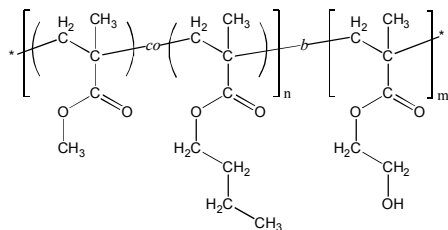


Sample Name:

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

Sample #: P10552-MMA_nBuMA_ran-b-HEMA

Structure:



Composition:

| | |
|-------------------------------|----------------------|
| $M_n \times 10^3$ (g/mol) | 28.0- <i>b</i> -49.0 |
| M_w/M_n | 1.15 |
| Molar ratio MMA : nBuMA | 60 : 40 (mol/mol) |
| Weight ratio MMA:nBuMA:HEMA | 19 : 25 : 56 (wt%) |
| T_g (MMA _n BuMA) | 65 °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.

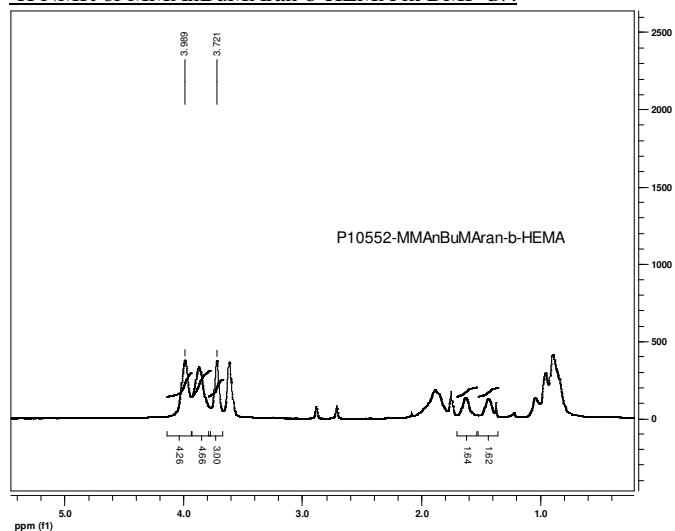
Characterization:

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 HEMA 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.

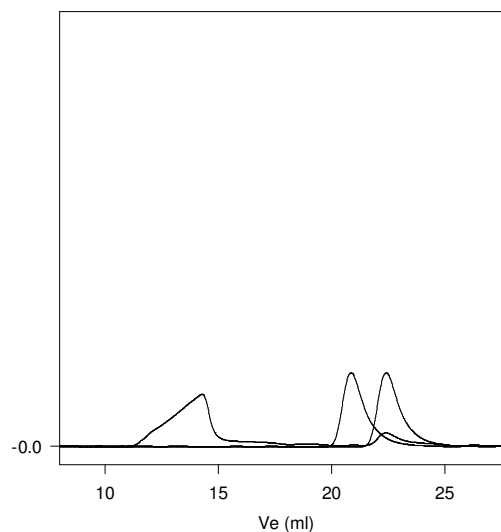
Thermal analysis of the sample was done on a TA Q100 differential scanning calorimeter (DSC) at a heating rate of 10°C/min. The glass transition temperature (T_g) was determined as a midpoint of step change in heat flow curve for the second heating scan.

¹H NMR of MMA_nBuMA_ran-b-HEMA in DMF-d₇:



SEC of MMA_nBuMA_ran [first block]:

P10552--MMA_nBuMA_ranHEMA



Size exclusion chromatography of

1. Random copolymer of MMA and nBuMA: Mn 28,000 Mw: 30,500 Mw/Mn 1.08

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

Mn 28,000-b-77,000 Mw/Mn 1.15

After Deprotection of HEMA TMS : Mn 28,000-b-49,000 Mw/Mn 1.15

In THF after deprotection, the SEC profile shows micellization