

## Live Webinar Q&A Sheet:

# Supporting Sustainability: Comprehensive Case Study on PLGA & PLA Polymer Characterization & Optimization Using Light Scattering Confirmation Dr. Stepan Podzimek and Julienne Regele

The recorded webinar may be viewed from the <u>Polymer Characterization</u> webinars page. These questions were submitted by live viewers. Additional information on SEC-MALS, DLS, FFF, CG-MALS and RT-MALS may be found on the Wyatt web <u>Library</u> under Webinars, Application Notes, Featured Publications and Bibliography, as well as on the corresponding <u>Product page</u> and <u>Solutions</u> page of our web site.

Please contact <u>info@wyatt.com</u> with any additional questions.

### **Questions & Answers**

### MACROECONOMY

- **Q.** What are the most promising applications of sustainable polymers in the near future?
- **A.** We see a lot of development in sustainable polymer materials for packaging applications. While this is a commodity material today, it is the largest segment of production with thins and thin films. Actually, PLA is a material that is ideal for that type of application.
- *Q.* How much of the drive for sustainable polymers is being driven by government regulations versus other factors?
- A. We certainly see many policies coming through, especially in Europe, to tackle this problem. However, organizations that sell products in plastic materials are also feeling the pressure from consumers to reduce or reuse plastic materials. There is still a lot of education that needs to happen in the public about recycling and how consumer choices impact the plastic recycling stream. To increase recycled materials used in products, you need a reliable cost effective stream of incoming material and that isn't quite there for all materials yet. Policy implementation to build better recycling infrastructure will enhance uptake.

### VISCOSITY

- Q. What is the difference between the intrinsic viscosity and viscosity?
- A. Intrinsic viscosity is traditionally used to characterize polymers. Intrinsic viscosity is the specific viscosity divided by concentration at the concentration approaching 0. Viscosity is a material quantity, similar to density and other constants, by definition it is the shear stress divided by the shear rate.
- Q. You mentioned that online viscometer can be used to measure hydrodynamic radius. What is the difference between hydrodynamic radius obtained by online viscometer and by dynamic light scattering?

- A. The hydrodynamic radius measured by DLS is the radius of a hypothetical sphere that would have the same diffusion coefficient as particles that are measured. Hydrodynamic radius obtained by viscometer is radius of sphere that would have the same product of molar mass and intrinsic viscosity as the molecules being measured. The two radii agree well and can usually be used interchangeably because they provide the same information.
- Q. What is the best way to determine the value of the drainage factor?
- A. You will need to measure the branching ratio based on the root mean square radius and branching ratio based on intrinsic viscosity, and then compare them. However, the procedure is mostly impossible for PLGA because it is too small to measure the root-mean square radius correctly.

### **MW AND SEC**

- Q. What SEC mobile phase would you recommend for the analysis of PLGA?
- A. Tetrahydrofuran (THF) is typically the most suitable solvent and for those samples which are not soluble in THF, the next choice is chloroform.
- R. What SEC mobile phase would you recommend for the analysis of PLGA?
- B. Tetrahydrofuran (THF) is typically the most suitable solvent and for those samples which are not soluble in THF, the next choice is chloroform.
- Q. On SLIDE 34, SEC-MALS of linear and branched PLA, what types of eluents and columns did you use? Did you use multiple columns?
- A. The results were acquired using two columns in series. The dimensions were 300 mm length and 8 mm inner diameter. They were packed with mixed packing. The separation range was about 100 g/mol to 2 million g/mol. The eluent was THF, and a flow rate of 1 ml/min. These conditions were used for all data shown today.
- Q. The MALS is only useful for Mw above a certain Mw?
- A. SEC is the most common technique for molar mass determination and is widely used and sometimes misused because the numbers can be far from true values. SEC-MALS is an absolute method that doesn't require or depend on standards like SEC with solely optical detection, like a refractive index detector. Modern MALS instruments do not have any low molar mass limit; the correct molar mass can be measured down to several hundred g/mol.
- Q. You referenced 90-degree angle to measure the Mw and other angles to measure branching. We calibrate the older models with the batch cell (20ml vial) using polysorbate (PS) standards at 90 degrees and obtain Mw of polymers in THF. Do you have an example of the branching effects and which angles are the most sensitive, to different types of branching?
- A. On the slide in the talk, the signals of the 90-degree detector and refractive index detector are overlaid on molar mass plot to show how the polymer elutes across the peaks, but all angles are used to measure molar mass. Different angles are not branching sensitive. It is the molecular size that is branching sensitive. In the case of PLA and PLGA the molecular size is measured as intrinsic viscosity. In the case of larger polymers, the size can be measured as the root mean square radius.

#### **GENERAL TECHNOLOGY**

- Q. What about measuring PLA bio composite molar mass?
- A. It is necessary to dissolve the PLA in composite. PLA can be solubilized in either THF or chloroform. The components that do not dissolve are then filtered and then the sample is injected in the SEC columns. Filtration is a critical step to protect the SEC columns.
- *Q.* Is it possible to use QELS/online DLS radius of hydration (Rh) calculations to obtain intrinsic viscosity (IV) in place of differential viscometry to obtain same branching information?
- A. QELS can be used, but the determination of hydrodynamic radius by online viscometer is mostly more sensitive. To characterize branching, the intrinsic viscosity need not be transferred to hydrodynamic radius. Branching is characterized from the Mark-Houwink plot. The intrinsic viscosity of branched molecules divided by the intrinsic viscosity of linear molecules at the same molar mass is called branching ratio g<sup>'</sup>. The branching ratio can be used to calculate the number of arms or number of branch units in the polymer molecule.
- *Q.* How would or do you calibrate for the branching -the degree of branching and the lengths and/or types of branching?
- A. Branching cannot be calibrated. The degree of branching can be quantified from the branching ratio g based on the root mean square radius or g' based on the intrinsic viscosity. There are various semi-empirical equations relating branching ratio with number of branch units in randomly branched polymers or number of arms in star-like polymers. The length of branches or type of branching cannot be determined by SEC-MALS-Viscosity.
- Q. Is it possible to use SEC with universal calibration instead of MALS detector?
- A. It is possible. The results from universal calibration are theoretically correct, but in reality, they are more affected by the brand broadening in columns and by non-steric separation mechanisms. The MALS is more reliable way to the true molar mass.
- *Q.* What are some ways I can use the DSC or rheometer to better understand how my polymer material will behave in processing conditions?
- A. DSC can be used to understand the curing process of your polymer material. This information is critical to identify process limitations, especially when it comes to temperature. Rheometers take polymer analysis to a next level to really understand how the material flows and deformations in response to different conditions. Like injection molding, you can mimic the stress condition in a rheometer and then set your conditions based on the polymer properties. There are lot of specific examples to look at on the polymer application page.