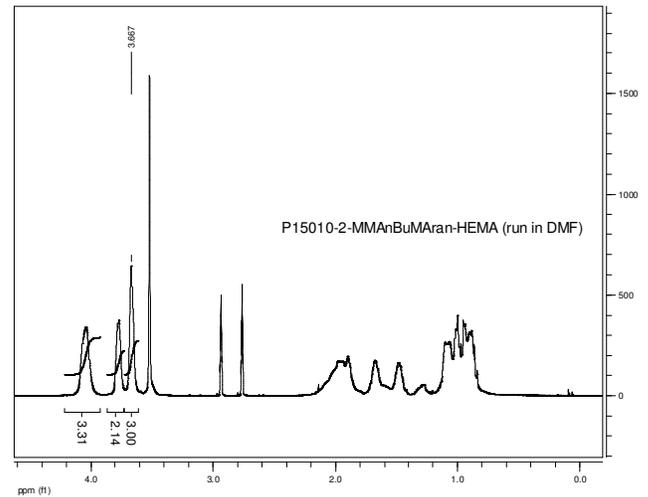
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMAAnBuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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.

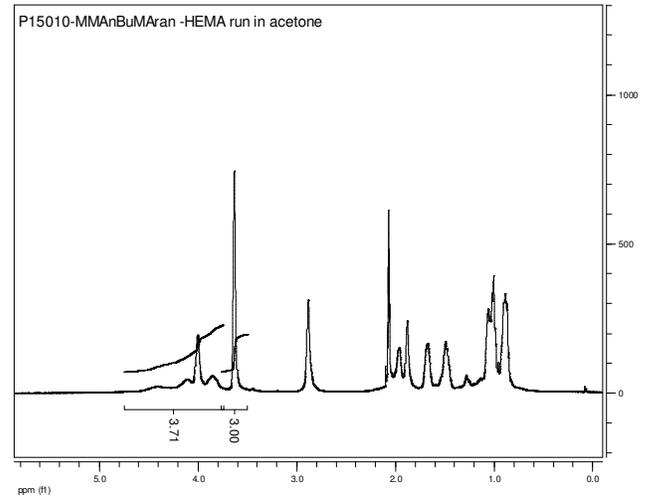
¹H NMR of MMAAnBuMAran [first block]:



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

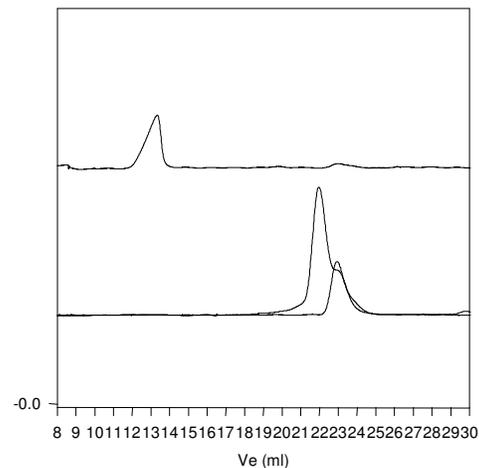


¹H NMR of MMAAnBuMAran-b-HEMA in acetone-d6:



SEC of MMAAnBuMAran and MMAAnBuMAran-b-HEMATMS:

P15010-MMAAnBuMAranHEMA



Size exclusion chromatography of
1. Random copolymer of MMA and nBuMA: M_n 26,500 M_w : 28,500 M_w/M_n 1.08
Poly(MMA-nBuMAran)-b-Poly(2-Hydroxy ethyl methacrylate (Protected with TMS))
 M_n 26,500-b-32,600 M_w/M_n 1.10
After Deprotection of HEMA TMS : M_n 26,000-b-21,000 M_w/M_n 1.10
In THF after deprotection, the SEC profile shows micellization

DSC of MMAAnBuMAran-b-HEMA:

