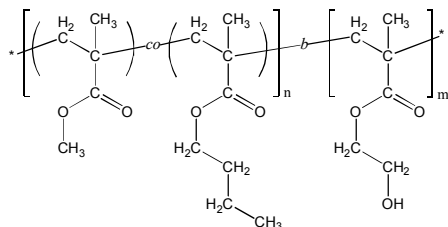


Sample Name:

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

Sample #: P9805-MMA_nBuMA_ran-b-HEMA

Structure:**Composition:**

$M_n \times 10^{-3}$ (g/mol)	22.0- <i>b</i> -15.5
M_w/M_n	1.10
Molar ratio MMA : nBuMA	54 : 46 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	27 : 32 : 41 (wt%)
T_g (MMA _n BuMA)	79 °C
T_g (HEMA)	157 °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.

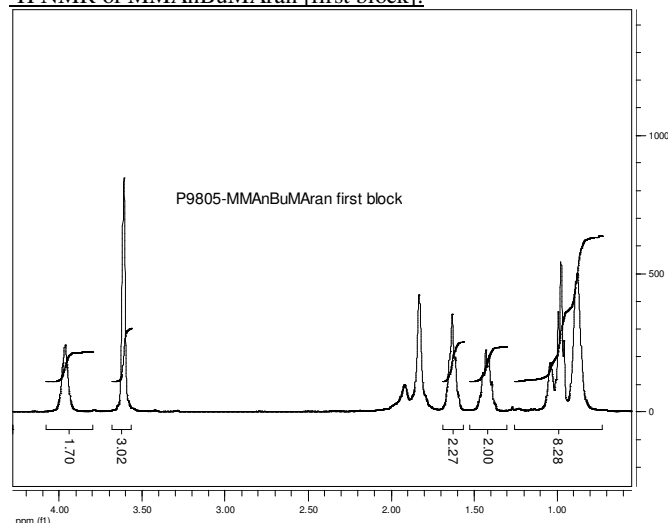
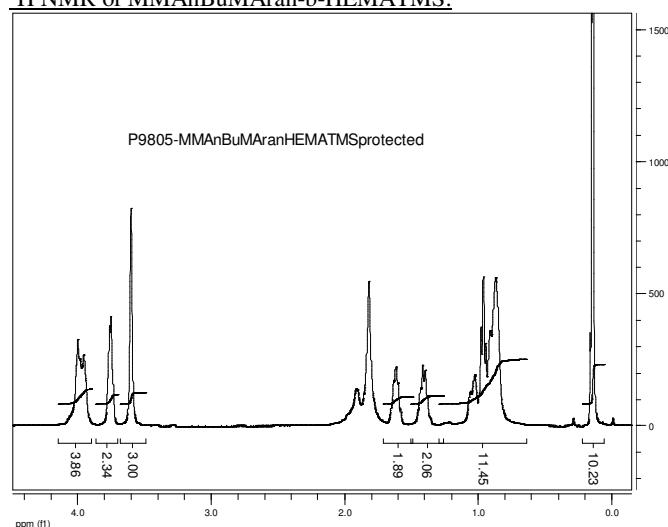
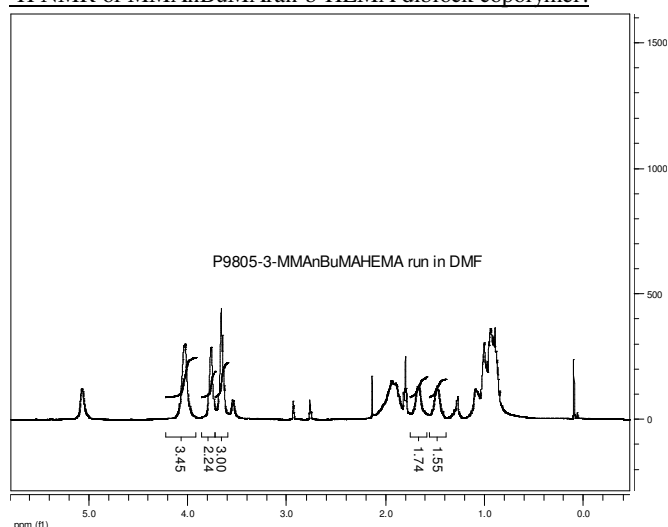
Solubility: The polymer is soluble in THF, DMF.

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 $\delta = 3.9$ 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 (MMA_nBuMA) block.

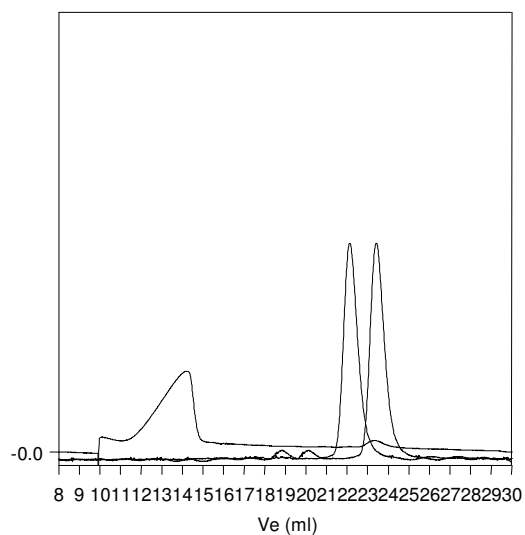
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA_nBuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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:** **^1H NMR of MMA_nBuMA_ran-b-HEMA diblock copolymer:**

SEC of MManBuMAran and MManBuMAran-b-HEMATMS:

P9805--MManBuMAranHEMA



Size exclusion chromatography of

1. Random copolymer of MMA and nBuMA: Mn 22,000 Mw: 23,500

Mw/Mn 1.08

2. Poly(MMA-nBuMAran)-b- Poly 2-Hydroxy ethyl methacrylate

(Protected with TMS)

Mn 22,000-b-24,100 Mw/Mn 1.09

After Deprotection of HEMA TMS : Mn 22,000-b-15,500 Mw/Mn 1.10

In THF after deprotection, the SEC profile shows micellization

DSC of MManBuMAran-b-HEMA:

