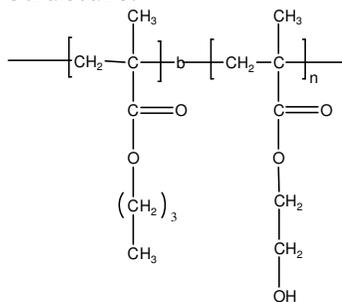


**Sample Name:**

**Poly( Methylmethacrylate –co-n-butyl methacrylate random -b-2-hydroxy ethyl methacrylate)**

**Sample #: P9455-MMAnBuMAran-b-HEMA**

**Structure:****Composition:**

Mn × 10 <sup>3</sup> MMAnBuMAran-b-HEMA	PDI
21.0-b-13.0	1.15
MMA:nBuMA	70:30 mol/mol
MMA:nBuMA:HEMA	38:24:38 wt%
T <sub>g</sub> for MMAnBuMA: 97°C	T <sub>g</sub> for HEMA: 117°C

**Synthesis Procedure:**

Poly(methylmethacrylate-n-butyl methacrylate random-b-2-hydroxy ethyl methacrylate) block copolymer is synthesized by living anionic polymerization with sequential addition of a mixture of MMA and n-butyl methacrylate followed by adding protecting hydroxyl HEMA (trimethyl siloxy ethyl methacrylate monomer). The obtained polymer was precipitated in methanol/acidic to deprotect the hydroxyl group.

**Characterization:**

SEC analysis of the obtained block copolymer in THF in presence of triethyl amine as eluent resulting in an ambiguity of the result because some of the trimethylsilyloxy ethyl methacrylate units are deprotected to convert hydroxy ethyl methacrylate.

The SEC analysis of the final polymer is carried out after protecting OH groups of hydroxy ethyl methacrylate to acetate group was treated with acetic anhydride in presence of pyridine. The SEC analysis of the obtained polymer gives more reliable results.

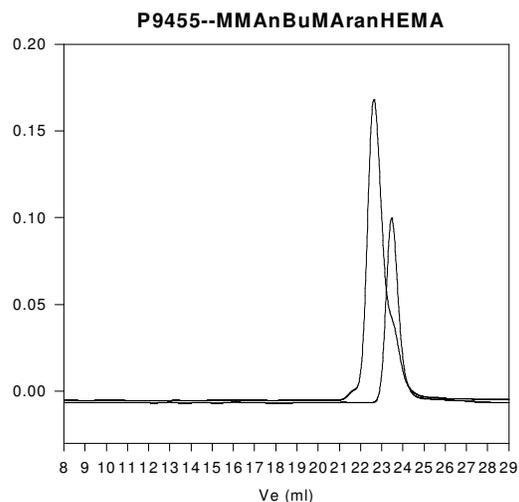
The final block copolymer composition by <sup>1</sup>H-NMR spectroscopy in CdCl<sub>2</sub> also yield the uncertainty of the analysis because of poor solubility of poly HEMA block in CdCl<sub>2</sub>. The composition of the obtained polymer therefore, carried out in CdCl<sub>2</sub> after protecting the OH group with acetic anhydride by comparing the peak area CH<sub>2</sub> alkyl ester (4 protons) group at 1.6 and 1.5 ppm and subtracting 6 protons values for nBuMA monomers (3 from α-CH<sub>3</sub> and 3 protons from terminal CH<sub>3</sub> alkyl ester group) between 0.9ppm to 1.2ppm to calculate 3 protons (α-CH<sub>3</sub>) from HEMA monomers. Block copolymer PDI is determined by SEC.

**Thermal analysis:**

Thermal analysis of the samples was carried out on a TA Q100 differential scanning calorimeter at a heating rate of 10°C/min. The midpoint of the slope change of the heat flow plot of the second heating scan was considered as the glass transition temperature (T<sub>g</sub>).

**Solubility:**

Polymer is soluble in DMF, THF.

**SEC of the block copolymer:**

Size exclusion chromatography of  
 1. Random copolymer of MMA and nBuMA: Mn 21000 Mw: 23000 Mw/Mn 1.10  
 Poly(MMA-nBuMAran)-b- Poly 2-Hydroxy ethyl methacrylate (Protected with TMS)  
 Mn 21,000-b-20500 Mw/Mn 1.10  
 After Deprotection of HEMA TMS : Mn 21000-b-13000 Mw/Mn 1.15

**DSC thermogram for the diblock polymer:**