
Dr. A. Ortín, Polymer Char, Valencia, Spain.

The determination of the solution viscosity of polymeric materials is very important to the industry, both to research and manufacturing, since it can be used to estimate molar mass providing important information relating to the physical properties of polymers. The relative viscosity of a dilute polymer solution to that of the pure solvent itself is measured and from it, the intrinsic viscosity ($\eta_\text{IV}$) of the polymer is calculated.

Due to the popularity of dilute solution viscosity measurements and the availability of those methods in many manufacturing laboratories, the IV of polymers has been traditionally used to specify and to control the production grades. It must be noted however, that the IV is not a property of the polymer itself, as the molar mass is, but rather a property of the polymer solution, influenced by the solvent and the temperature.

The IVA (intrinsic viscosity analyzer) is a fully automated instrument for viscosity measurements of polymeric materials in solution. It is compatible with typically used organic solvents such as decalin, tetralin, tri-chlorobenzene (TCB) and ortho-dichlorobenzene among many others. Dissolution temperature and analysis temperature can be programmed independently from ambient to 200ºC, so that a wide range of polymers, even most crystalline ones, can be analyzed with convenience and safety.

Intrinsic Viscosity Determination

The IVA instrument performs the polymer intrinsic viscosity measurement by means of a two-capillary relative viscosity detector, which concept was developed and patented by Yau in the 80s (US 4793174), as a robust method in contrast to temperature, pressure or solvent flow rate variations. Capillary viscometers rely on the principle that the pressure drop ($\Delta P$) due to the flow ($Q$) of a fluid across a capillary tubing of length $L$ and radius $r$, is proportional to the absolute viscosity of the flowing fluid ($\eta$), according to Poiseuille’s law:

$$\Delta P = \frac{8QL}{\pi r^4}\eta$$

Absolute viscosity of fluids is important to many industries and can be measured using different types of capillary viscometers. However, in polymeric materials the interest is on the relative viscosity of a dilute polymer solution given that from it, the intrinsic viscosity of the polymeric material can be derived.

In the first place, the relative viscosity ($\eta_{\text{rel}}$) is defined as the ratio of the polymer solution viscosity to that of the pure solvent:

$$\eta_{\text{rel}} = \frac{\eta_{\text{solution}}}{\eta_{\text{solvent}}}$$

This is a dimensionless quantity which represents to what extent the added polymeric material increases the viscosity of the solvent. The relative viscosity of the solution is proportional to the amount or concentration ($C$) of polymer it contains, while the intrinsic viscosity is defined to remove that effect. The specific viscosity ($\eta_{sp}$) of the solution and the polymer intrinsic viscosity ($[\eta]$) are calculated according to the Equations:

$$\eta_{sp} = \eta_{\text{rel}} - 1$$

$$[\eta] = \lim_{C \to 0} \frac{\eta_{sp}}{C}$$
The intrinsic viscosity has units of inverse density (dL/g for instance). It is defined at the limit of infinite dilution (zero concentration), and sometimes calculated by extrapolation of relative viscosity measured at different concentration levels. A more practical and efficient approach is based on a single-point relative viscosity measurement, taken at a defined concentration low enough to eliminate the need for extrapolation, or using a model equation to obtain the extrapolated value. Among several models and equations, the Solomon-Ciutà Equation, which does not require additional parameters, can be used:

\[
\eta_r = \frac{1}{C} \left( \frac{1}{C} - 1 \right) \ln \frac{\eta_r}{\eta_0}
\]

The relative viscosity is calculated as a function of time as the injected solution goes through the system, and any influence of flow-rate variations (such as high frequency pulsations) or thermal effects are cancelled out directly by the reference capillary, resulting in very high sensitivity and long-term stability.

### IVA - Intrinsic Viscosity Analyzer

The IVA constitutes a precise and convenient approach to IV measurement, due to the automation of all the analytical procedures, from vials filling to reporting of results. Samples are put in solid form into 20 mL vials and brought to the instrument autosampler tray, with capacity of 42 vials. The operator enters the samples identification data, selects the analytical method and starts the analysis that proceeds unattended until all the vials defined in the instrument run queue are analyzed. Under software control, the instrument takes care of adding solvent to the vials, controlling the dissolution time per vial, injecting each solution and rinsing of the capillary lines. Thanks to the compact design without cold spots, the solution travels safely throughout all the system without any risk of precipitation. A new run can be immediately started after finishing the previous one, achieving a throughput of 40 samples a day in standard operation conditions.

