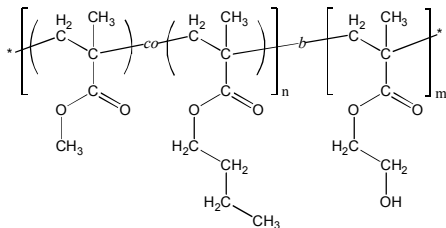


Sample Name:

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

Sample #: P6746-MMA_nBuMA_ran-b-HEMA

Structure:



Composition:

$M_n \times 10^3$ (g/mol)	15.0- <i>b</i> -7.0
M_w/M_n	1.10
Molar ratio MMA : nBuMA	90 : 10 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	59 : 9 : 32 (wt%)
T_g	120 °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.

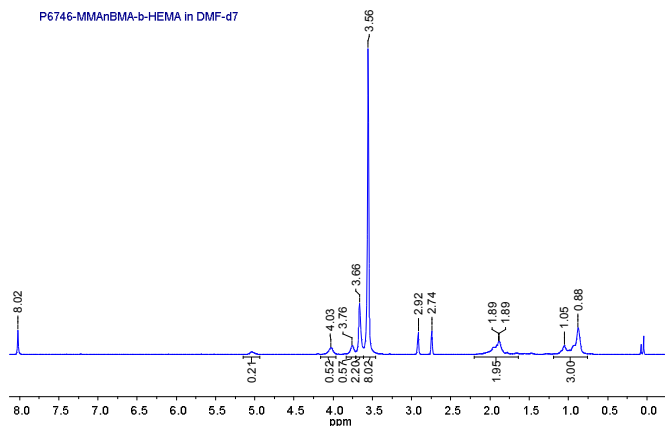
Characterization:

The polymer composition was determined by ^1H NMR. MMA:nBuMA molar ratio was calculated by comparing the integration of the $-\text{OCH}_2$ -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 $-\text{OCH}_2$ - 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.

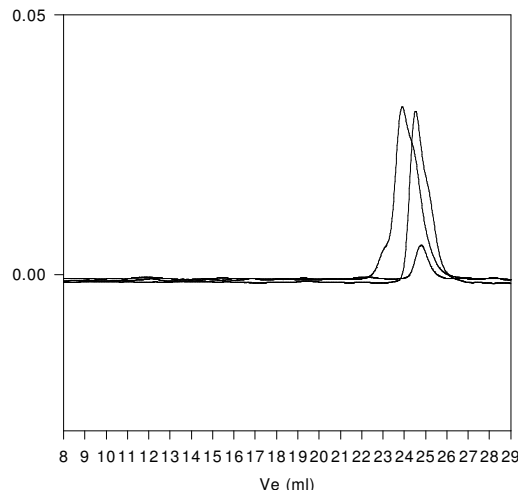
Thermal analysis of the sample was done on a TA Q100 differential scanning calorimeter (DSC) at a heating rate of 10°C/min. The glass transition temperature (T_g) was determined as a midpoint of step change in heat flow curve for the second heating scan.

^1H NMR of MMA_nBuMA_ran-b-HEMA (400 MHz, DMF-d₇):



SEC of MMA_nBuMA_ran and MMA_nBuMA_ran-b-HEMATMS:

P6746--MMA_nBuMA_ranHEMA



Size exclusion chromatography of

1. Random copolymer of MMA and nBuMA: M_n 15000 M_w : 16500 M_w/M_n 1.08

Poly(MMA-nBuMA_ran)-b- Poly 2-Hydroxy ethyl methacrylate (Protected with TMS)

M_n 15000-b-11000 M_w/M_n 1.10

After Deprotection of HEMA TMS : M_n 15000-b-7000 M_w/M_n 1.10

In THF after deprotection, the SEC profile shows no micellization and the elution retarded

DSC of MMA_nBuMA_ran-b-HEMA:

