GPC of Polythiophene

Introduction:
Polythiophenes are conductive polymers with a backbone structure that consists of 5 member conjugated rings containing sulfur and polymerized at the 2 and 5 positions. The resulting material lends itself to varied uses in sensors, MEMS-based actuators, batteries, corrosion inhibition, EMI shielding, and electrochromic camouflage coatings.

SEC/GPC analysis of polythiophene can be difficult because of potential chemical interactions with the GPC column. Additionally, the polymers may fluoresce depending on the exact nature of the substitutions on the polymer backbone.

Sample Preparation:
A polythiophene sample was weighed into a vial and 10ml of THF was added to the vial. The vial was then capped and heated to 50°C while stirring for 1 hour. The solution was then hot filtered into a 2ml vial, which was placed in an autosampler tray controlled at a temperature of 45C. The elevated temperature must be maintained because the polythiophene precipitates from solution at room temperature.

Chromatography Instruments and Conditions:

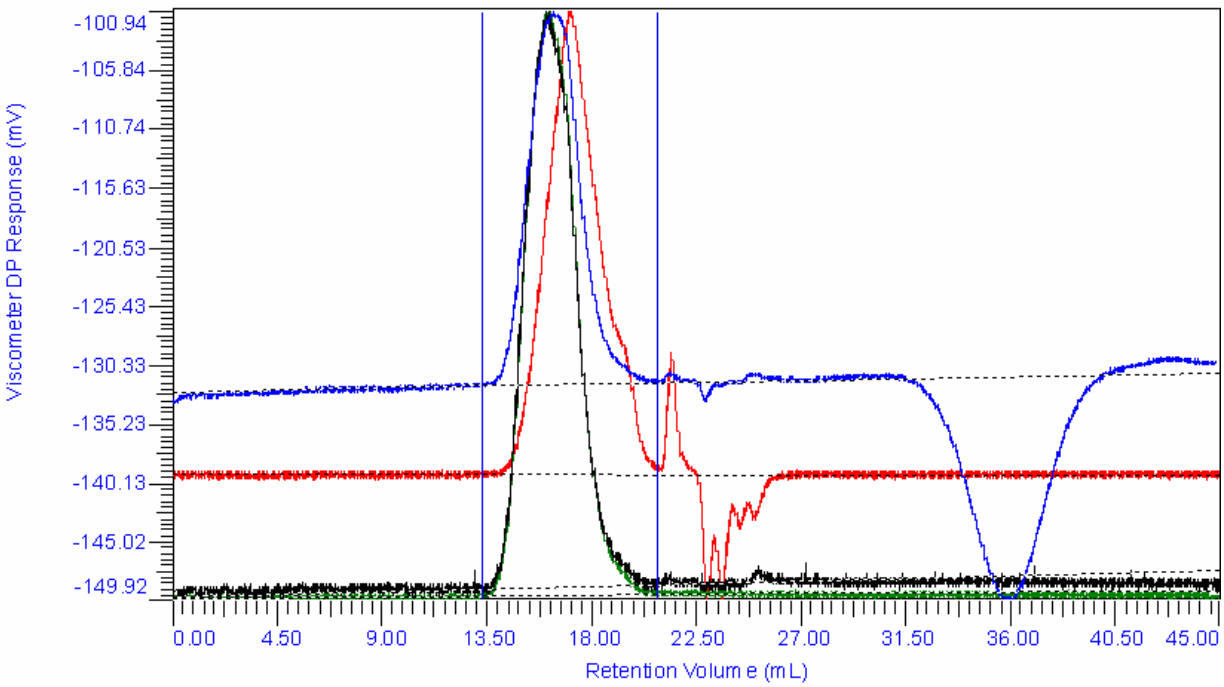
Pump/Autosampler:	Viscotek GPCMax-II Temperature 45°C.
Detectors:	Viscotek Model 302 Triple Detector Array:
	(RI, Viscometer, Light Scattering) Temperature 45°C.
Columns:	Viscotek I-MBHMW-3078 (x2) Temperature 45°C.
Mobile Phase:	THF
Flow Rate:	1 ml/min.
Injection Volume:	100 µl

I-Series columns were selected because of their superior inertness compared with standard SEC columns.

Results:
The sample solution observed to be ‘fluorescent orange’ colored. Therefore, preliminary measurements were made of the fluorescence at 670 nm, which is the wavelength of the diode laser employed in the light scattering detector. The fluorescence at this wavelength was found to be negligible.

Good signal to noise ratios were observed on all detectors and no peak tailing was observed (Figure 1). The lack of tailing suggests that the sample is not being retained by the I-series columns.

