MATERIALS ANALYSIS

CHARACTERIZATION OF POLYESTERS BY AGILENT 1260 INFINITY MULTI-DETECTOR GPC/SEC SYSTEM

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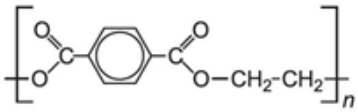
ABSTRACT

Polyesters are one of the most widely used industrial polymers. Popular applications include clothing, food packaging, water and bottles for carbonated soft drinks. One of the most commonly used polyesters for these applications is Polyethylene Terephthalate (PET). The annual world wide production of PET is approximately 40 million tonnes and is growing at ca 7% per year. Of this, approximately 65% is used to manufacture fibres, 5% for film and 30% for packaging. The diverse range of properties exhibited by polyesters depends on their structure, molecular weight, and molecular weight distribution.



INTRODUCTION

The mechanical and chemical resistance properties of PET make it difficult to dissolve and challenging to characterize using GPC. PET was traditionally analysed using high temperature GPC with organic solvents such as m-Cresol. In recent years the use of the fluorinated alcohol, Hexafluoroisopropanol (HFIP) has become the preferred solvent for GPC because it will dissolve PET at ambient temperature. HFIP has its drawbacks however, since it is both very expensive and has a high viscosity.

In this application we overcome these issues by initially dissolving the polymer in HFIP, but then running the analysis in Chloroform. When dissolving a polymer in one solvent, but then analysing in a different solvent, there is always a concern that these conditions may promote interaction with the packing material.

In this application we use advanced GPC detection techniques, in particular Light Scattering to generate molecular weights independent of the column calibration.

Calibration of the Detectors in Advanced GPC

Information needed for advanced GPC	Values
Dn/Dc of standard	Dn/Dc of PS in Chloroform is 0.16
RI of the eluent	RI of Chloroform=1.44
Accurate concentration and molecular weight of standard	Mp : 113300 1mg/ml Polystyrene

Agilent Technologies

Instrumentation:

Agilent 1260 Infinity Quaternary Pump (G1311B)
Agilent 1260 Infinity High Performance Autosampler (G1367E)
Agilent 1260 Infinity Thermostatted Column Compartment (G1316A)
Agilent 1260 Infinity GPC/SEC Multi-Detector Suite (G7800A)
MDS Viscometer Detector (Option 032)
MDS Light Scattering Detector (Option 033)
MDS Refractive Index Detector (Option 031)

Method of Analysis	
Flow :	1 ml/min
Detector :	1260 MDS Viscometer, LS, RI
Column Temp :	30 ˚C
Detectors Temp. :	30 ˚C
Inj. Volume :	100ul
Eluent :	100 % Chloroform
Column :	2 X PL Gel Mixed B, 7.5mm X 300 mm, with Guard

Column Calibration	
RT	**Mw**
13.2	483400
13.7	224900
14.2	113300
14.8	51150
15.2	29150
15.8	13270
16.4	6940
17.0	2780
17.7	1320
18.0	860
18.5	370

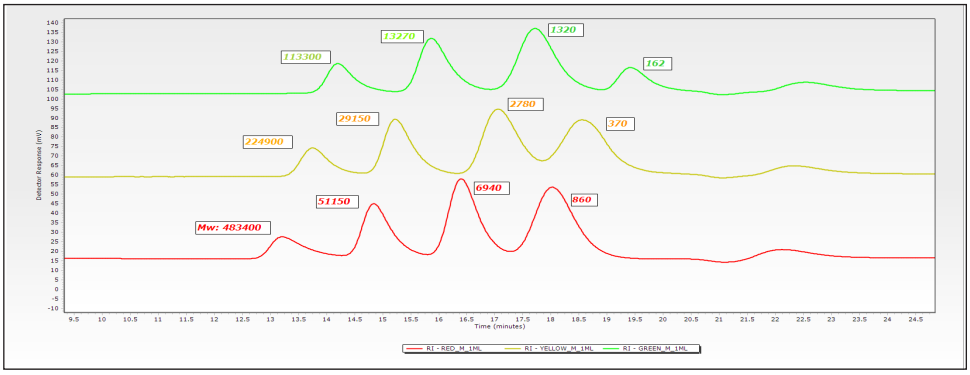


Figure 1: EasiVial chromatogram

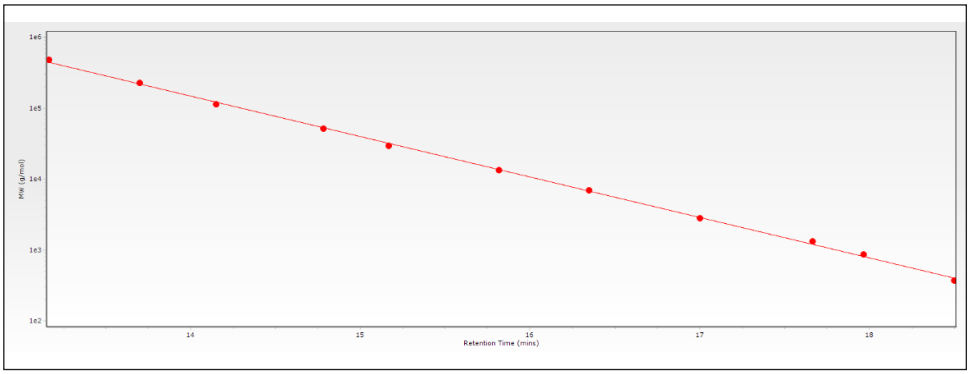


Figure 2: EasiVial column calibration

To allow us to perform conventional GPC calculations we also choose to calibrate the GPC column using a series of pre-weighed polystyrene standard mixtures (EasiVial). This enables us to generate a 12 point calibration from three injections, by simply adding a specific volume of solvent to vials containing known amounts of polymer standards.

SAMPLE PREPARATION AND ANALYSIS

600ul of HFIP was added to 43mg of polyester sample in a 10ml volumetric flask. This was then allowed to dissolve for 3 hours and then chloroform was added up to the mark. 100ul of the sample was then injected into the GPC system. A typical chromatogram of the PET sample is shown in Figure 3, highlighting the excellent response from all three detectors.

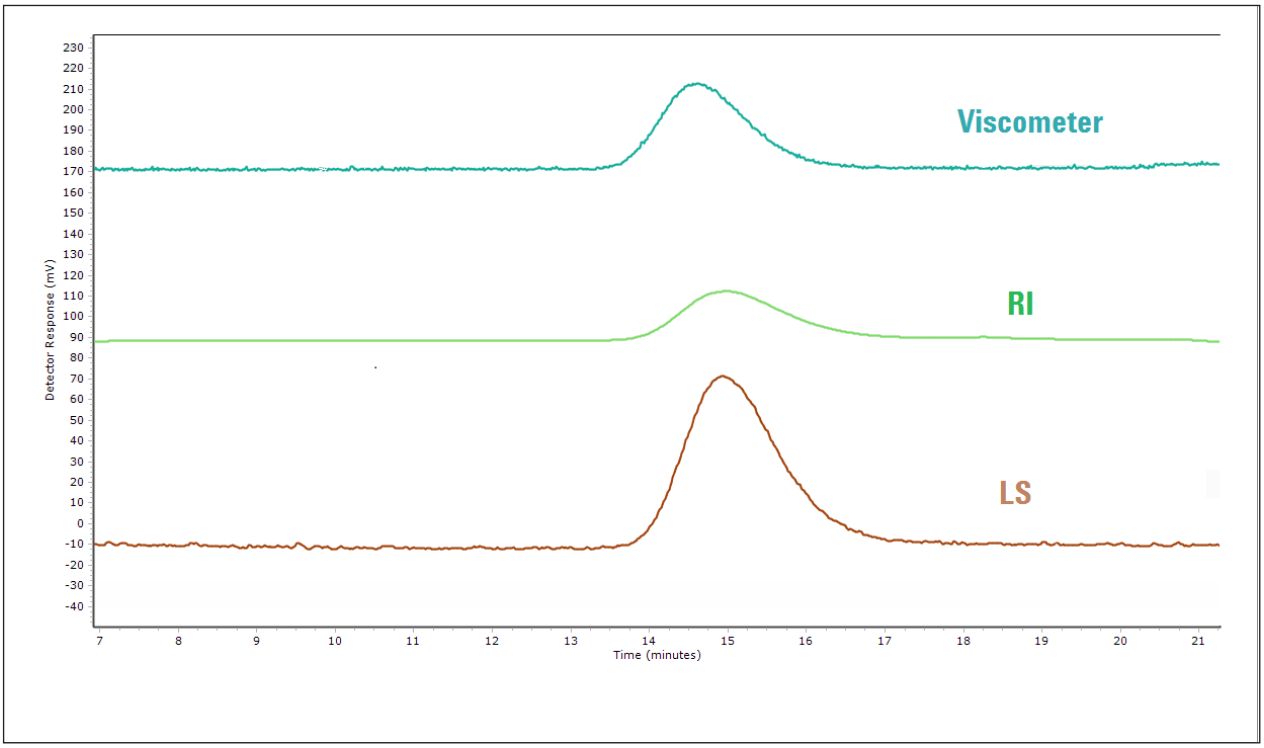


Figure 3: Multi detector signal for Polyester sample

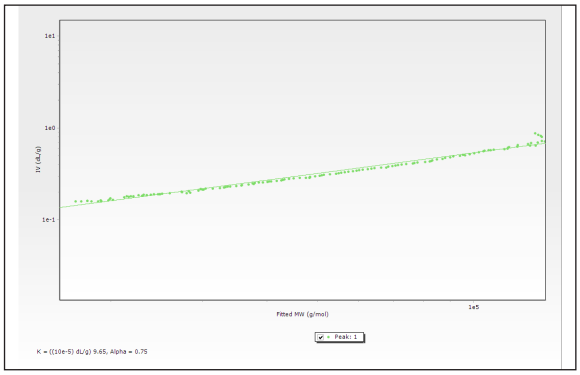


Figure 4: MH plot for the polyester sample

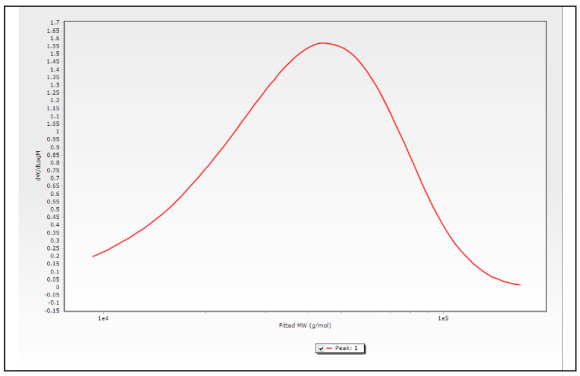


Figure 5: Molecular weight distribution of the polyester sample

RESULTS

The sample was analysed using triple detection, which includes the responses from DRI, Viscosity and Light Scattering detectors.

The molecular weight averages for this sample are shown in the table below.

The Mw's reported are with a high degree of confidence because we are using the Light Scattering detector in this calculation. Molecular weights obtained using this detector are not reliant on a column calibration.

	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
PET Sample	43945	33099	44544	57456	70224	55772	1.3

The Mark-Houwink (MH) plot and Molecular Weight Distribution plots are shown in Figures 4 and 5.

The MH plot generated from the combination of the viscosity and refractive index detectors, shows the relationship of the polymer IV and molecular weight. This plot can provide structural information of the polymer. A linear plot as in this example indicates that there is no change in structure across the molecular weight distribution of the PET.

CONCLUSIONS

The method of dissolution and analysis of the PET sample by firstly dissolving in HFIP followed by analysis in Chloroform produces reliable molecular weight information.

The expected molecular weight of this material was 45,000, and this compares favourably with the 44,544 calculated by the triple detection analysis for this sample.

In addition, the MH plot has a slope of 0.75 which suggests that the polymer is in a good solvent and has a random coil conformation. The quality of the data from all detectors supports the conclusion that the method of sample dissolution and analysis is reliable for this type of PET material.

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