NOTES POLYMER

Published by Waters Corporation for Polymer Scientists and Plastics Engineers Worldwide

Viscometry option adds new power 150CV PLUS GPC SYSTEM to Millennium GPC software

NOW GET MORE INFORMATION ABOUT YOUR POLYMER IN A SINGLE ANALYSIS THAN EVER BEFORE

Waters 150CV plus is a fully integrated GPC System for analyzing polymers at temperatures from ambient to 150°C. It features both refractive index and viscometry detectors to give you more information about your polymer sample from a single injection than you could get with either detector alone. With this system you can determine:

- Universal Calibration
- Absolute Molecular Weight
- Intrinsic Viscosity
- Branching Index (a measure of long chain branching)

Data acquisition, processing, and report generation is managed by the Millennium Chromatography Manager Software. The software acquires data from the system's refractive index and viscometry detectors to give you information never available before.

The viscometry detector in Waters 150CV plus is a proprietary single capillary design based on Poiseuille's Law:

$$P = [(8/\pi)(L/r^4)](F)(\eta)$$

Where: P = Pressure Drop Across the Capillary

L = Capillary Length

r = Capillary Radius

F = Flow Rate

η = Viscosity of the Fluid

The viscometry detector is designed to prevent shear thinning during an analysis, giving you more accurate results by calculating the correct intrinsic viscosity values. The viscometry detector does not require splitting the flow path prior to entering the detector and detects the entire mass of the polymer to give you accurate intrinsic viscosity information.

MILLENNIUM CHROMATOGRAPHY MANAGER SOFTWARE — TAKING DATA AND CONVERTING IT INTO MEANINGFUL INFORMATION

Millennium Chromatography Manager Software was first introduced in 1992 and has become the best-selling chromatography data management software product ever. Well over 7,000 copies of the software have been sold worldwide in both PC and client server versions since its introduction. In early 1995, Waters introduced Millennium 2.1 Software, which features a new application for calculating GPC/Viscometry data. Millennium software is popular with analytical chemists because it is a Microsoft Windows®-based product

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VOL 6, NO. 1 • WINTER 1996

Also in this issue

Benchtop HPLC system identifies WATERS INTEGRITY™ SYSTEM and quantifies additives in medical plastics.

GIVING YOU MASS SPECTRAL DATA ON POLYMER ADDITIVES WHERE AND WHEN YOU NEED IT.

Until recently, polymer chemists untrained in mass spectroscopy who needed to confirm the identity of additives in polymer formulations or identify degradation products had one of three choices: send their sample out for analysis by an expert mass spectroscopist, confirm test results with one or more complementary techniques, or rely on confirmatory information based on reference standards and trust in their ability to provide accurate data.

In 1994, Waters™ introduced the Integrity System, the first benchtop HPLC system to feature a particle beam mass spectral detector. For the first time, bench chemists could conveniently obtain electron impact mass spectral information on their HPLC samples in a matter of minutes rather than wait days or weeks. Raw data could be processed in real time and viewed in a manner identical to photodiode array detector data. Using computerized libraries of mass spectra, compounds under investigation could be reliably and accurately identified.

The following article describes work currently underway in Waters applications laboratories using Waters Integrity

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Waters

Solving plastics processing and end-use problems with GPC together with viscometry detection

Figure 1: Molecular Weight Distribution and Branching Index (g') of a commercial resin

The sharp drop in g' at higher molecular weight indicates significant long chain branching and accounts, at least in part, for the poor performance of this material.

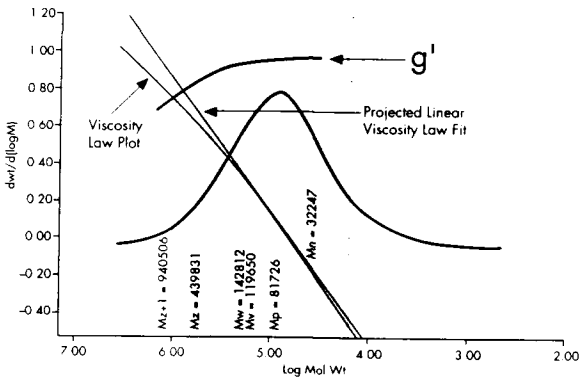
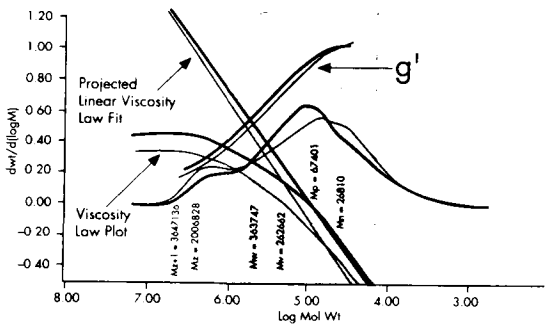
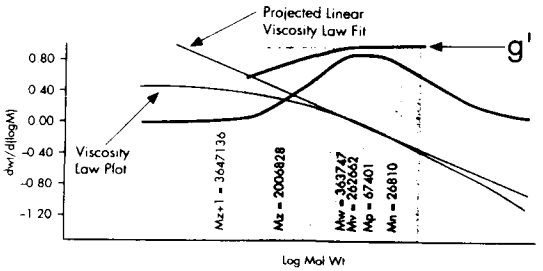


Figure 2: Comparison of two resins



With the Millennium GPC Viscometry software it is easy to compare the characteristics of multiple samples to account for differences among them. In this example the samples were quite similar but not identical. Both had bimodal molecular weight distributions and similar branching indicies with very high levels of long chain branching.

Figure 3: Evaluation of a metallocene catalyzed linear low density polyethylene



The 150CV plus GPC system is a versatile instrument. It is suitable for analyzing polymers such as this linear low density polyethylene and other polyolefins which are only soluble at elevated temperatures. Operating from ambient to 150°C, it can also be used to characterize polyamides, vinyls, polystyrenes, acrylics, polycarbonates, as well as uncured epoxies, urethanes and elastomers.

A VERSATILE TOOL FOR THE PLASTICS ENGINEER

It is well-known that polymer molecular weight distributions influence melt processability and end-use properties in a major way. Beyond the basic distribution as determined by traditional gel permeation chromatography, GPC, the relative linearity or branching of the polymer can alter the behavior even when the number or weight average molecular weight values are in the desired range.

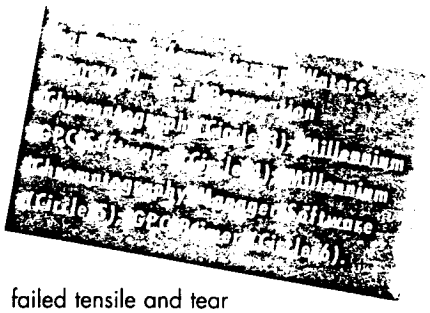
One way to obtain this structural information on a polymer is by incorporating a viscometer detector into a GPC system to give you branching and distribution information at the same time. Waters 150CV plus Gel Permeation Chromatograph incorporates such a viscometry detector as well as a version of Millennium GPC Software Millennium that processes the information from the viscometer. This powerful tool gives the plastics engineer valuable insight into the polymer structure. More information about the viscometry software can be found in the article beginning on page 1 in this publication.

THE ROLE OF BRANCHING INDEX VALUES IN PREDICTING POLYMER PROCESSING PERFORMANCE

The viscometer makes it possible to determine the branching index of the polymer, a measure of the degree of long chain branching in the sample. This factor exerts a significant influence on the melt elasticity of the polymer, causing significant differences in processability between branched and linear polymers[1]. For example, a branched polyethylene will exhibit tension stiffening upon drawing while a linear PE will exhibit tension thinning under the same conditions, resulting in a decrease in viscosity with subsequent necking and potentially premature failure at the draw point. An explanation of this difference in behavior is that entanglement of the branches prevents the polymer chains from aligning under stress, while the linear polymers can move more readily.

DEMONSTRATING BRANCHING'S EFFECT

Of course branching, and the corresponding effect it has on melt processability, is not always desirable. Figure 1 illustrates the molecular weight distribution and long chain branching of a low density polyethylene used to make heavy gauge trash bags. The resin had a low Melt Flow Index and



failed tensile and tear strength tests. This probably resulted from fabrication at temperatures that were too low for this material.

Similarly the overlay of two LDPE paper coating resins in Figure 2 indicates a high degree of branching. In addition to the branching, there are significant shoulders in the high MW region of the MW distribution curve. Both of these characteristics undoubtedly contributed to poor melt flow and the reported slowing of the coating machines to unacceptable rates.

In another evaluation, a metallocene catalyzed linear low density polyethylene (LLDPE) sample was studied. Figure 3 shows the distribution and branching index for this material. Millennium software provides considerable insight into the polymer structure for convenient comparison and interpretation of processing problems. All of the results shown in this report were obtained with Waters 150CV plus, a versatile, self-contained GPC system with integral refractometer and viscometry detection and the ability to operate at temperatures ranging from ambient to 150°C.

IMPROVE YOUR DECISION-MAKING ABILITY WITH INFORMATION FROM WATERS 150CV PLUS GEL PERMEATION CHROMATOGRAPH

The Waters 150CV plus with Millennium GPC/viscometry software provides the plastics engineer with a convenient yet powerful means of solving processing problems or, more proactively, avoiding them for even greater productivity and profitability. The Oracle® relational data base which is a standard feature of the Millennium software also enables the creation of control charts and long term trend analyses.

REFERENCES

1. N.G. McCrum, C.P.Buckley and C.B. Bucknall, *Principles of Polymer Engineering*, Oxford Science Publishing, Chapter 7, **1988**

NEW POWER TO MILLENNIUM GPC SOFTWARE continued from page 1

making it easier to use than its DOS-based predecessors. It features an Oracle® relational database which makes file management and retrieval remarkably straightforward[1]. It also features data trending and tracking capabilites so that you can monitor results of numerous analyses over time, automated integration routines for both RI and viscometry channels, and the Millennium Report Publisher™ which allows you to display printed results in standardized or customized formats. As an added convenience, Millennium even automatically calculates the inter-detector delay volume, a crucial parameter for accurate multi-detector calculations.

PROVEN UNIVERSAL CALIBRATION

In conventional GPC analysis, a plot of log (M) (molecular weight) vs. T (retention time) or V (retention volume) is constructed using narrow dispersity polymer standards. These standards are typically polystyrene or poly(methylmethacrylate) when analyzing organic-soluble polymers, and poly(ethylene oxide) or polysaccharides for aqueous GPC. The molecular weights obtained for your sample by this conventional GPC narrow standard calibration curve will be "relative" to the calibrant instead of "absolute" for the specific polymer being analyzed.

In the mid-1960's, Benoit began work on the concept of Universal Calibration[2]. In this calibration routine, the log hydrodynamic volume (η)(M) — the product of intrinsic viscosity and molecular weight — is plotted vs. retention time or elution volume. The theory postulates that any series of linear narrow standards that are random coils in solution (and do not exhibit any non-size exclusion effects such as adsorption or hydrogen bonding in the column set), will all fit the same calibration curve independent of polymer type. The Universal Calibration Curve in Figure 1 was developed with polystyrene narrow standards.

VISCOSITY LAW RELATIONSHIP — FOR DETERMINING BRANCHING

Once the Universal Calibration curve has been generated, the Millennium software then calculates and displays the Viscosity Law Plot, a plot of log M vs. log η as it did in Figure 2 for a mix of polystyrene standards. This relationship (log η vs. log M) is referred to as the Mark-Houwink law, and is expressed as:

$$\eta = k(M)^{\alpha}$$

The Mark-Houwink constants, k and α, represent the intercept and slope of the

continues on page 4

Figure 1: Calculating and plotting the Universal Calibration Curve with narrow polystyrene standards

As the standard or sample polymer is analyzed, the viscometry detector continually measures the pressure drop across the capillary, so that the intrinsic viscosity (η_i) at slice point i,[3,4] can be calculated

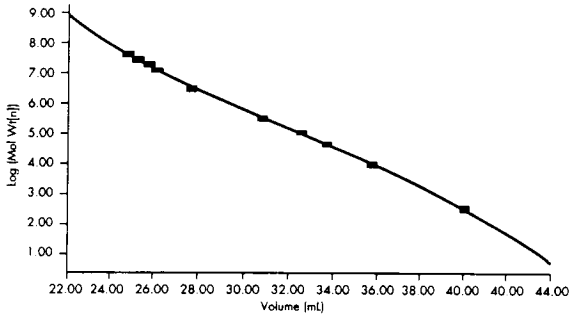


Figure 2: Viscosity Law Plot for polystyrene standards

This Viscosity Law Plot was developed with the same polystyrene standards used to produce Figure 1.

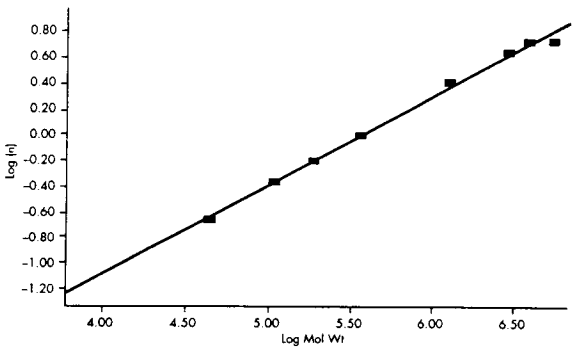


Figure 3: Detector signals for a run of NBS 1475

These are the unprocessed traces from both detectors. This information is permanently stored in the relational database of the Millennium Chromatography Manager software and can be retrieved at any time for evaluation or reprocessing.

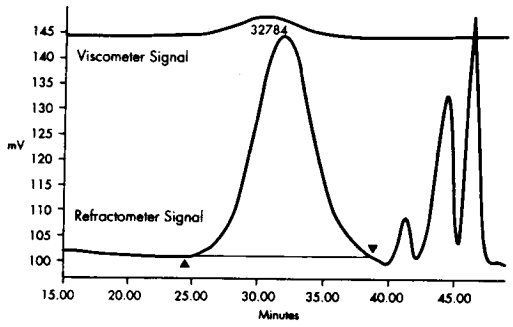


Figure 4: Molecular Weight Distribution, Viscosity Law Plots, and Branching Index for NBS 1475

The linear Viscosity Law Plot for each sample is produced by extrapolating the linear segment of the actual plot that occurs in the low molecular weight range where long chain branching is unlikely. The branching index, g', is calculated as $[\eta_{br}] / [\eta_{lin}]$.

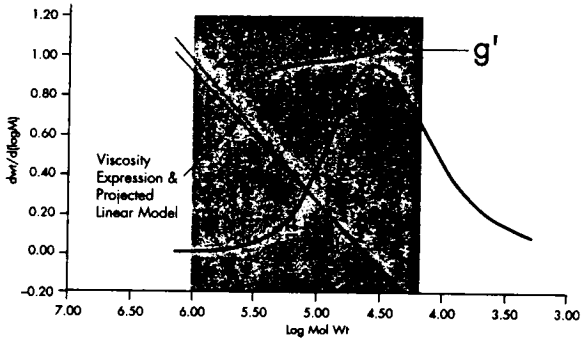
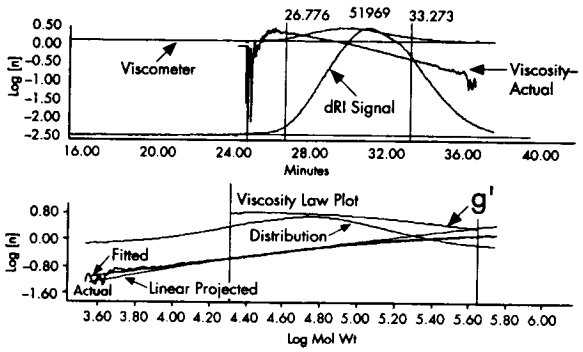


Figure 5: Molecular Weight Distribution, Viscosity Law Plots and Branching Index for NBS 1476

With Millennium you can display a complete set of results or selectively show a single characteristic of the sample. Multiple options for viewing data exist, depending on your needs and preferences.



plot, respectively. In some cases, these empirical constants may be found in the CRC Polymer Handbook[5] for several polymer/solvent/temperature combinations.

Once the Universal Calibration for the narrow standards has been established, you are then ready to determine molecular weight averages and branching characteristics of polymer samples.

COMPARING A LINEAR AND A BRANCHED POLYMER

The Microsoft Windows environment makes the integration of the polymer sample very easy. Figure 3 shows the RI and Viscometry channels for a run of NBS 1475, a well-characterized linear polyethylene broad standard, with known M_w, M_n, and η values to show the accuracy of the 150CV plus. Figure 4 illustrates the resulting molecular weight distribution, with the molecular weight averages displayed. The actual Viscosity Law Plot for this polymer is shown together with the linear plot. Since the polymer is linear, the two plots almost superimpose and their ratio (g') remains close to unity over the measured range, indicating little if any long chain branching.

In Figure 5, a similar analysis is shown for another polyethylene standard, NBS 1476, in this case a branched polymer. Millennium allows you to view test results in a variety of ways such as this two-window presentation chosen from the "Review" screen. In this instance, the g' values declined to below 0.7, giving evidence of significant long chain branching.

Refining the calculations is a very easy process with the Millennium Chromatography Manager. After the initial run, the results can be reprocessed by setting the acceptable data region cursors to exclude the high and low ends where the concentration of the eluting polymer is very low, typically about 5% of the total area under the curve. Then the "Recalculate" function is used to produce updated values of MW, intrinsic viscosity, k, α and g'. This user-specified data region can be used for subsequent analyses as part of the defined integration parameters. Other parameters you

can select include the order of curve fit for the viscosity law plot. First Order is recommended if you know the polymer is linear and Second Order if you suspect that it is branched.

The excellent performance of the 150CV plus and associated Millennium GPC Viscometry software is summarized in Table I, in which the values determined in this work show excellent agreement with generally accepted values for these two polymers.

In addition to the accuracy data shown in Table I, the GPC 150CV plus system is exceptionally reproducible. Figure 6 illustrates overlays of six injections each from three different sample vials of NBS 706, a well- characterized polystyrene broad standard. Because of its broad distribution at the low MW end, it is considered difficult to obtain number average (Mn) molecular weight precision better than 5%. In this work with 18 replicate injections, the reproducibility was outstanding, with Mn precision of 2.75%, while the weight average (Mw) values only varied by 0.45% and the Z-average (Mz) was also less than 1%, at 0.79%

ADDITIONAL VERSATILITY FOR POLYMER CHARACTERIZATION

The Millennium GPC Viscometry software is also very useful for characterizing polymers that do not have a constant refractive index increment, dn/dc, over their entire MW range. This is the case with copolymers that can vary in composition as molecular weight changes and also with low MW polymers. For these situations the viscometer alone can be used to determine number average (Mn) molecular weight, without using the concentration detector.

This calculation was first described by Goldwasser in 1989[6]. Millennium uses a method developed by Lesec which is similar to one described by Yau in 1990[7]. Mn is obtained using only the sample concentration, (C), the viscometry signal, (Vis_i), and the hydrodynamic volume Universal Calibration curve (HV_i):

$Mn=C/\Sigma(Vis_i/HV_i)$:

EVERYTHING YOU NEED IN ONE PACKAGE

The Millennium Chromatography Manager with viscometry software allows you decide how you want to work. You can either manually process your raw data and select the best regions for integration, or you can set an integration method to automatically reduce the data and print out a fully customized report. The combination of Millennium relational data base, System Suitability™ option, flexible calibration routines and integration events, plus the Windows ease of use, makes this new software package the most complete, versatile choice available for the investigator who is serious about polymer characterization.

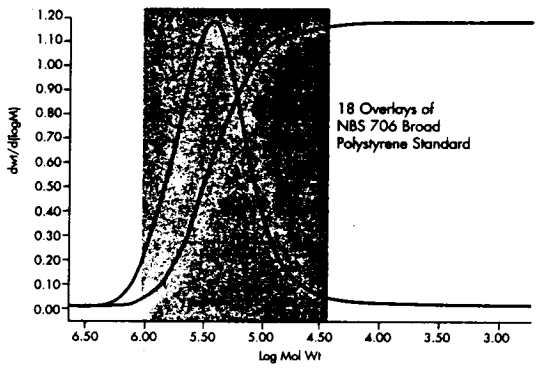
For more information on the following Waters products, circle the appropriate number(s) on the attached reply card:
Waters 150CVplus Gel Permeation Chromatograph (Circle 3);
Millennium GPC Software (Circle 4;
Millennium Chromatography Manager Software (Circle 5).

Table I

Polymer	NBS 1475		NBS 1476	
	Accepted Value	Experimental Value	Accepted Value	Experimental Value
Mw	53,000	56,900	102,000	95,800
Mn	18,300	17,400	23,700	23,400
Intrinsic Visc.	1.01	1.03	0.90	0.88
Alpha	0.70	0.69	—	—

Figure 6: Comparison of multiple molecular weight determinations

Another way to display the results of the analysis is to show the amount of each MW fraction as a distribution or as a cumulative trace. The area of the curve bracketed in color is the area that was integrated.



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