MATERIALS ANALYSIS

CHARACTERIZATION OF POLYPHENYLENE SULPHIDE USING THE AGILENT PL-GPC 220 HIGH TEMPERATURE GPC SYSTEM WITH TRIPLE DETECTION

Solutions for Your Analytical Business

Markets and Applications Programs

Authors

Adrian Boborodea

Senior Scientist,
Certech ASBL, Belgium.

Alan Brookes

GPC Instruments
Sales Manager EMEAI

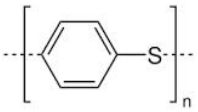
Abstract

In this Application Note we demonstrate how the Agilent PL-GPC 220 High Temperature GPC System with triple detectors (differential refractive index, viscometer and light scattering) can be used to reliably measure the true molecular weight distributions of common commercial grades of polyphenylene sulphide (PPS) samples.

In addition, the instrument allows the generation of Mark Houwink parameters, which were found to correlate well with the values provided by literature for linear PPS.

INTRODUCTION

Polyphenylene Sulphide (PPS) is a polymer chain built from alternating sulphur atoms and phenylene rings in a para-substitution pattern:



PPS is a crystalline polymer having an outstanding chemical resistance and high-temperature stability. The mechanical properties of the commercial grades depend on the molecular weight and on the structure of the resin, which can be branched or linear, gel permeation chromatography with multiple detectors being the method of choice to evaluate these characteristics.

The separation in GPC is a function of Vh, the hydrodynamic volume of the polymer, which is proportional with the product between molecular weight and the intrinsic viscosity. For conventional GPC, the true molecular weight of the unknown sample is not measured, and has to be calculated by calibrating the column with well characterized standards. When viscometry and light scattering (LS) are available as on-line detectors, the molecular weight of the sample can be directly measured, and indeed it is not necessary to perform the column calibration. However, the detectors do have to be calibrated. Before applying this procedure it is also necessary to measure the interdetector time delay (IDD), a crucial parameter for accurate evaluation of true molecular weights.

When trichlorobenzene (TCB) is used for polyolefin analysis by high temperature GPC, the instrument is calibrated using a polystyrene standard for which the concentration, the molecular weight, dn/dc, and the intrinsic viscosity are known. This standard provides good signals in all three detectors (differential refractive index, viscometer and light scattering). However, the TCB boiling point of 214°C, and limited solubility of PPS means that TCB is unsuitable as a GPC solvent for PPS. PSS does however dissolve readily at temperatures of around 250°C in 1-chloronaphthalene (1-CN) which has a boiling point of 260°C. Therefore, in this case we can use 1-chloronaphthalene (1-CN) as a suitable GPC eluent for the analysis of PPS. However, as presented in Figure 1, the PS standards have a much lower dn/dc in this solvent compared with TCB. Note the low signal for these PS standards for the RI and LS detectors as seen below as a result of the low dn/dc of PS in 1-CN.

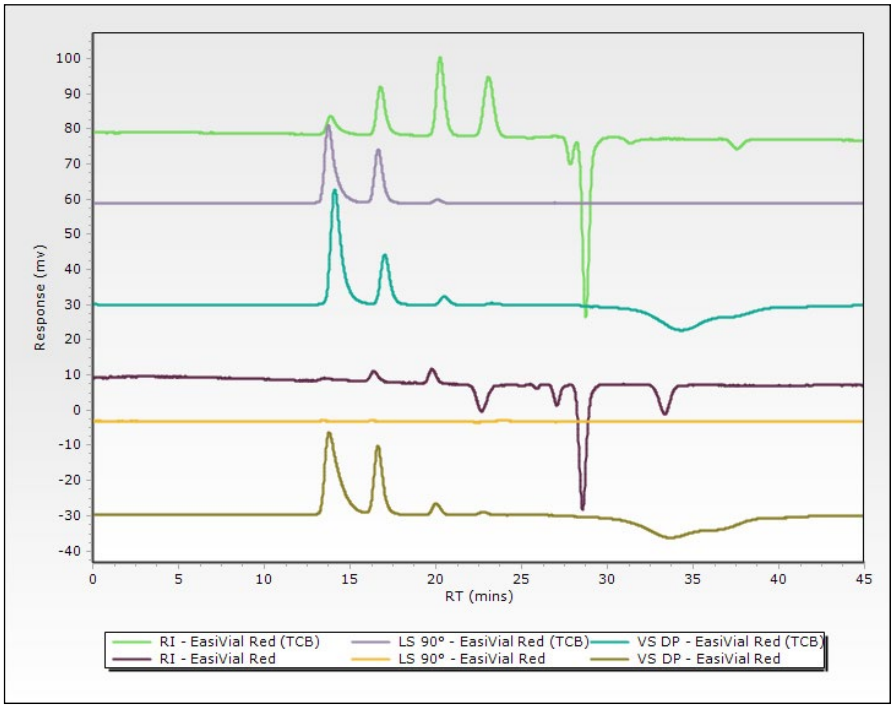


Figure 1: Comparison of chromatograms obtained by triple detection for EasiVial Red analyzed in 1-CN and in TCB.

This very low value of dn/dc for PS in1-CN is a major challenge, and has proven to be a problem in developing the muti-detector analysis of PPS by GPC. Because the LS signal is proportional with its $(dn/dc)^2$, the PS peak elution and response is difficult to measure, and therefore it is not possible to accurately measure Interdetector Delay (IDD) and calculate the LS calibration constant with PS standards.

It is important to note that even with this low dn/dc value for PS in 1-chloronaphthalene, the integrated high performance differential refractive index detector in the Agilent PL-GPC 220 High Temperature GPC System, has very low drift combined with good signal/noise, which still allows the identification of the peak retention times of PS standards. Therefore, for comparative studies, the conventional approach using Refractive Index detection permits the evaluation of relative molecular weights based on conventional calibration and Mark Houwink parameters provided in literature (1):

- K_PS= 18.6*10-5 dL/g; alpha_PS = 0.657
- K_PPS = 8.91*10-5 dL/g; alpha_PPS = 0.747

Using the Agilent GPC software, this is a relatively simple procedure, and easy to apply by following the step by step tutorial provided with the instrument.

However, the conventional calibration does not provide the true molecular weights or information regarding the structure of PPS samples. In order to evaluate these properties it is necessary to add supplementary detectors and to calibrate the instrument.

In this Solution Note we present the procedure to measure the true molecular weights and Mark-Houwink parameters of PPS samples using multi-detector GPC with advanced detection techniques. Alternative solutions and supplementary details on the method can be found in (2).

EXPERIMENTAL

Instrumentation

Agilent PL-GPC 220 High Temperature GPC System equipped with a differential refractive index detector, viscometer and light scattering detectors.

Method for Analysis

Detectors used	LS , VS, DRI
Mobile phase	1–chloronaphthalene (1-CN)
Columns	3 x PLgel 10 µm Mixed-B 300 x 7.5 mm
Standards	EasiVial PS-L for IDD and SRM 1475a for detector calibrations
Samples	PPS 30k, PPS 40k and PPS 50k (commercial grades PPS)
Concentration	2 mg/mL
Temperature	210˚C
Injection volume	200 µL
Flow Rate	1.0 mL/min
Software	Agilent GPC/SEC Software

IDD calibration

Because the IDD depends on the flow rate and the tubing volume between detectors, a possible solution to measure this parameter is to inject a PS standard when the instrument is running at the same flow rate (1 mL/min) in another solvent such as TCB or THF. In our case we used the second peak in the chromatograms obtained in TCB (Figure 1). We obtained 9 s between the light scattering and refractive index detectors, and 23 s between light scattering and viscometer.

