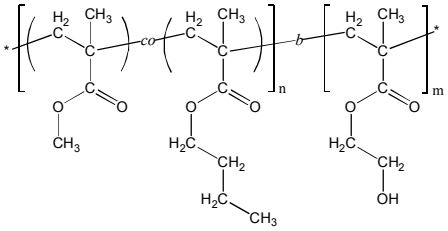
## Sample Name:

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

## Sample #: P18661-MMAnBuMAran-b-HEMA

**Structure:**



**Composition:**

| | |
|---|---|
| $M_n$ x $10^3$ (g/mol) | 22.5-*b*-25.0 |
| $M_w/M_n$ | 1.15 |
| Molar ratio MMA : nBuMA | 68 : 32 (mol/mol) |
| Weight ratio MMA:nBuMA:HEMA | 28 : 19 : 53 (wt%) |

### 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.

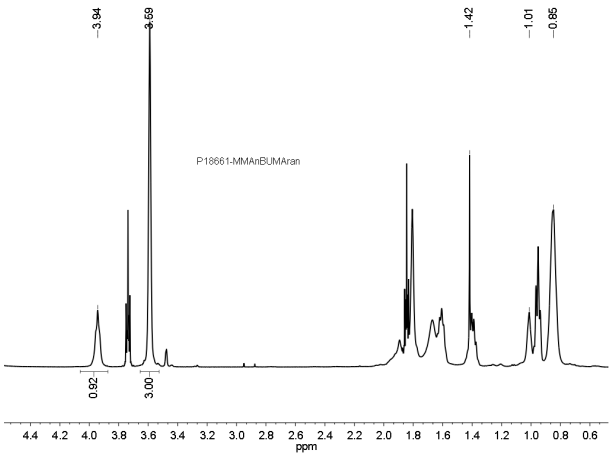
### Characterization:

The polymer composition was determined by $^1$H NMR. MMA:nBuMA molar ratio was calculated by comparing the integration of the -$OCH_2$- 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 -$OCH_2$- protons of HEMATMS to the integration of methoxy group of MMA and using SEC data for the first (MMAnBuMA) block.

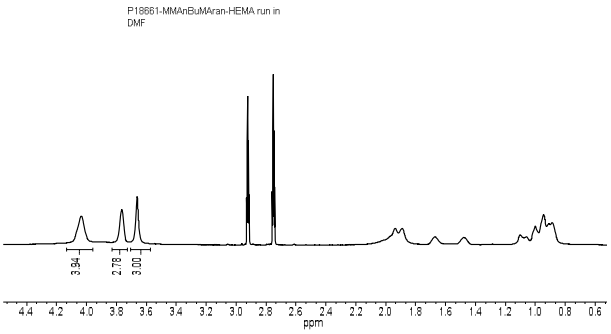
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMAnBuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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.

$^1$H NMR of MMAnBuMAran [first block]:



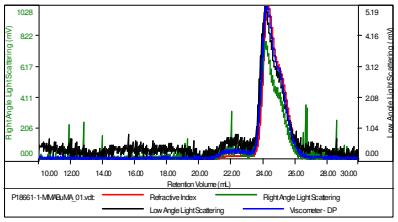

$^1$H NMR of MMAnBuMAran-b-HEMA diblock copolymer:



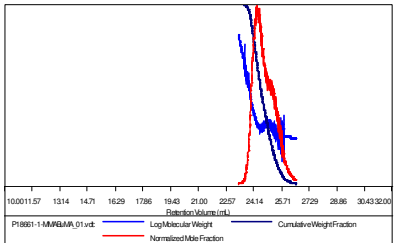

SEC of MMAnBuMAran [first block]:

**Sample ID: P18661-MMAnBUMAran**

| | |
|---|---|
| Concentration (mg/mL) | 7.6513 |
| Sample dn/dc (mL/g) | 0.0850 |
| Method File | PS80K-Apr15-2014-0000.vcm |
| Column Set | 3x PL 1113-6300 |
| Solvent | THF |



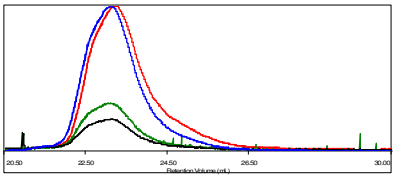

| Sample | Mn | Mw | Mp | Mw/Mn | IV |
|---|---|---|---|---|---|
| P18661-1-MMABuMA_01.vdt | 22,343 | 23,239 | 22,919 | 1.040 | 0.0614 |




SEC of MMAnBuMAran-b-HEMATMS:

**Sample ID: P18661-2-MMABuMA-HEMATMS**

| | |
|---|---|
| Concentration (mg/mL) | 10.1294 |
| Sample dn/dc (mL/g) | 0.0840 |
| Method File | PS80K-Apr15-2014-0000.vcm |
| Column Set | 3x PL 1113-6300 |
| Solvent | THF |




| Sample | Mn | Mw | Mp | Mw/Mn | IV |
|---|---|---|---|---|---|
| P18661-2-MMABuMA-HEMATMS_01.vt | 51,805 | 59,191 | 59,720 | 1.143 | 0.1072 |