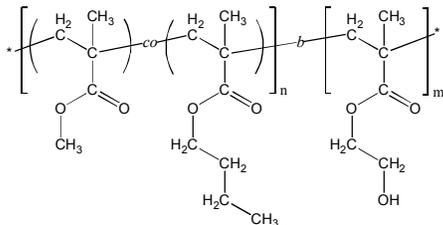


Sample Name:

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

Sample #: P9333-MMA*n*BuMA*r*an-*b*-HEMA

Structure:



Composition:

$M_n \times 10^3$ (g/mol)	23.0- <i>b</i> -22.0
M_w/M_n	1.10
Molar ratio MMA : nBuMA	65 : 35 (mol/mol)
Weight ratio MMA:nBuMA:HEMA	29 : 22 : 49 (wt%)
T_g (MMA <i>n</i> BuMA)	85 °C
T_g (HEMA)	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:

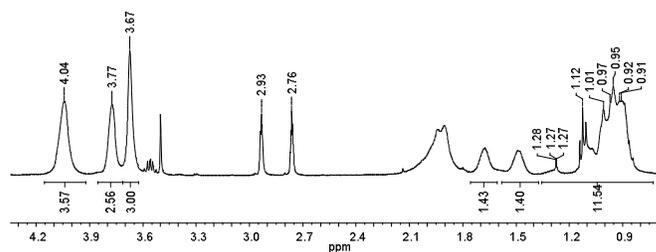
The polymer composition was determined by ^1H NMR. MMA:nBuMA molar ratio was calculated by comparing the integration of the $-\text{OCH}_2-$ protons of nBuMA (at $\delta = 3.9$ ppm) to the integration of methoxy group of MMA (at $\delta = 3.6$ ppm). Molecular weight of the second (HEMA) block was calculated 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*n*BuMA) block.

The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA*n*BuMA-*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.

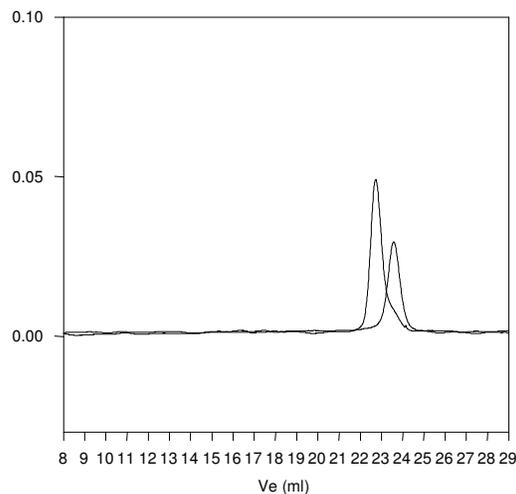
^1H NMR of MMA*n*BuMA*r*an-*b*-HEMA in DMF-*d*7:

P9333-HMMA*n*BuMA-HEMA in DMF



SEC of MMA*n*BuMA*r*an and MMA*n*BuMA-*b*-HEMATMS:

P9333--MMA*n*BuMA*r*anHEMA



Size exclusion chromatography of

1. Random copolymer of MMA and nBuMA: M_n 23,000 M_w : 24,300 M_w/M_n 1.06
Poly(MMA-*n*BuMA*r*an)-*b*- Poly 2-Hydroxy ethyl methacrylate (Protected with TMS)
 M_n 23,000-*b*-34,000 M_w/M_n 1.10
After Deprotection of HEMA TMS : M_n 23,000-*b*-22,000 M_w/M_n 1.10

DSC thermogram of MMA*n*BuMA-*b*-HEMA:

