MATERIALS ANALYSIS

COMPARISON OF MOLECULAR WEIGHT ANALYSES OF OLIGOMERIC HINDERED AMINE LIGHT STABILIZER (HALS) USING CONVENTIONAL AND ADVANCED DETECTION GPC TECHNIQUES

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Solution Note

Materials

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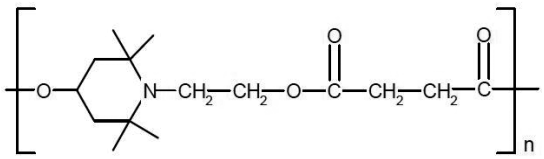
Introduction

TINUVIN 622 is the light stabilizer of choice for many applications calling for low volatility and minimal migration because of its oligomeric structure and elevated molecular weight. Furthermore TINUVIN 622 is effective as an antioxidant and contributes significantly to the long-term heat stability of polyolefins and tackifier resins. Chemically it is a Butanedioic acid, dimethylester, polymer with 4-hydroxy-2,2,6,6- tetramethyl-1-piperidine ethanol

TINUVIN 622



TINUVIN 622 is a highly effective additive in a wide range of applications including polyolefins (PP, PE), olefin copolymers such as EVA, blends of polypropylene with elastomers, polyacetals, polyamides and polyurethanes. TINUVIN 622 is specified with a number average molecular weight (Mn) of 3100 - 4000.

In this Solution Note we use multi detector GPC to highlight the ability to generate true molecular weights for a relatively low molecular weight polymer using advanced detection techniques.

Conventional GPC/SEC is a comparative technique

Conventional GPC employing a single concentration detector is actually a comparative technique. During the analysis the detector tells you how much material elutes from the column at any given time. That is then converted into a molecular weight and then into a molecular weight distribution by reference to a calibration curve of molecular weight as a function of retention time. If the standards used in the calibration are of the same chemistry as the sample, then accurate molecular weights are obtained. However, if the standards and the sample vary chemically, the results are only comparative.

What does multi-detector GPC/SEC provide?

Multi-detector GPC employing a concentration detector with a viscometer, a light scattering detector or both addresses the limitations of conventional GPC. Multi-detector GPC allows:

- The calculation of molecular weights that are not dependent on the chemistry of any standards used in calibration, and
- The determination of other polymer properties that cannot be measured by conventional GPC/SEC.

GPC/SEC with a Viscometer?

The most common form of multi-detector GPC employs a concentration detector with a viscometer. The viscometer measures the solution viscosity of materials as they elute from the column. Combining this with concentration information from the other detector provides significant insight about the behavior of polymer molecules in solution.

What is a Viscometer?

A viscometer used in GPC is a device for measuring the viscosity of a solution containing a polymer sample relative to viscosity of the solvent alone. In most standard designs this is done by forcing the solution and a reference solvent through narrow capillaries and measuring a pressure drop.

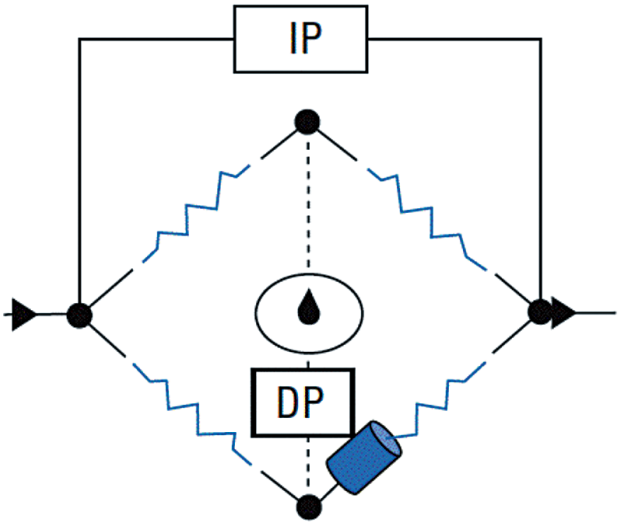


Figure 1: Four-capillary bridge viscometer.

Four-capillary bridge viscometer

The industrial standard design for viscometers for GPC is known as the four-capillary bridge design. This is a fluidic equivalent of the electrical circuit known as a Wheatstone bridge.

The viscometer consists of four linked capillaries in two flow paths, both of which branch from the fluid line out of the GPC columns. The two flow lines are independent but join after the two capillaries, to flow to waste. Both flow paths are identical except for the placement of a delay column after the first capillary on one of the flow paths.

This is a large internal volume column packed with glass beads. A pressure is measured across the entire bridge known as the inlet pressure (IP). A second pressure measurement is made between the two flow paths known as the differential pressure (DP).

Intrinsic viscosity in GPC and SEC

The benefit of measuring the intrinsic viscosity in GPC is that it allows the determination of molecular weights via the Universal Calibration. This is an approach that permits the calculation of accurate molecular weights regardless of the chemistry of the standards employed in the calibration.

The Universal Calibration makes use of the fact that the intrinsic viscosity and the molecular weight are related to the size of the molecules in solution by hydrodynamic volume = k x molecular weight x intrinsic viscosity.

Hydrodynamic volume is a measure of molecular size and k is a constant. Therefore, if a calibration curve is generated for a set of standards plotting log (intrinsic viscosity x molecular weight) versus retention time, that is equivalent to plotting log size vs. retention time. And since the column separates on the basis of size in solution, the same calibration curve will be generated regardless of the standards employed – a Universal Calibration, as shown in figure 2.

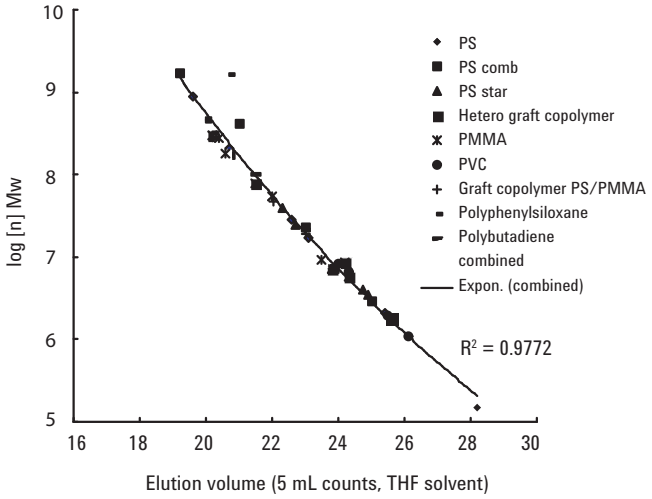


Figure 2: Universal calibration plot.
(Ref : Grubisic, Rempp, Benoit, J. Polym. Sci., Part B, Polym. Lett., 5:753 (1967)

The result is that any calibrants can be used to generate the calibration, as long as they perform pure SEC in the column and are not retained due to interactions. When analyzing samples, the concentration and specific viscosity of a slice of a peak are determined from the response of the concentration detector and viscometer, respectively. The specific viscosity is converted into intrinsic viscosity, and this value along with the retention time is compared to the calibration curve to generate a true molecular weight for the sample.

Viscometry in practice

Viscometry is a relatively simple technique to perform. Solvents and samples do not need to be prepared in any special way, as long as the instrument is purged correctly. Viscometers will generally operate well under most conditions without special attention. However, care must be taken when transferring viscometers into different solvents, especially viscous solvents where flushing at vastly reduced flow rates may be required. GPC with viscometry works well for most samples of appreciable molecular weight, and can also be used to analyze copolymers and other blends as long as concentrations are accurately known.

Viscometry summary

GPC employing viscometry is an excellent technique for measuring molecular weights of samples that are not the same chemistry as the standards available. It also works well for copolymers and can be used to probe the behavior of polymer molecules in solution.

GPC/SEC with a Light Scattering Detector?

Static light scattering in GPC involves irradiating the material eluting from a column with a laser beam and measuring the intensity of resulting scattered light. A more complex technique than viscometry, static light scattering does have some practical limitations. However, the combination of a GPC separation with a concentration detector and a light scattering detector can reveal a great deal of information about polymer molecules in solution.

What is a static light scattering detector?

A static light scattering detector comprises a sample cell, a laser beam, and one or more detectors to collect the scattered laser light. The detectors are set at some angle to the incident beam depending on the design of the detector.

During operation the laser beam irradiates the sample and the detector collects the resulting scattered light from relaxation of the molecule. The intensity of scattered light is measured as the Raleigh ratio, the excess scattering of the sample and solvent combination over that of the solvent alone. The Raleigh ratio is directly proportional to the molecular weight of the solute molecule scattering the light.

A simplified version of the light scattering equation describing the Raleigh ratio (RΘ) is shown in figure 3. We can see that the response from the detector is directly proportional to the molecular weight, a constant K, dn/dc, and the concentration.

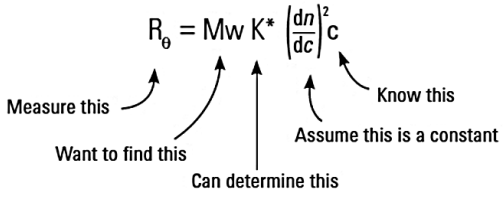


Figure 3: Light scattering equation.

It is clear from this equation that the value of dn/dc is of vital importance in light scattering calculations. In addition, it is evident that the response is directly proportional to the molecular weight, so low-molecular-weight samples and/or low dn/dc sample and solvent combinations will lead to poor light-scattering data. However, if the dn/dc is good and the light scattering detector is stable and sensitive, lower molecular weight materials can be investigated successfully.

Light scattering summary

GPC/SEC employing light scattering is an excellent technique for measuring molecular weights of samples, and does not require any column calibration. However, obtaining good quality light scattering data requires stringent laboratory practice and the response from the detector is very dependent on molecular weight and dn/dc. Due to the latter, light scattering does not work well for copolymers. However, for many samples GPC with light scattering can be used to probe the behavior of polymer molecules in solution through the conformation plot. Triple detection takes advantage of all the benefits of light scattering and viscometry, and is considered the most advanced form of multi detector GPC.

Triple detection

Triple detection is the name given to the GPC/SEC analysis of polymers employing a concentration detector, a viscometer and a light scattering detector. In this approach:

- Molecular weights are calculated as in GPC with light scattering,
- Intrinsic viscosity is also determined from viscometry.

The advantage of this method is that all the data is available, opening up the investigation of the sample by the Mark-Houwink plot or the conformation plot. It is thus possible to use the intrinsic viscosity to estimate the size of the molecule under analysis and therefore correct the calculated molecular weight. Triple detection is considered the most advanced form of multi-detector GPC.

Experimental

Instrumentation

1260	Infinity Quaternary Pump	(G1311B)
1260	Infinity Standard Degasser	(G1322A)
1260	Infinity Autosampler	(G1367E)
1260	Infinity Themostatted Column	(G1316A)
1260	Infinity Multi-Detector Suite	(G7800A)
	MDS Viscometer Detector	
	MDS Light Scattering Detector	
	MDS Refractive Index Detector	

Method for Analysis

Detectors used	MDS LS , VS, DRI
Mobile phase	THF
Columns	2x PLgel 3 µm Mixed-E 300 x 7.5 mm
Standards	EasiVial PS-L
Temperature	40 ˚C (column and detector)
Injection volume	100 uL
Flow Rate	1.0 mL/min
Agilent GPS/SEC software version 1.2	

Instrument/Detector Calibration

Instrument calibration was performed with a single well characterized polystyrene standard with known dn/dc, IV, concentration and molecular weight. Following this, a Universal calibration was performed with a range of polystyrene standards prepared with accurate concentrations and known molecular weights allowing the calibrated viscometer to generate the IV values for the Universal Calibration.

The Conventional calibration curve and Mark Houwink plot are shown in Figures 4 and 5.

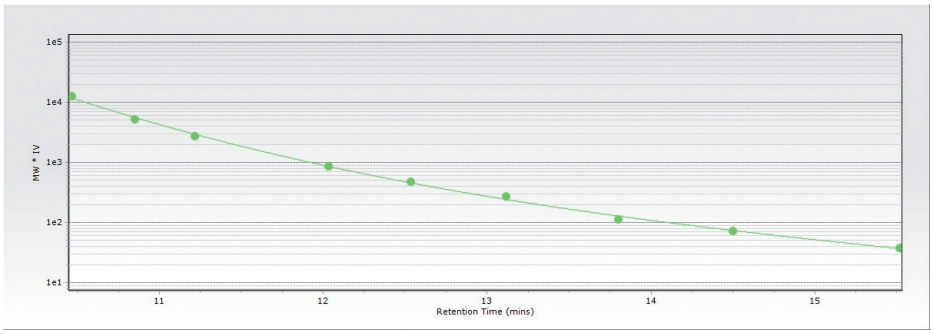


Figure 4: Conventional Calibration.

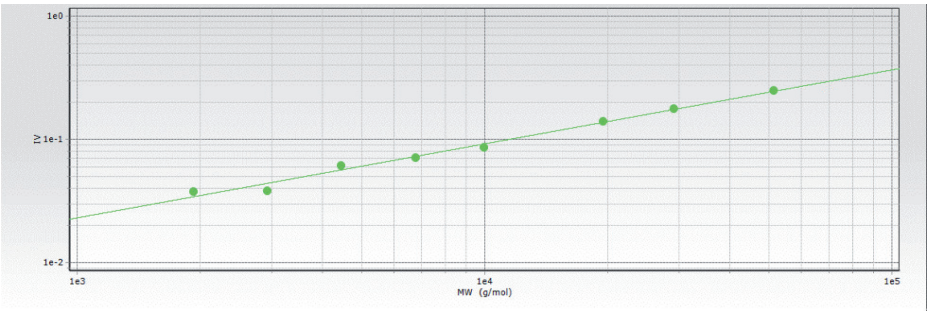


Figure 5: Mark Houwink Plot.

Polystyrene Calibration

The table below shows the PS standards used for Universal Calibration.

RT	Mp
10.45	51150
10.83	29150
11.20	19540
12.02	9970
12.52	6770
13.10	4430
13.78	2930
14.48	1930

An RI Chromatogram showing separation of 4 polystyrene standards from one of our pre-prepared EasiVial products is shown in Figure 6. Good resolution of each of the polystyrene standards is achieved together with oligomeric detail for the lowest molecular weight polymer standard.

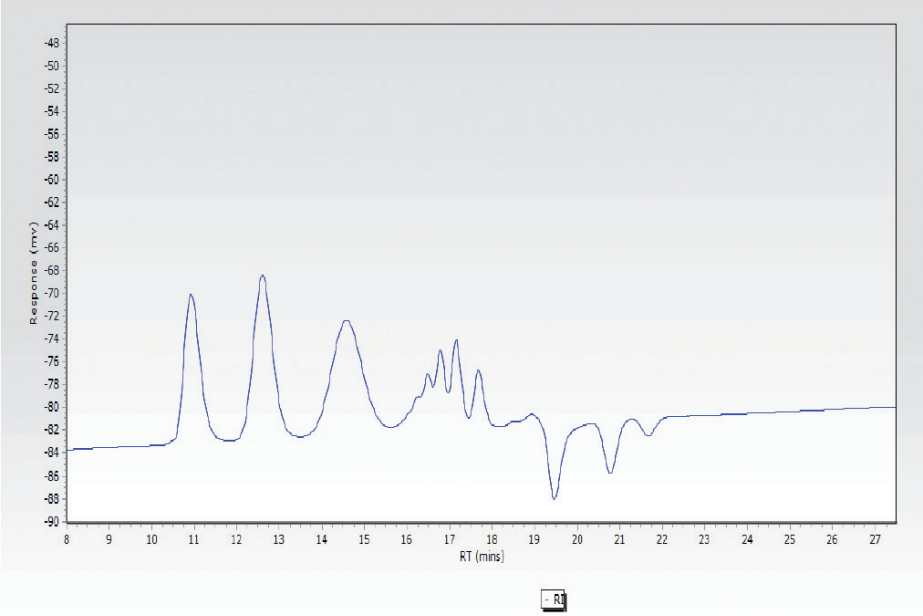


Figure 6: EasiVial Chromatogram.

Analysis of TINUVIN 622

A multi detector chromatogram of Tinuvin 622 is shown in Figure 7.

Good response was obtained from all three detectors, in particular the 90deg LS detector which gave excellent response for this low molecular weight material.

