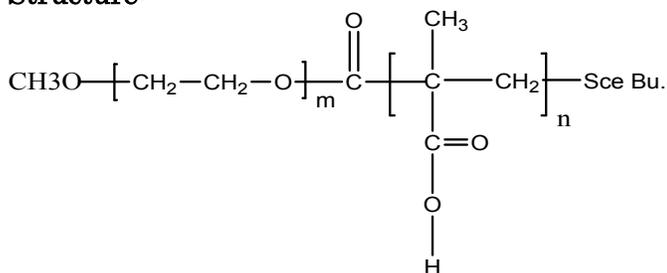


**Sample Name:** Poly(ethylene oxide -b- methacrylic acid)

**Sample #:** P8060-EOMAA

**Structure:**



**Composition:**

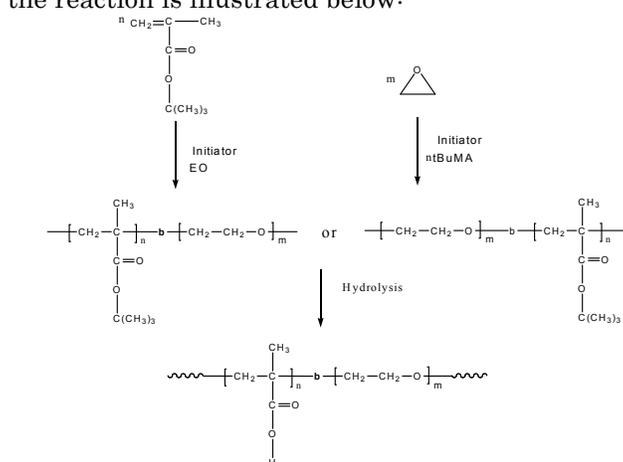
Mn x 10 <sup>3</sup> PEO-b-PMAA	PDI
3.0-b-1.2	1.15

**Synthesis Procedure:**

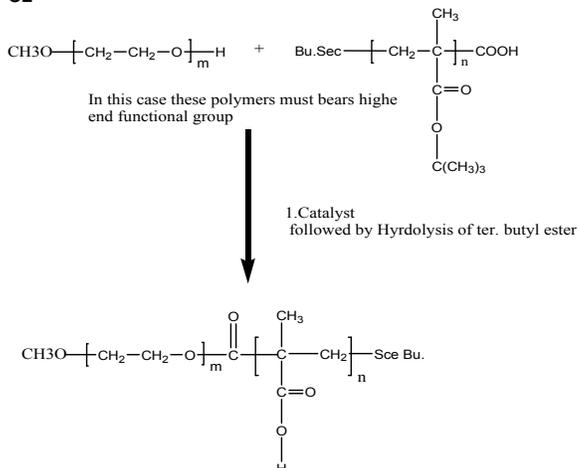
Poly(ethylene oxide -b- methylacrylic acid) is prepared by 2 different routes:

A. By living anionic polymerization of sequential addition of EO and tBuMA (ethylene oxide or t-butyl methacrylate) followed by hydrolysis of the t-butyl group<sup>1</sup> or

B. by chemical coupling reaction of the corresponding functionalized polymer. The scheme of the reaction is illustrated below:



or



**Characterization:**

An aliquot of the first anionic block was terminated before addition of the second block and analyzed by size exclusion chromatography (SEC) to obtain the molecular weight and polydispersity index (PDI). The final block copolymer composition was calculated from <sup>1</sup>H-NMR spectroscopy by comparing the peak area of the ethylene oxide protons at about about 3.6 ppm with the tert.butyl protons at about 1.4 ppm.

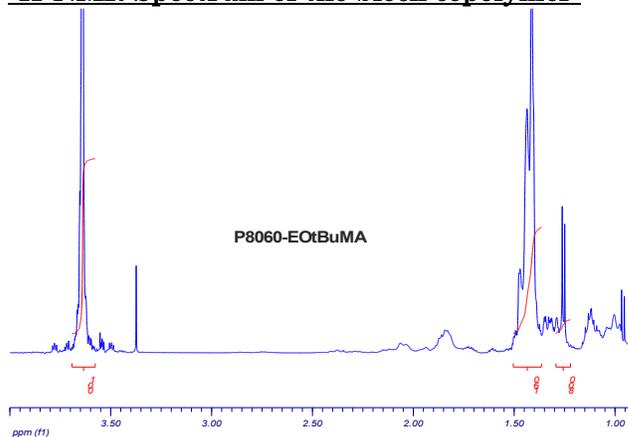
**Hydrolysis:**

To cleave the tert.butyl ester moiety the hydrolysis was carried out in dioxane using acid catalyst. The degree of hydrolysis was checked by FTIR the disappearance of characteristics at 1362 cm<sup>-1</sup>.

**Solubility:**

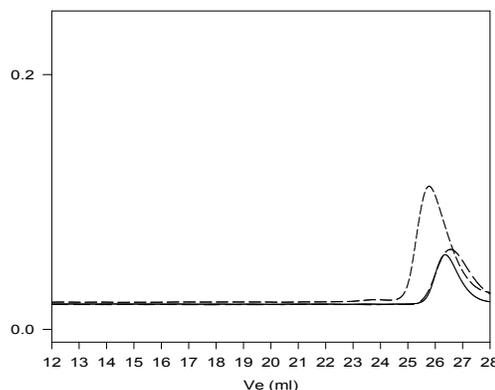
Poly(ethylene oxide -b- methacrylic acid) is soluble in water, THF, methanol, ethanol and precipitate out in hexane, ether.

**<sup>1</sup>H-NMR Spectrum of the block copolymer:**



**SEC of the block copolymer:**

P8060A-EOtBuMA Precursor for P8060-EOMAA



Size exclusion chromatography of poly(tert-butyl methacrylate-b-ethylene oxide)

- COOH terminated Poly(tert-butylmethacrylate), M<sub>n</sub>=2200 M<sub>w</sub>=2500, PI=1.11
- Poly ethylene glycol methylether: Mn 3000 Mw: 3200 PI=1.06
- - - After the linking reaction: Poly (Ethylene oxide-b-tert-Butyl methacrylate): Mn 3000-b-2200 PI=1.15
- After hydrolysis of the ster fuction: PEO-b-MAA Mn: 3000-b-1200 Mw/Mn 1.15

**References:**

J. Wang, S. K. Varshney, J. Jerome and Ph. Teyssie "Synthesis of AB (BA) ABA and BAB Block copolymers of tert-butylmethacrylate (A) and ethylene oxide (B) " *CA Vol 117, 16, 151478, J. Polym. Sci., Part A: Polym. Chem. Ed., 1992, 30, 2251-2261.*

## Thermal analysis of the P8060-EOMAA

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 ( $T_g$ ).

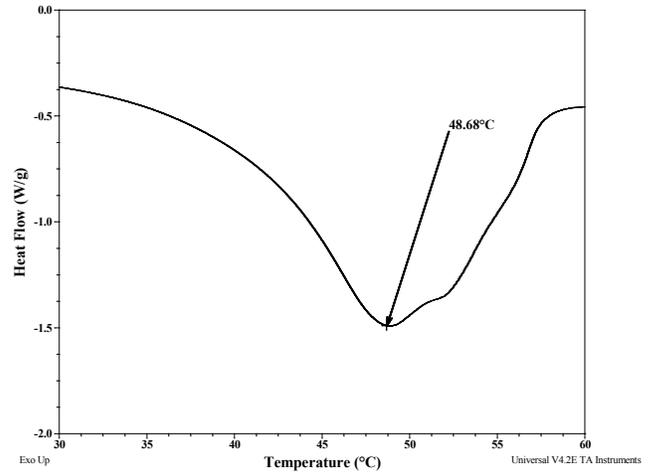
### Melting and crystallization curve for the sample

The melting temperature ( $T_m$ ) was taken as the maximum of the endothermic peak whereas the crystallization temperature ( $T_c$ ) was considered as the minimum of the exothermic peak.

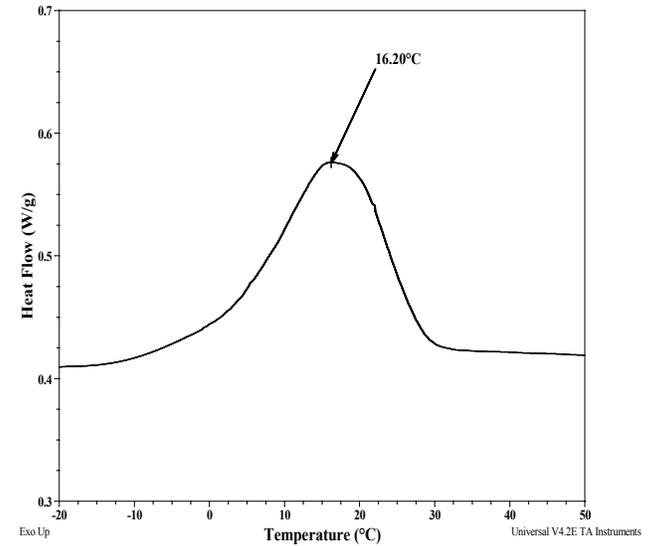
### Thermal analysis results at a glance

Sample	$T_m$ (°C)	$T_c$ (°C)	$T_g$ (°C)
EO Block	49	16	-41
AA block	-	-	Not distinct

### Melting curve for the polymer:



### Crystallization curve for EO block:



### Thermogram for the EO block:

