Live Webinar Q&A Sheet:

Multi-Detector SEC Characterization of Polymer Architectures

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

Please contact info@wyatt.com with any additional questions.

Q: *When would you use the z-average molar mass or the z+1 average?*

A: These are used in the analysis of branched polymers. Also, when companies get a customer complaint about a polymeric product and there are no differences found between production runs in M_n and M_w data, M_z and M_{z+1} can reveal differences.

Q: *It is quite common to find synthetic branched polymers, because they are designed that way. What about natural polymers – are branched polymers common in nature? Would they be star, comb, dendrimers or something else? Can their branching be analyzed by SEC-MALS as well?*

A: Yes – for example starch and amylopectin are branched. Their branching properties are analyzed in the same way as synthetic polymers, using MALS or MALS + viscometry.

Q: *Besides the extra time of analysis, are there any disadvantages to using 6 columns in your SEC system? Do you think it is feasible or necessary to have so many in routine analysis?*

A: In my opinion SEC-MALS is good for research but not for routine analysis at a demanding level of quality. As I have shown elsewhere, in industry that you cannot even get 3 sigma with SEC data, let alone 6 sigma. For research, I believe 6 columns are necessary for good data.

Q: *You mentioned that the UV detector is used to determine composition of a copolymer. Please explain how that is done.*

A: In a copolymer such as isobutylene-co-isoprene or co-styrene, isobutylene does not have a UV response but the other components do. So you can see the isoprene or styrene by UV, and you can take the UV-RI ratio across the distribution to calculate the mass ratio of the copolymer. With the addition of MALS information, the molar mass of each component can be calculated.

Q: *If there is no literature value of dn/dc, what is the best way to determine it?*

A: Using the RI detector in batch mode – make a series of concentrations and plot *n* vs c, and the slope gives *dn/dc*.

Q. *What criteria do you typically use in selection of GPC peak start/stop to measure g' (RI or MALS S:N ratio, or Mark-Houwink plot or other).*

A. On the high side (larger retention volume) I use the lowest detectable LS signal and on the low side (lower retention volume) I use the lowest detectable RI signal to set the integration limits.

Q: *Is there one, generally accepted molar mass at which to report g' or the number of arms?*

A: Not to my knowledge, this would not have much validity the number of arms in a star polymer or similar branched structure depends on various factors as well as molar mass.

Q: *What is the significance of M_v versus M_w in evaluating a polymer?*

A: The use of M_v is due to historical reasons, since in the past viscosity measurements were commonly used to get molecular weight data. It is generally close in value to M_w.

Q: *Can SEC-MALS be used for separation, identification and characterization of highly branched polysaccharides? Or do they have to be linear bio-polymers or homo-polymers?*

A: Yes, SEC-MALS will readily determine the molar mass, size and conformation of highly branched polysaccharides. You would need corresponding linear polymers of the same molar mass in order to get *g* and *h* branching ratios, but you can measure ρ using SEC-MALS-DLS as well as the Mark-Houwink-Sakurada conformational parameters using SEC-MALS-IV.

Q: *You say that we should not ignore the M_z values, but what does the M_z values tell you about your polymer?*

A: Since it is weighted towards the higher molar masses, M_z gives information on the upper size range and magnifies differences between polymer samples that might have similar M_w or M_n. Additionally, as I showed in the webinar, you can correlate low shear viscosity with M_w and M_z.

Q: *If you would not have had branching of PIB across the whole molecular weight range, would you expect a loss or decrease in UV signal at some point on the chromatogram? Do you compare that against some known branched standard to get a relative view of intensity?*

A: Yes – you could see where in the distribution you have no UV-active groups (the branching points). We compared the theoretical branching points with those measured using link destruction. In theory you could make some star-branched standards, but randomly-branched standards may not be possible to make.

Q: *What are the uses of a cyclical polymer?*

A: They have theoretical interest as well as practical. For example, in your car tire, rolling resistance is associated with polymer end groups. In a ring you have no end groups so in principle you could reduce rolling resistance and save gas.

Q: *How do you get the branching number if Rg< 10 nm?*

A: An online differential viscometer is used with MALS to determine the hydrodynamic radius R_h, and the branching ratio *h* is given by the ratio of R_h between and linear and branched samples of the same molar mass.

Q: *You mentioned that you used polystyrene (PS) to calibrate your SEC columns for accuracy, but PIB is very different from the PS standard. Can you please explain how you can account for the difference between the PS calibration standard and the PIB analyte?*

A: With MALS, column calibration is not necessary. Rather, we use the PS standard for quality control of the instruments, not for calibration – if I see a deviation from the nominal PS values, I know that something is wrong with my set-up.

Q: *My sample is dissolved in water. It's hard to dissolve in solvent. How should I perform MW measurements?*

A: Water-based SEC-MALS is very commonly done, all you need is the right SEC column and the same system described in the webinar (without continuous distillation, of course).

Q: *Was the Universal Calibration work done with a viscometer detector? If so, can you explain why the Universal Calibration results are so different from the MALS results?*

A: In Universal Calibration, the hydrodynamic volume V_h is derived from the elution volume, the intrinsic viscosity is measured with an online viscometer, and molar mass is calculated from the known relationship between V_h, *M* and intrinsic viscosity. The calculation assumes that the polymer sample has a linear conformation just like the PS standard used for calibration. However, a branched polymer will generally have a different relationship between V_h, *M* and intrinsic viscosity, so if you compare your polymer to linear PS standards you will under- or over-estimate the molecular weight of your branched polymer.

Q: *Any suggestions about experiments for distinguishing between a single ring versus a connected ring with multiple rings (de Genne's Olympic Rings)?*

A: This is a million-dollar question we are actively working on. Rheology may be the key.

Q: *The detection limit of R_g is >10 nm. Is it depending on the system? or theoretical limit?*

A: The limit is set by the wavelength and the range of angles measured. The MALS instrument covers nearly the entire range of angles (extending the range entails much lower signal-to-noise and is not very practical), so in order to reduce the detection limit, a shorter wavelength light source is needed.


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