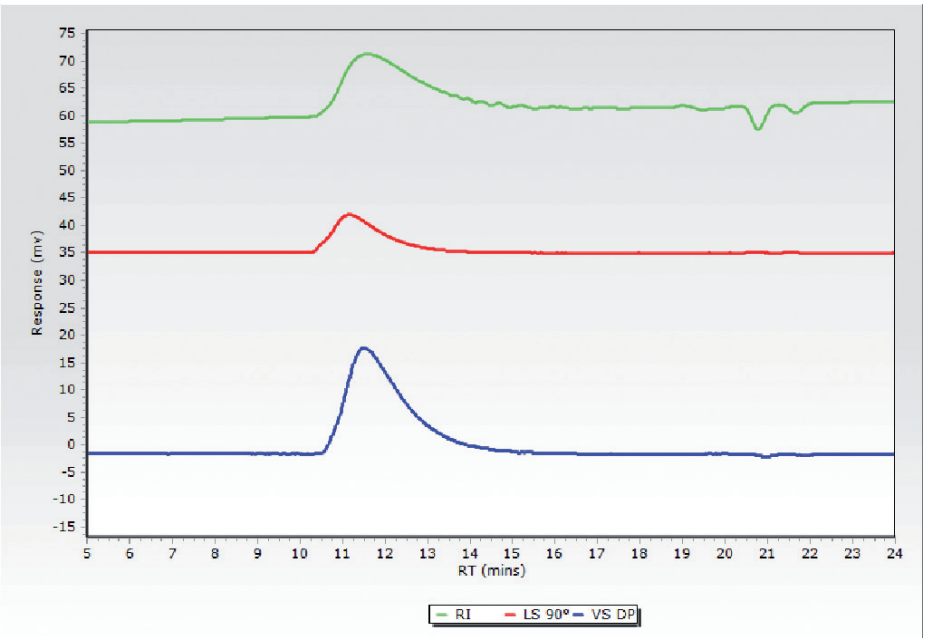


Figure 7: Tinuvin 622 Multi Detector Chromatogram.

The RI molecular weight distribution of Tinuvin 622 is shown in Figure 8.

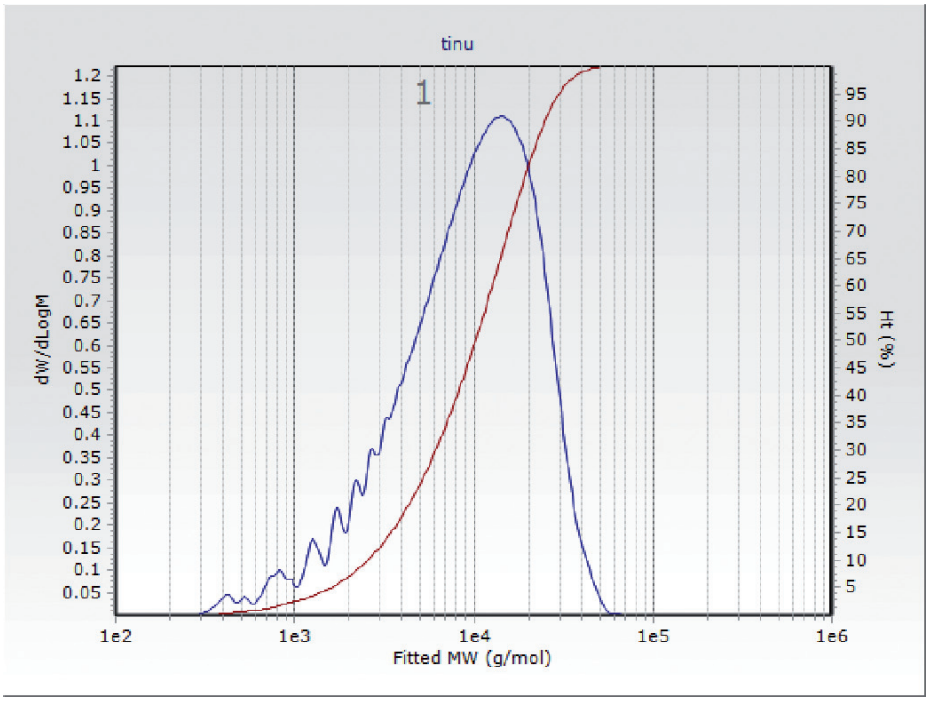


Figure 8: Molecular Weight Distribution Plot of Tinuvin 622.

TINUVIN 622 Molecular Weight Averages

The molecular weight averages of Tinuvin 622 were calculated using four different methods and compared below.

Method	Mp	Mw	Mn	PD
Conv	16190	12282	5335	2.3
Universal	9826	7361	3490	2.1
LS	8321	6281	3440	1.8
Triple	8593	6477	3441	1.9

Conventional GPC provides molecular weights based on the Polystyrene Calibration curve, therefore they are Polystyrene equivalent molecular weights. However, these values are higher than the expected Mn value specified for this polymer of between 3100 and 4000.

By using advanced detection techniques such as Viscometry, and/or Light Scattering we can calculate true molecular weights for this polymer. There is good agreement between the three advanced detection calculation methods, with all generating an Mn of around 3400. This falls within the expected Mn of this particular polymer, and highlights the benefits of employing advanced detectors in GPC.

Conclusion

The analysis of Tinuvin 622 is achieved by conventional GPC/SEC, however the resultant molecular weight is overstated when analyzing against a Polystyrene calibration. By investigating the polymer using advanced detectors such as Viscometry and Light Scattering, we can arrive at the expected molecular weight values, and therefore have a better understanding of the molecular weight distribution of the additive.

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