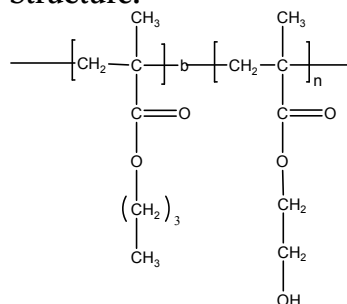


Poly(n-butyl methacrylate-b-2-hydroxy ethyl methacrylate)

Sample #: P10471-nBuMAHEMA

Structure:



Composition:

| | |
|---------------------------------------|--|
| Mn $\times 10^3$ nBuMA-b-HEMA | PDI |
| 30.0-b-19.0 | 1.18 |
| T _g for nBuMA block: 53 °C | T _g for HEMA block: 103 °C |

Synthesis Procedure:

Poly(n-butyl methacrylate-*b*-2-hydroxy ethyl methacrylate) block copolymer is synthesized by living anionic polymerization with sequential addition of n-butyl methacrylate and protecting hydroxyl HEMA (trimethyl siloxy ethyl methacrylate monomer). The obtained polymer was precipitated in methanol/acidic to deprotect the hydroxyl group.

Characterization:

SEC analysis of the obtained block copolymer in THF in presence of triethyl amine as eluent resulting in an ambiguity of the result because some of the trimethylsiloxyl ethyl methacrylate units are deprotected to convert hydroxy ethyl methacrylate.

The SEC analysis of the final polymer is carried out after protecting OH groups of hydroxy ethyl methacrylate to acetate group was treated with acetic anhydride in presence of pyridine. The SEC analysis of the obtained polymer gives more reliable results.

The final block copolymer composition by $^1\text{H-NMR}$ spectroscopy in CdCl_2 also yield the uncertainty of the analysis because of poor solubility of poly HEMA block in CdCl_2 . The composition of the obtained polymer therefore, carried out in CdCl_2 after protecting the OH group with acetic anhydride by comparing the peak area CH_2 alkyl ester (4 protons) group at 1.6 and 1.5 ppm and subtracting 6 protons values for nBuMA monomers (3 from $\alpha\text{-CH}_3$ and 3 protons from terminal CH_3 alkyl ester group) between 0.9ppm to 1.2ppm to calculate 3 protons ($\alpha\text{-CH}_3$) from HEMA monomers. Block copolymer PDI is determined by SEC.

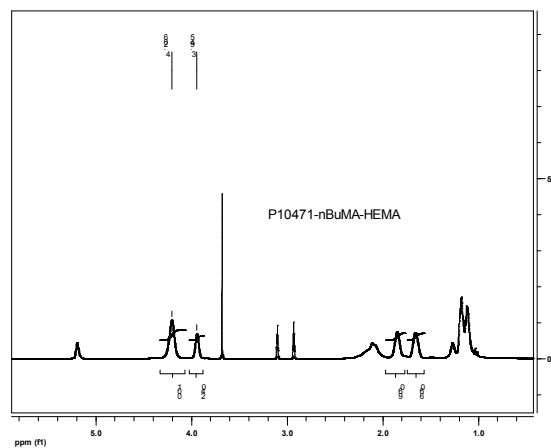
Thermal analysis:

Thermal analysis of the samples was carried out on a TA Q100 differential scanning calorimeter at a heating rate of 10°C/min. The midpoint of the slope change of the heat flow plot of the second heating scan was considered as the glass transition temperature (T_g).

Solubility:

Polymer is soluble in DMF, THF.

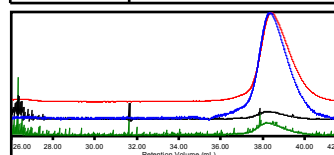
¹H-NMR Spectrum of the block in DMF:



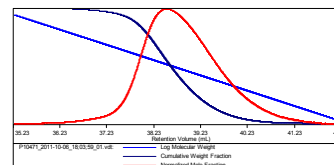
SEC of the block copolymer:

Sample ID: P10471-1

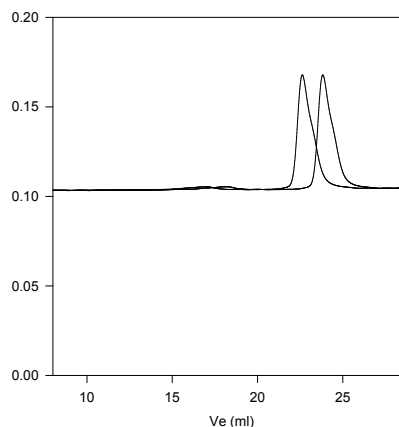
| | |
|-----------------------|---------------------|
| Concentration (mg/mL) | 5.4975 |
| Sample dn/dc (mL/g) | 0.0760 |
| Method File | PS80K-July-0000.vcm |
| Column Set | 3x PL 1113-6300 |
| System | System 1 |



| Sample | Mn (Da) | Mw (Da) | Mp (Da) | Mw/Mn | IV (dL/g) |
|-----------------------------------|---------|---------|---------|-------|-----------|
| P10471_2011-10-06_18:03:59_01.vdt | 30,397 | 32,180 | 32,674 | 1.059 | 0.2429 |



P10471--nBuMAHEMA



Size exclusion chromatography of

1. Poly nBuMA: Mn 30,000 Mw: 32,000 Mw/Mn 1.06

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

Mn 30,000-b-39,500 Mw/Mn 1.18
After Degradation of UEMA-TMO

After Deprotection of HEMA TMS : Mn 30,000-b-19,000 Mw/Mn 1.18
The deprotected polymer does not elute in THF

The deprotected polymer does not elute in THF.

DSC thermogram for the polymer:

