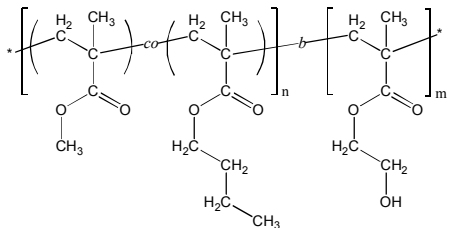


Sample Name:

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

Sample #: P10561-MMA_nBuMA_ran-b-HEMA

Structure:



Composition:

| | |
|-------------------------------|----------------------|
| $M_n \times 10^3$ (g/mol) | 29.5- <i>b</i> -13.0 |
| M_w/M_n | 1.19 |
| Molar ratio MMA : nBuMA | 50 : 50 (mol/mol) |
| Weight ratio MMA:nBuMA:HEMA | 29 : 41 : 31 (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.

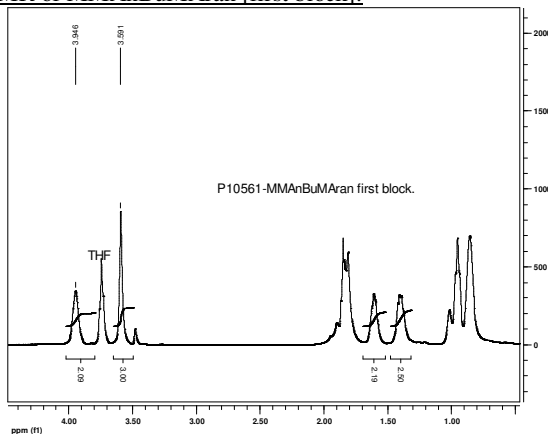
Characterization:

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 HEMATMS to the integration of methoxy group of MMA and using SEC data for the first (MMA_nBuMA) block.

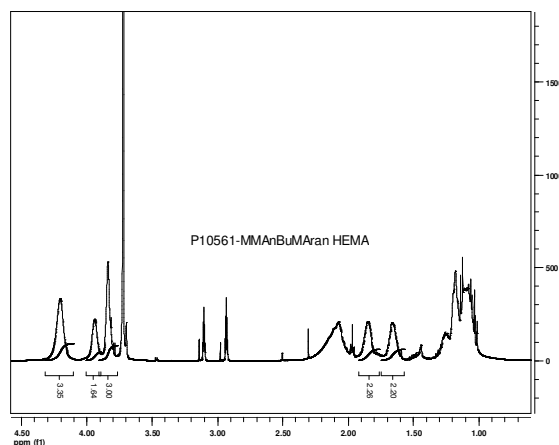
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA_nBuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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]:



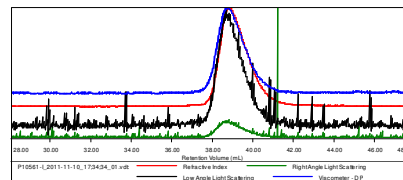
¹H NMR of MMA_nBuMA_ran-b-HEMA in DMF-d₇:



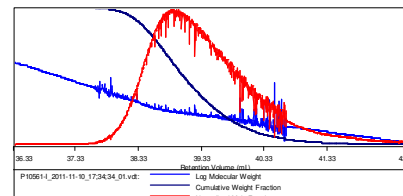
SEC of MMA_nBuMA_ran [first block]:

Sample ID: P10561-I-MMA_nBuMA

| | |
|-----------------------|--------------------|
| Concentration (mg/mL) | 5.3809 |
| Sample dn/dc (mL/g) | 0.0800 |
| Method File | PS80K-Oct-0000.vcm |
| Column Set | 3x PL 1113-6300 |
| System | System 1 |

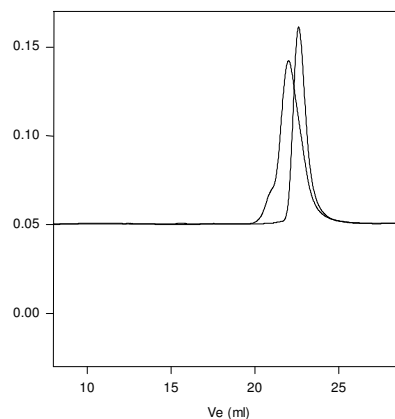


| Sample | Mn (Da) | Mw (Da) | Mp (Da) | Mw/Mn | IV (dL/g) |
|--------------------------------------|---------|---------|---------|-------|-----------|
| P10561-I_2011-11-10_17:34:34_01.v.dl | 29,495 | 32,048 | 32,016 | 1.067 | 0.2428 |



SEC of MMA_nBuMA_ran and MMA_nBuMA_ran-b-HEMATMS:

P10561-MMA_nBuMA_ran-HEMA



Size exclusion chromatography of
1. Poly MMA_nBuMA_ran: Mn 29,500 Mw/Mn 1.08
Poly(MMA_nBuMA_ran-b- Poly 2-Hydroxy ethyl methacrylate (Protected with TMS)
Mn 29,500-b-20,200 Mw/Mn 1.19
After Deprotection of HEMA TMS : Mn 29,000-b-13,000 Mw/Mn 1.19
The deprotected polymer does not elute in THF.