Calibration of detectors

To calibrate the detectors, it is necessary to inject a standard with known concentration, dn/dc, molecular weight and intrinsic viscosity. We chose PE SRM 1475a standard, which is usually used as control sample in the GPC laboratories running high temperature analyses of polyolefins. The chromatograms in Figure 2 and the following parameters in 1-CN were used for the calibration of detectors:

Detectors used	LS , VS, DRI
Mobile phase	1–chloronaphthalene (1-CN)
Columns	3 x PLgel 10 µm Mixed-B 300 x 7.5 mm
Standards	EasiVial PS-L for IDD and SRM 1475a for detector calibrations
Samples	PPS 30k, PPS 40k and PPS 50k (commercial grades PPS)
Concentration	2 mg/mL
Temperature	210°C
Injection volume	200 µL
Flow Rate	1.0 mL/min
Software	Agilent GPC/SEC Software

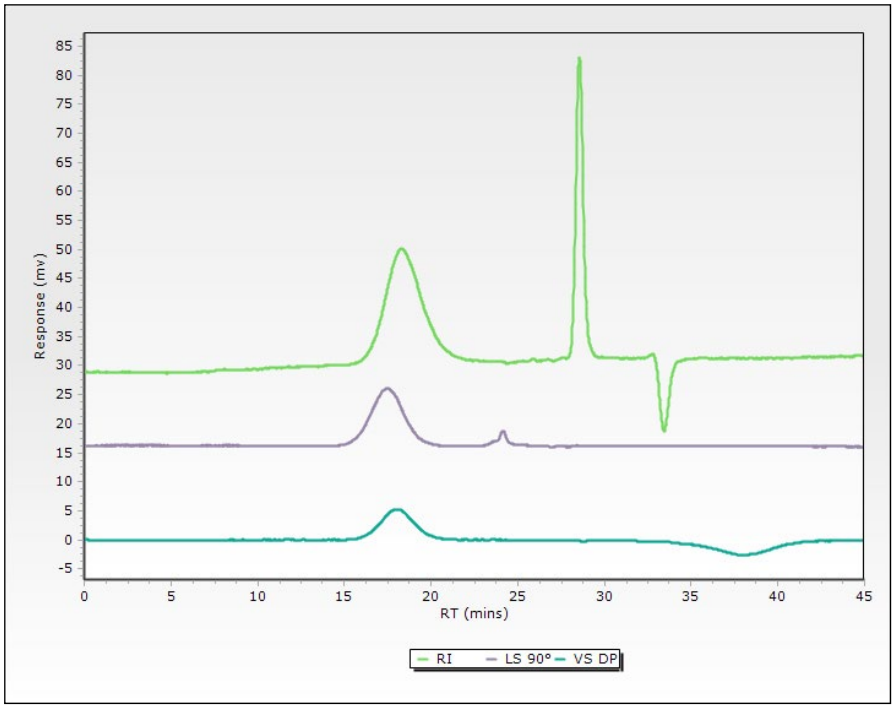


Figure 2: Chromatograms of PE SRM 1475a in 1-CN for the calibration of detectors.

Sample chromatograms

Each sample was injected twice and typical chromatograms are given in Figure 3. An excellent reproducibility was obtained for all detectors, which also proves that no degradation was introduced whilst the samples were held in the autosampler prior to injection. This is due to the fact that Agilent's autosampler oven has two temperature zones, the samples held at 150°C initially, and then being re-solubilized only 1 hour prior to analysis at 210°C. This way, thermal degradation of the samples is avoided and reproducibility of results is excellent.

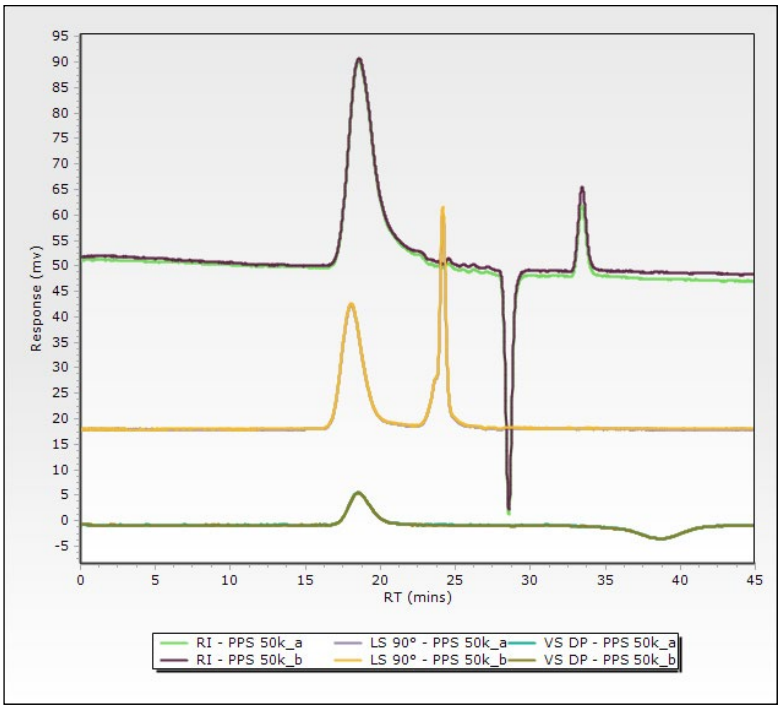


Figure 3: Overlay of two injections of PPS 50k in 1-CN showing an excellent reproducibility in all detectors.

Molecular weight distributions

With the instrument calibration done, the obtained chromatograms with triple detection are enough to evaluate the molecular weight distributions. A clear difference was recorded between different commercial PPS samples, as presented in Figure 4.

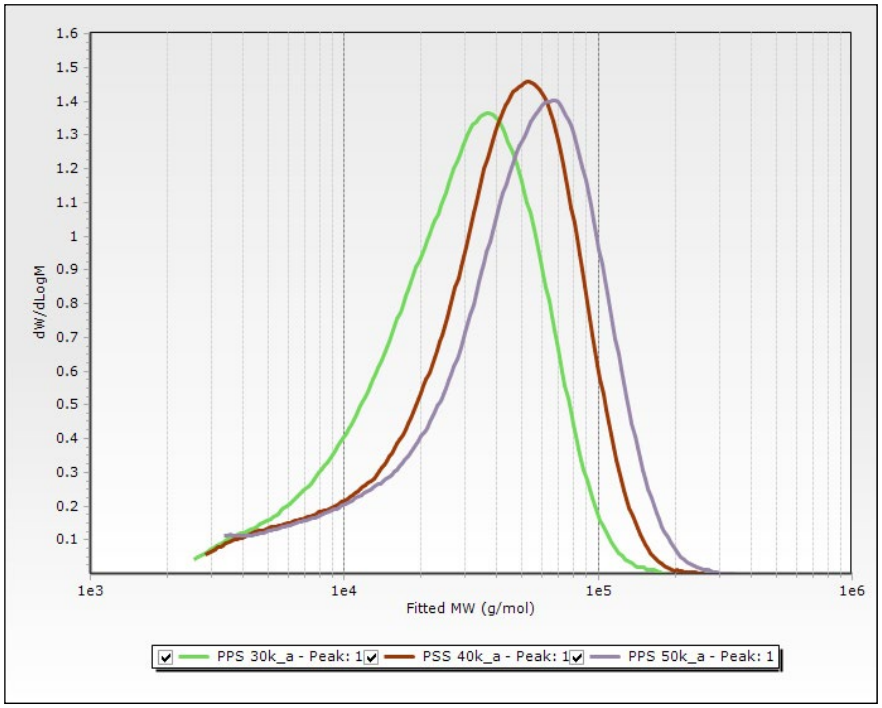


Figure 4: Overlay of molecular weight distributions of the PPS samples

Calculated molecular weight averages for samples

The molecular weight distributions allow calculation of all average molecular weights (Mn, Mw, Mz, Mz+1). In the following table these values were compared with the previously obtained results provided by conventional calibration (2):

Calibration :	Conventional		Triple detection	
Sample	**Mn**	**Mw**	**Mn**	**Mw**
PPS 30k (first)	13300	30600	19600	34200
PPS 30k (second)	13800	30600	21000	35800
PSS 40k (first)	16000	43500	25600	48100
PSS 40k (second)	16000	43300	27100	49200
PPS 50k (first)	14500	49500	29400	58500
PPS 50k (second)	14800	49500	26700	57900

Mark Houwink parameters

The major advantage of the triple detection is the possibility to evaluate not only the molecular weight but also the structure of the PPS samples. The Mark Houwink plots given in Figure 5 show good reproducibility and the obtained parameters are similar with the ones provided by literature for linear PPS.

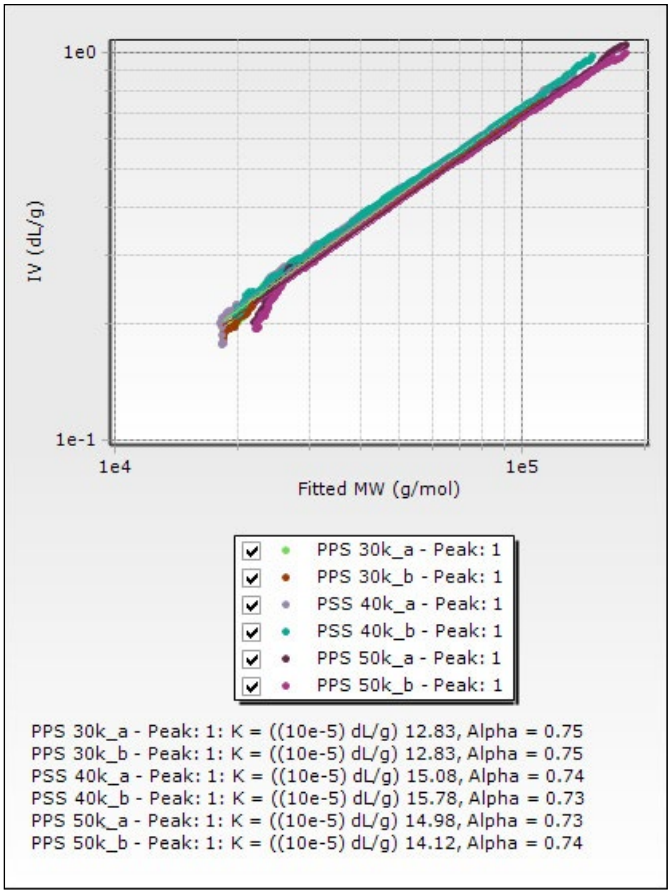


Figure 5: Overlay of Mark-Houwink plots of the PPS samples

Conclusions

The low drift and high signal/noise of the integrated DRI detector in the Agilent PL-GPC 220 High Temperature GPC System allows conventional calibration with PS standards, even when the dn/dc value of PS in 1-chloronaphtalene is very low. However, the obtained relative molecular weights can be used only for comparative purposes, with no information regarding the sample structure.

This solution note demonstrates that the Agilent PL-GPC 220 High Temperature GPC System, with triple detection, is a reliable instrument for accurate measurements of the true molecular weights of commercial PPS samples. Moreover, it allows evaluation of the Mark Houwink parameters of PPS samples, providing critical information on sample structure which show excellent correlation with the literature reference values for linear PPS.

CERTECH

Certech is a contract research organisation offering a wide range of services to industries in the field of environment, materials formulation & technology and process intensification.

Certech's mission is to provide help, support and services to small and large industrial enterprises, by offering analysis and measurements, problem-solving, contract research, product and process development capabilities.

Certech's vision is to deliver innovative solutions in product and process improvement or development, by exploiting sustainable chemistry, to meet future societal and industrial needs.

Certech is a key member of the Agilent Partner Labs Network, collaborating on method development and providing application consultancy.

REFERENCES

1. C. J. Stacy - Molecular Weight Distribution of Polyphenylene Sulfide by High Temperature Gel Permeation Chromatography – J. Appl. Polym. Sci., Vol. 32, 3959-3969 (1986)

2. A. Boborodea, A. Brookes - Characterization of Polyphenylene Sulphide Using Gel Permeation Chromatography with Triple Detection – Int. J. Polym. Anal. Charact., Vol. 20, issue 2, 172–179 (2015)

certech
centre de ressources technologiques en chimie

Visit Partner Lab at www.certech.be

Solutions for your analytical business
Markets & Applications Programs
www.solutions-to-win.com

The Measure of Confidence

Published in USA, February 10, 2015
5991-5570EN

Agilent Technologies