Figure 1: Triple Chromatogram of Polythiophene



Results from duplicate injections of this sample are presented in Table I below.

Table I. Results

Injection No.	dn/dc (ml/g)	Mw	Mn	Mz	PDI	R_h (nm)	IV (dl/g)	M-H a	M-H Log K
1	0.242	41,677	18,797	84,258	2.217	6.078	0.424	0.826	-4.154
2	0.238	41,607	18,856	83,429	2.207	6.037	0.416	0.843	-4.239
Avg.	0.240	41,642	18,827	83,844	2.212	6.058	0.420	0.8345	-4.1965

R_h is the hydrodynamic radius (wt-average) and IV is the whole polymer intrinsic viscosity. Molecular weights were calculated based on the measured dn/dc value of 0.24. dn/dc is measured from the integrated RI signal as follows.

[1] $$\frac{dn}{dc} = \frac{RI.Area \cdot n_0}{RI.Cal \cdot V_{inj} \cdot Conc}$$

RI.Cal is the calibration constant of the RI detector, n_o is the refractive index of the solvent, V_{inj} is the injection volume, and Conc is the sample concentration injected.

The columns labeled M-H refer to the Mark-Houwink parameters which relate intrinsic viscosity and molecular weight according to the following empirical equation.

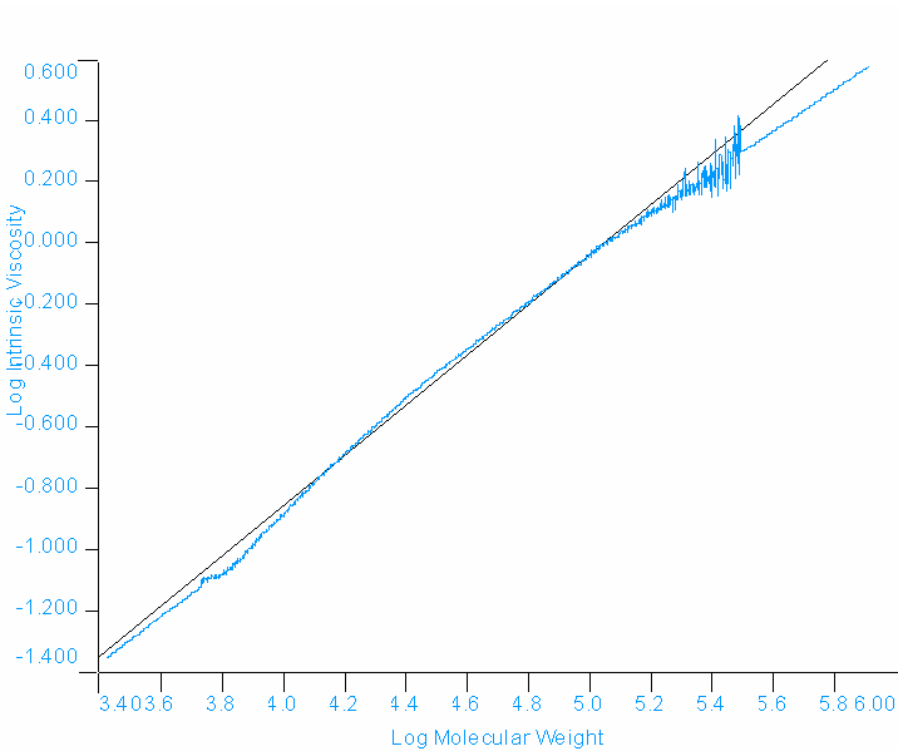
[2] $$[IV] = KM^{a}$$

Taking the log of both sides:

$$[\ 3\ ] \qquad Log[IV] = a * LogM + LogK$$

A plot of log IV vs. log M therefore yields a straight line of slope "a" and intercept of log K. See Figure 2. Flexible chain polymers yield "a" values in the range of 0.7. The "a" value of 0.83 found for this polythiophene indicates that it has a stiff chain.

Figure 2. Mark-Houwink plot for Polythiophene



Conclusions:
The polythiophene can be successfully characterized in THF at 45C using the I-series columns. The polymer will fall out of solution at room temperature; therefore temperature control of the sample vial, columns and detectors is necessary. The TDA coupled with the GPCMax-II fulfills this need.

Keywords: Triple Detection, TDA-302, GPCMax, Temperature Control, I-Series Columns, GPC, SEC, Fluorescence, Polythiophene, Conductive Polymers, Light Emitting Polymer, Light Scattering, Mark-Houwink