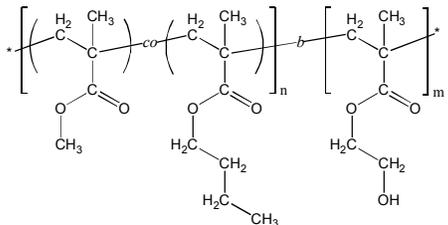


Sample Name:

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-b-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.

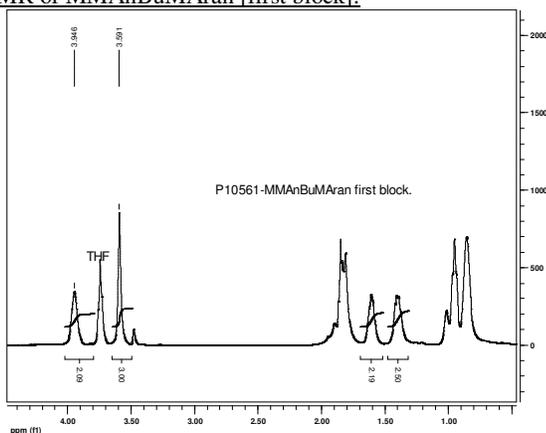
Characterization:

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.

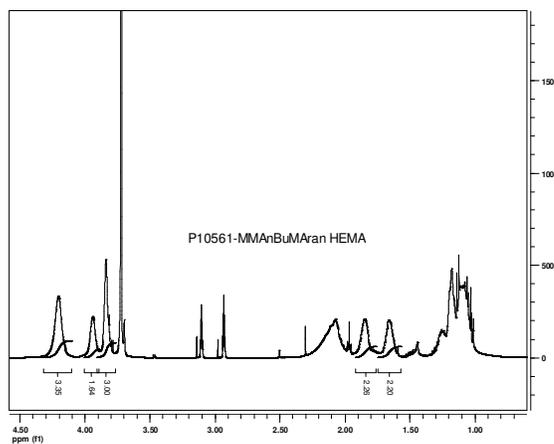
The average molecular weight and polydispersity index were determined by size exclusion chromatography (SEC). For SEC analysis, the MMA_nBuMA-b-HEMA block copolymer can be treated with acetic anhydride in presence of pyridine to convert the hydroxy-groups to acetate groups.

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]:



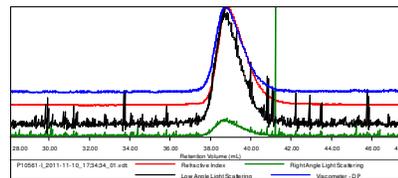
¹H NMR of MMA_nBuMA_ran-b-HEMA in DMF-d₇:



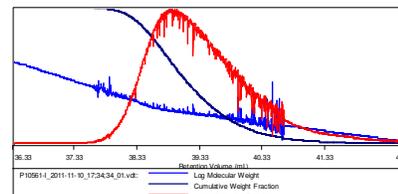
SEC of MMA_nBuMA_ran [first block]:

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

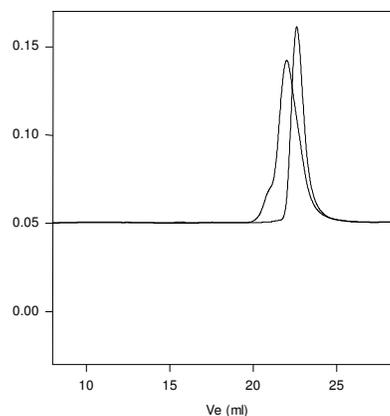


Sample	Mn (Da)	Mw (Da)	Mp (Da)	Mw/Mn	IV (dL/g)
P10561-I_2011-11-10_173434_01.vd	29,495	32,048	32,016	1.087	0.2428



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: 31,500 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.