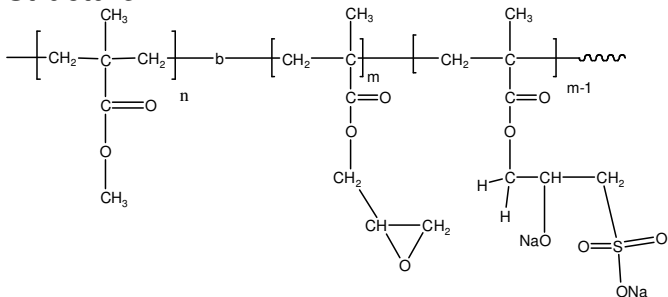


Sample Name:

Poly(Methyl methacrylate-b-Glycidyl methacrylate) – Sulfonated Dialized Polymer

Sample #: P18477B-MMAGMA-Na2SO3

Structure:



Composition:

Mn × 10 ³ MMA-b-GMA-Na2SO3	PDI
4.2-b-15.5 (before sulfonation)	1.4
PMMA microstructure	Sndio:hetero:iso 73 : 20 : 7
Degree of sulfonation (by ¹ H NMR and titration)	appr. 70% 2.8 mmole SO ₃ ⁻ /g

Synthesis Procedure:

Poly(methyl methacrylate-b-glycidyl methacrylate) block copolymer was synthesized by group transfer polymerization with sequential addition of methylmethacrylate and methylglycidyl methacrylate. The obtained polymer was precipitated into methanol. The polymer was sulfonated by refluxing the obtained diblock copolymer with tetrabutyl ammonium bromide and sodium sulfite (molar ratio MMA-GMA / TBAB / Na₂SO₃ = 1 : 1 : 2) in CH₃Cl/dionized water for 12h. The settled down polymer glue was decanted and washed with cold water/CHCl₃ mixture, followed by drying under reduced pressure for 48h at 48°C.

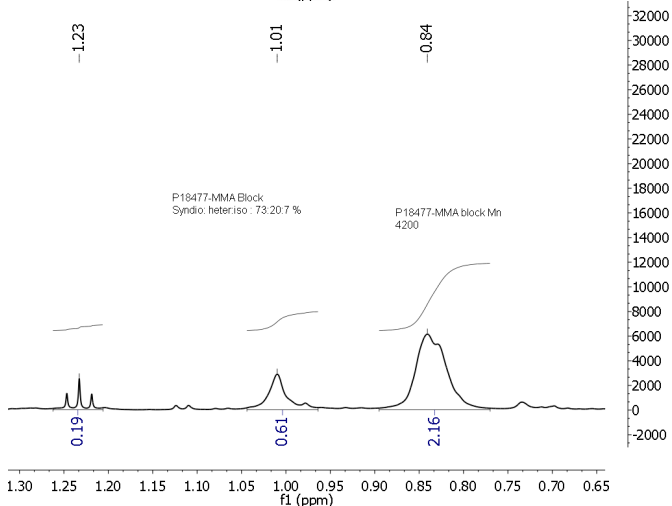
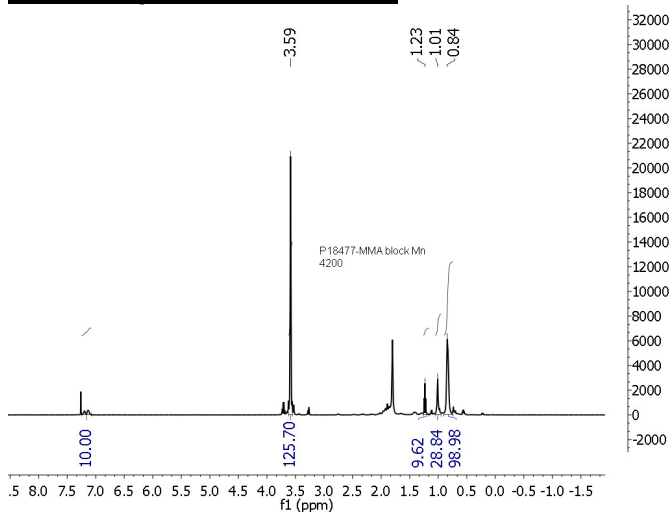
Solubility:

The block copolymer is soluble in THF and CHCl₃.

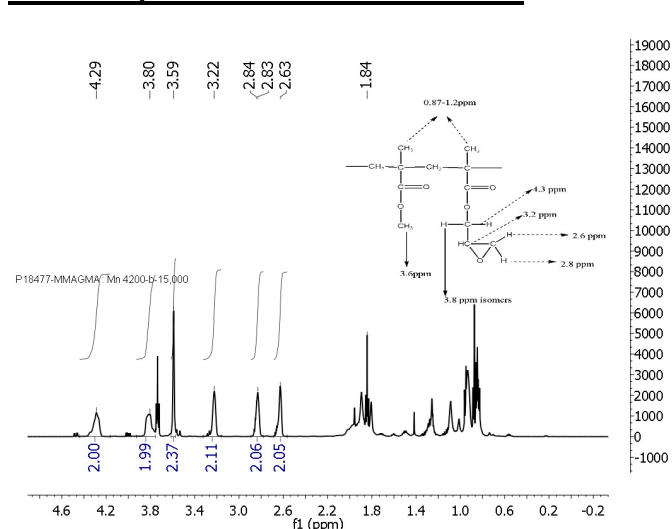
Characterization:

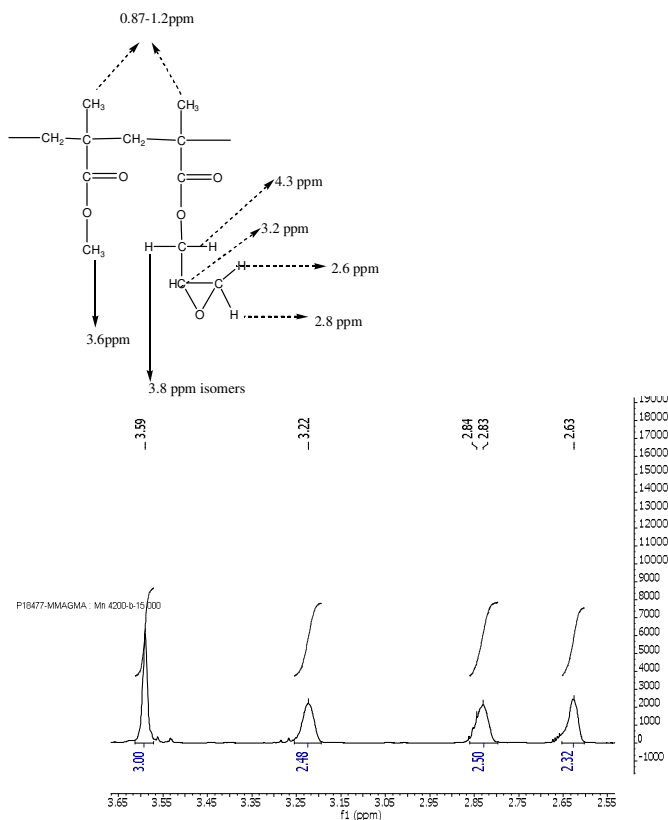
SEC analysis of the obtained block copolymer was carried out in THF in presence of triethyl amine as eluent and using light scattering detector to determine the absolute molecular weight and polydispersity. The composition of block copolymer was determined by ¹H NMR in CDCl₃ by comparing methyl group from MMA block at 3.6 ppm and methylene group from GMA block at 2.8 and 2.6 ppm.

¹H NMR spectrum of PMMA:

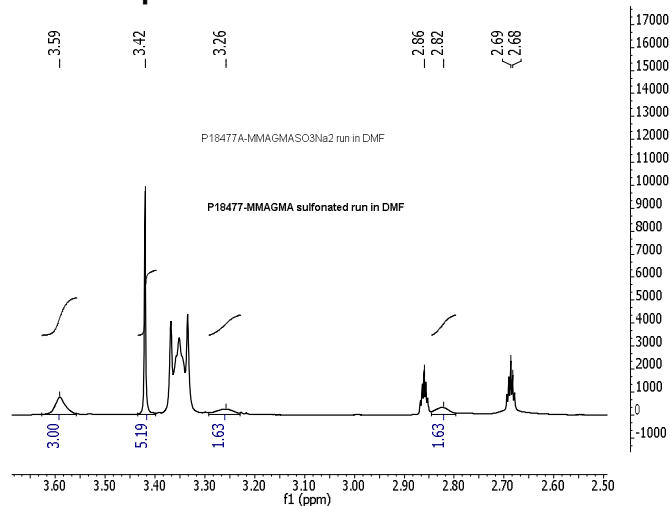


¹H NMR spectrum of PMMA-b-PGMA:





¹H NMR spectrum in DMF:

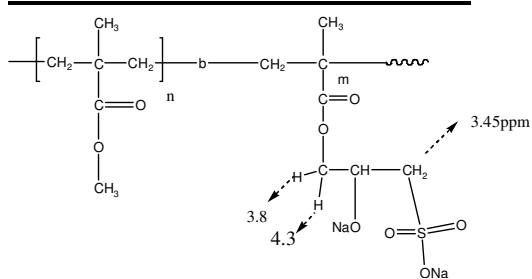


Degree of sulfonation:

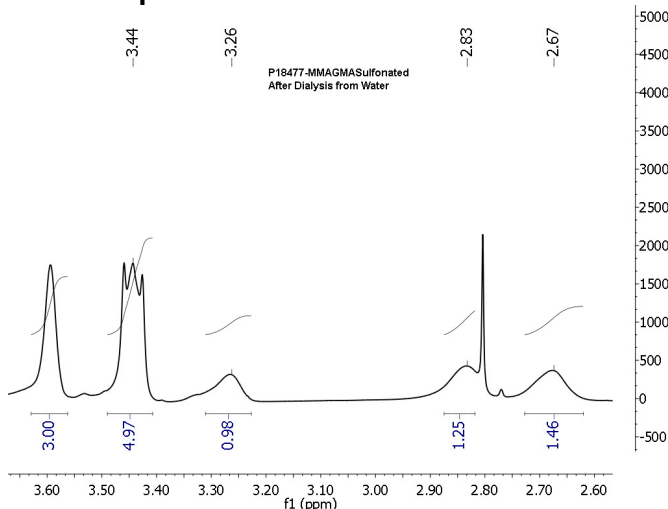
The degree of sulfonation of PGMA block was determined from the ratio between total integration of epoxy protons before and after reaction with Na₂SO₃:

- from ¹H NMR in spectra acetone:
 $(1.63 + 1.63) / (2.48 + 2.5 + 2.32) = 3.69 / 7.3 = 50\%$;
- from ¹H NMR spectra in DMF:
 $1.63 \times 3 / (2.48 + 2.5 + 2.32) = 4.89 / 7.3 = 67\%$

PMMA-b-PGMA after sulfonation:

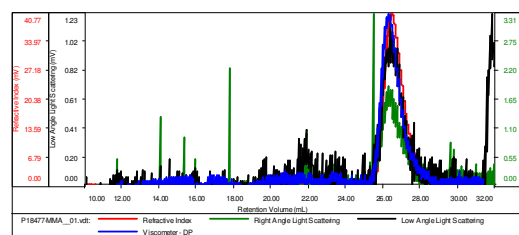


¹H NMR spectrum in acetone:

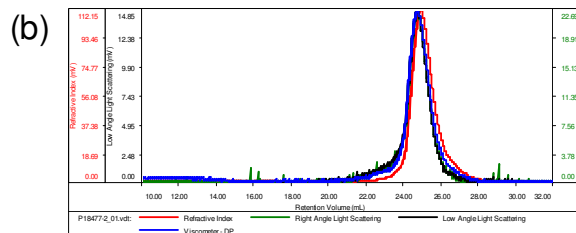


SEC-LS elugrams in THF of (a) PMMA block, and (b) PMMA-b-PGMA diblock copolymer:

Concentration (mg/mL)	1.3449
Sample dn/dc (mL/g)	0.1080
Method File	PS80K-Feb10-2014-0000.vcm
Column Set	3x PL 1113-6300
System	System 1



Sample	Mn	Mw	Mp	Mw/Mn	IV
P18477-MMA_01.vcl	4,777	5,019	4,995	1.051	0.1185



Sample	Mn	Mw	Mp	Mw/Mn	IV
P18477-2_01.vcl	20,184	28,424	27,847	1.408	0.1647