In order to maintain the polymeric sample integrity along the dissolution and measurement processes, the Sample Care protocols successfully implemented by the manufacturer in other analytical applications, are also part of the IVA method. Those include the ability to purge the vial atmosphere with an inert gas (Nitrogen) before dissolution starts, and minimizing the time spent at high temperature by keeping every vial inside of the oven only for the programmed dissolution time. The vials remain in an external tray at room temperature until the scheduling software requests their transfer to the dissolution oven. Efficient heat transfer to the vial, together with preheating of the solvent prior to delivery to the vial, help in shortening the time required for dissolution. Oxidative and thermal degradation is thus minimized, ensuring that accurate intrinsic viscosity is measured even for the most challenging ultra-high molar mass materials, or oxidation-prone polymers, such as polypropylene.

No solvent needs to be handled by the analyst at any moment and no vapors are released to the atmosphere given all the system is airtight at all times. Thus, a higher standard in safety and health is set thanks to the IVA fully automated approach.

For increased safety level, the instrument is equipped with three vapor sensors in different compartments, in order to detect any potential leaks of solvent and stop the analysis in such event. Over-temperature protection, as well as heater failure protections are included into the instrument dedicated electronics as well as monitoring software.

### Results and Applications

The viscosity measurement is performed by the built-in two-capillary viscometer placed inside of an oven with extremely precise and stable temperature control (0.01°C). The instrument fluidic design is rather simple, having a single valve inside the oven, which results in high reliability.

The IV results obtained by IVA are in good agreement with the ISO 1628-3:2010 method, as can be verified in Figure 3, for a series of polypropylene samples with medium to high viscosity values, analyzed in TCB at 150°C.
An infrared (IR) detector is optionally incorporated for online accurate quantification of the injected mass which otherwise needs to be entered as weighed using an analytical balance. The IR detector is suitable for detection of polymers with aliphatic CH groups, and that can be dissolved in solvents that are IR transparent. An important group in this category are polyolefins, such as polyethylene and polypropylene as well as copolymers.

**Application example: intrinsic viscosity of UHMWPE**

Maybe one of the most challenging polymers for analysis is ultra high molar mass polyethylene (UHMWPE). Those are high crystallinity materials with extremely high values of IV, only soluble at elevated temperatures in organic solvents. Special care must be taken in sample preparation to prevent degradation, which would reduce the apparent viscosity, and also in the analysis given the high specific viscosity of the solutions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>IV (dL/g)</th>
<th>std (IR)</th>
<th>std (balance)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>11.38</td>
<td>0.2</td>
<td>0.7</td>
</tr>
<tr>
<td>B</td>
<td>21.00</td>
<td>0.4</td>
<td>2.6</td>
</tr>
<tr>
<td>C</td>
<td>28.67</td>
<td>0.7</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Table 1. Intrinsic viscosity (IV) for three industrial UHMWPE samples analyzed by IVA in TCB at 140ºC. Standard deviation based on 6 replicates when using the measured injected mass by IR, or using the nominal mass given by the analytical balance.

Three different materials were analyzed at a low concentration level of 0.25 or 0.15 mg/mL in TCB, for limiting the viscosity of the solutions. Dissolution time was 1 hour with gently shaking, at 140ºC under nitrogen atmosphere, in order to minimize thermal and oxidative degradation. Results are presented in Table 1, together with standard deviation, when using the IR detector for quantifying the injected mass, and when using the nominal weight given by the analytical balance, in the IV calculation. An improvement in the precision is clearly seen when the actual mass measured by the IR detector is considered, given it eliminates any errors associated with handling small amounts of polymer by the operator, but also due to the possible presence of non-soluble particles.

Other UHMWPE materials from industry, even with higher viscosities ranging from 30 to 50 dL/g, were also successfully analyzed in the IVA instrument. The dissolution time was increased up to 3 hours and, in the extreme cases, the measurement flow rate was reduced in order to keep the backpressure in the system within acceptable range. The estimated molar mass averages from IV determination were in excess of 10 million g/mol, beyond the typical application range of high temperature Gel Permeation or Size Exclusion Chromatography (GPC/SEC). As it happens in many cases of industrial interest, viscometry was the only path to characterize and rank those products according to their molar mass.

**Conclusion**

A new fully automated Intrinsic Viscosity Analyzer (IVA) has been developed to fulfill the need in the industry for an efficient, precise and safe approach to dilute solution viscosity determinations. A wide range of polymers soluble from ambient to 200ºC can be analyzed in a variety of solvents.

The instrument performs all the needed steps without user intervention nor solvent handling throughout the whole process for up to 42 samples, paying special attention to the sample condition and minimizing the degradation.

The two-capillary serial design is self-cleaning and self-calibrating, which ensures long term, robust and precise viscosity results, removing the need for manual rinsing or cleaning. When applicable, the IR detection helps in improving the accuracy and precision of the method. Measurement of intrinsic viscosities in excess of 30dL/g for UHMWPE was achieved with convenience.

Published in: Petro Industry News, April/May Issue 2015.
Solutions for Polyolefin Characterization

CRYSTAF®: An instrument designed for intensive use in the analysis of the Chemical Composition Distribution in Polyolefins.

TREF®: A completely automated apparatus for the analysis of the Chemical Composition Distribution in Polyolefins. It provides complementary information to CRYSTAF data in the analysis of some complex resins.

CRYSTAF-TREF®: CRYSTAF and TREF techniques are available in the same equipment for a full Chemical Composition Distribution characterization.

CEF®: A high throughput equipment to analyze the Chemical Composition Distribution in Polyolefins, using a new approach combining CRYSTAF and TREF separation mechanisms.

PREP mc®: An automated instrument to perform semipreparative fractionation according to composition by TREF or CRYSTAF, or molar mass.

PREP C20®: New column-based preparative fractionation instrument, capable to fractionate up to 20 grams of polymer.

CRYSTEX® QC: A truly automated system based on TREF-separation concept for soluble fraction measurement ethylene content and intrinsic viscosity in PP/PE plants control.

CRYSTEX® 42®: A high-throughput and easy to use system for simultaneous measurement of the soluble fraction, ethylene content and intrinsic viscosity in a fully automated process for up to 42 samples.

IVA®: Reliable and automated instrument for Intrinsic Viscosity Analysis of polymers with dissolution temperature up to 200°C.


CFC®: A fully automated Cross Fractionation Chromatograph (TREF+GPC) for the analysis of Bivariate distribution in Polyolefins.

GPC One® Software: The most comprehensive GPC/SEC Calculations Software integrating all detectors’ signals.

Data Unit 200®: Versatile signals acquisition device to link any vendor GPC instrument with Polymer Char’s GPC One®.

TGIC®: An adsorption high temperature HPLC technique for the analysis of low crystallinity Polyolefins.

SGIC 2D®: An adsorption high temperature HPLC technique combined with GPC and infrared detection for the analysis of composition and molar mass interdependence of Polyolefin resins.

IR4®: Integrated reliable and simple to use infrared (IR) detector to measure concentration and composition.

IRS MCT®: Integrated and modern IR detector with an MCT element (thermoelectrically cooled) for high sensitivity analysis.

Analytical Services: Polymer Char laboratory, a global reference in the field, counts on the latest technologies for Polyolefin Characterization.

Company Profile

Polymer Char is devoted to the development of state-of-the-art instrumentation for Polyolefin Analysis.

The company offers the broadest and most modern range of instruments and services for polymer analysis and more specifically, for the structural characterization of Polyolefins, such as Molar Mass Distribution (GPC-IR®, GPC-QC®, GPC One®), Chemical Composition Distribution (CRYSTAF, TREF, CEF®), Bivariate Distribution by Cross-Fractionation Chromatography (CFC®), High Temperature HPLC (TGIC®, SGIC 2D®), Soluble Fraction Determination (CRYSTEX®, CRYSTEX® QC and CRYSTEX® 42®), Preparative Fractionation (PREP mc®, PREP C20®), Intrinsic Viscosity (IVA®) or integrated Infrared Detection (IR4®, IRS MCT®).

Polymer Char is also well known for its advanced approach to virtual instrumentation software that, together with excellent remote control capabilities and its strong commitment to Customer success, places the company at the leading edge on instrumentation diagnostics and technical support.

Together with its global network of partners and distributors, Polymer Char supplies, trains and supports Customers worldwide. The company provides analytical services in 35 countries and its instruments are present today in over 20 countries within the Americas, Europe, Africa, Middle East and Asia Pacific, predominantly serving Polymer Producers and Processors, Government and Academic Research Laboratories, Contract Research Organizations, Analytical and Testing Laboratories, and Chemical Instrumentation Manufacturers.

In the last two decades and with an annual investment of up to 20% of its manpower resources on R&D, Polymer Char has played a key role in the development of most of the existing Polyolefin analysis technologies, such as CRYSTAF, CRYSTEX®, CEF®, CFC®, and GPC with IR detection. Each new project, each new analysis, underpins Polymer Char as the Polyolefin Characterization Company.