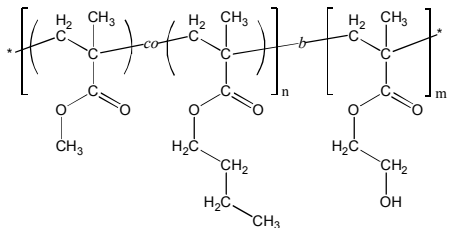


Sample Name:

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

Sample #: P9767-MMA_nBuMA_ran-b-HEMA**Structure:****Composition:**

$M_n \times 10^3$ (g/mol)	19.0- <i>b</i> -19.0
M_w/M_n	1.16
Molar ratio MMA : nBuMA	65 : 35 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	28 : 22 : 50 (wt%)
T_g (MMA _n BuMA)	86 °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.

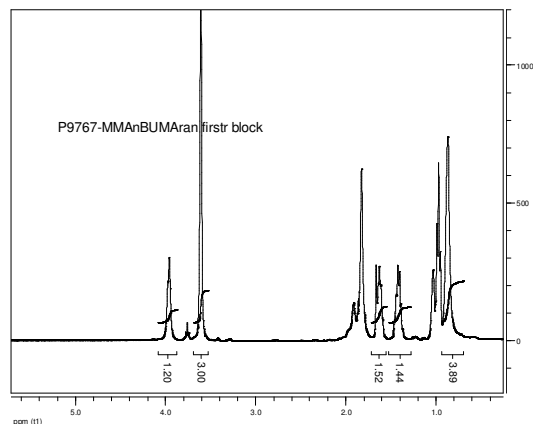
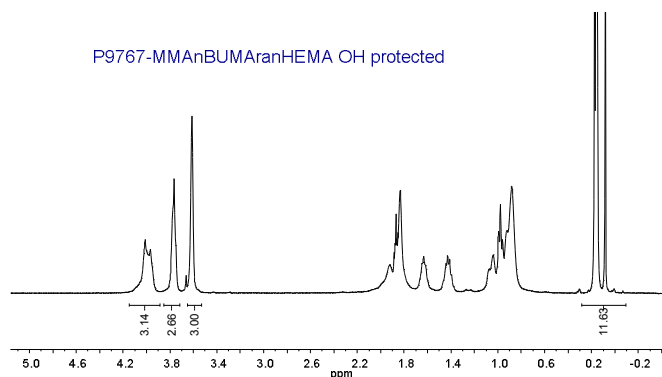
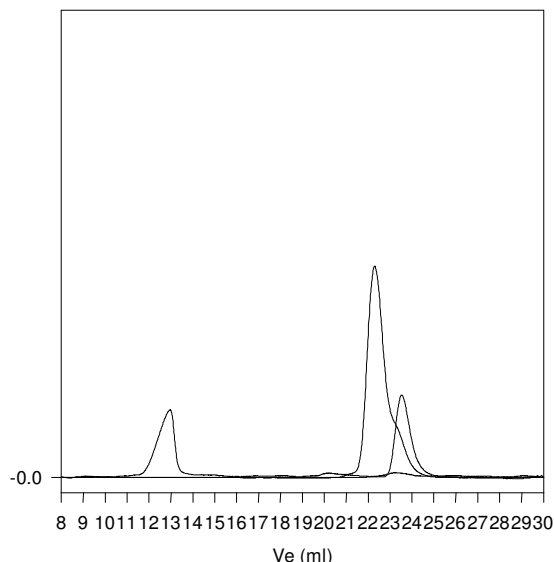
Solubility: The polymer is soluble in THF, DMF.

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-HEMATMS:****SEC of MMA_nBuMA_ran and MMA_nBuMA_ran-b-HEMATMS:****P9767- MMA_nBuMA_ran-b-HEMA**

Size exclusion chromatography of

1. MMA_nBuMA_ran block Mn 19,000 Mw: 21,000 Mw/Mn 1.10

2. MMA_nBuMA_ran-b-HEMATMS: 19,000-29,500 Mw/Mn : 1.16

After deprotection of the hydroxyl group:

MMA_nBuMA_ran-b-HEMA : Mn 19,000-*b*-19,000 Mw/Mn 1.16

Shows micellization in THF

DSC of MMA_nBuMA_ran-b-HEMA: