Live Webinar Q&A Sheet:
Shining a Light on Conjugated Polymers with GPC-MALS

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 FFF may be found in the Wyatt website Resources section under Webinars, Application Notes, and Bibliography, as well as on the corresponding Product page and Solutions page of our web site.

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SEC-MALS

Q: *To calculate the MW from MALS you need the polymer's dn/dc value. How was this done, bearing in mind that a pure substance is required for this and that dn/dc typically varies rapidly in the low molecular weight region, i.e between degree of polymerization (DP) of 10 and 40? Did you perform any offline measurements of dn/dc?*

A: No—we purified the polymer by recycling preparative GPC, and then ran analytical GPC-MALS and used the 100% mass recovery method to determine dn/dc. You are right that dn/dc can change on going from small oligomers to polymers for some cases, but our materials are all DP >20, and given the large dn/dc of our polymers in THF, any changes with DP would be negligible.

Q: *The fit degree in these plots changes the MW and dispersity a lot. What is the best approach to selecting an angular fit degree?*

A: If the fit quality is good ($R^2 \geq 0.999$), and the sample of interest is within the range of the calibration standards, the order of the polynomial shouldn't matter. I recommend using the minimal order that gives a good fit quality. In our case, we used a third-order fit, and $R^2 = 0.9998$.

Q: *Can ASTRA's conjugate analysis feature, which combines MALS, RI and UV, be used to determine the conjugation ratio in these copolymers?*

A: There is interest in fine-tuning the optoelectronic properties of P3HT by copolymerizing it with electron-poor moieties. The conjugate analysis in ASTRA® utilizes the combination of UV and RI concentration detectors to determine mass fractions of two-component copolymers, by utilizing the extinction coefficient for each component in combination with the dn/dc of each component. You could take the polythiophene homopolymer and determine its parameters, then take the benzotriazole homopolymer and determine its extinction coefficient and dn/dc. Provided the variables are different enough, (usually differences in the UV extinction coefficient provide the discrimination), you could determine the mass fraction of each component in the copolymer. Based on the unique UV absorption spectra for these two homopolymers we saw today, this analysis could work and could be interesting to compare to the mass fraction via NMR analysis.

Q: *If you can use either UV or RI for concentration measurement of the polymer, which is preferable, and why?*

A: I'd use RI—UV absorbance for some polymers can saturate the detector (or be outside the linear regime), making it difficult to use; also you can automatically get dn/dc from RI data.

Q: If you measure the polymer's absorbance at the MALS laser wavelength, what is the minimum value for which you would decide to use ASTRA's absorbance correction?

A: Rather than absorbance, an even better metric is the minimum extinction coefficient at this wavelength, and that's still difficult to use. The short answer is to use the decrease in the DAWN MALS instrument's forward monitor to gauge whether or not you need to use the correction. A dip of more than 1-2% would justify the correction.

Q: How much of the forward monitor light do you expect to lose due to scattering as a percent when there is no absorbance?

A: Essentially you should see almost no change in the forward monitor if there's no absorbance, typically not more than 1-2%.

Column calibration and universal calibration

Q: *What are the limitations of Universal Calibration and how would you choose between it and GPC-MALS?*

A: Universal calibration has some specific advantages for molar mass determination, especially for strongly fluorescent samples. But ultimately it is still a calibration-based technique that requires generating a calibration curve, whereas MALS does not need reference kits and is considered the gold standard for absolute molar mass characterization of polymers. In fact, MALS is often used to certify the molar mass of standards that are then used for universal calibration.

Going beyond just molar mass determination, the combination of MALS and viscometry really unlocks a comprehensive characterization toolkit. You can determine Mark-Houwink-Sakurada coefficients for novel materials, you can determine the RMS radius from MALS or the hydrodynamic volume from intrinsic viscosity and use that information for branching analysis or insight into polymer structure and conformation. Together, you can create a very robust system.

Q: If we characterize well our calibrations standard by SEC-MALS and if the standards are the same kind of polymer as the tested product, will we have the right MW, hydrodynamics radius, distribution, and polydispersity of our samples?

A: Yes—if your product is the same material as the calibration standards, you will have accurate results.

Q: *Was the molecular weight determined by refractive index (RI) or light scattering (LS), and how much difference does it make?*

A: Absolute MW cannot be determined from RI alone or from LS alone—we used either MALS or viscometry, together with RI, and the results were within 10%.

Q: *Could you please compare the analysis of molecular weight by NMR, GPC-MALS, GPC-RI and GPC-Viscometry? When you say universal curve, does mean that you can apply it to any polymer? What if a polymer does not absorb in UV-VIS?*

A: NMR end-group analysis is great if you (a) have end-groups, and (b) can resolve them—neither of which necessarily holds true. GPC-MALS is generally robust, but can present problems when the sample absorbs the light used to do the scattering. GPC-RI does not provide absolute molecular weights, so is not reliable unless your calibration standards are the same as the sample of interest. GPC-Viscometry enables universal calibration, which does mean that you can apply it to any polymer, including those that don't have much of a UV-Vis cross-section.

In all of the GPC-hyphenated methods, usually an RI detector is used to determine the concentration, but any accurate and linear concentration-sensitive technique appropriate for the analyte will work, such as UV or infrared absorption.

Q: *Are there any polymer standards available that would permit accurate analysis of rod-like samples by analytical GPC with column calibration?*

A: That would be a great question to ask NIST folks about—I bet there are rod-like calibrants. However, using calibration would automatically give relative MW values—not absolute—which would compromise accuracy. The most accurate analysis of your sample by conventional calibration requires a standard that is close in structure to what you are studying, this is partly why conventional calibration can be so challenging—as many families of macromolecules lack a suitable reference standard and not all rod-like polymers are similar to each other. You also want a controlled polymerization so you can accurately describe the molar mass when generating the calibration curve.

Keep in mind that even with a suitable standard, something as minor as broader peaks due to higher injection volumes will lead to different results compared to the same sample with a smaller injection—that's just the nature of conventional calibration curve. A lot of these limitations can be overcome with universal calibration as we've seen today, and even more so with MALS.

With that said, you may be able to find controlled-polymerized conjugated polymers, poly(arylenes), or polysulfones polymer standards that are at least more rod-like than polystyrene. But this is definitely a challenge of column calibration overall.

Application-specific

Q: *What is the best way to analyze the small species oligomers/high m-e species that become evident at longer elution times?*

A: This depends on what, specifically, you need to analyze. There are columns that are designed to provide good separation of low molecular weight species—one could use such a column and integrate the spectrum. Alternatively, one could use MALDI-TOF or LC-MS. Some oligomers are isolable and separable by column chromatography. Preparative GPC is also an option.

Q: I usually analyze environmental micro and nanoplastics using GPC-UV-MALS-RI and the signal in the concentration detector is too low for a good reading. What is the usual concentration range that you use to perform calibration of polymers?

A: 1-3 mg of polymer per mL of solution.

Q: *Do both methods show bands in SDS-PAGE?*

A: Synthetic polymers are not, in general, suitable for SDS-PAGE. This technique is popular among proteins scientists because proteins tend to contain discrete populations (leading to 'bands'), are never branched, and tend to have similar charge per unit length upon denaturation in SDS. Polymers are generally quite heterogeneous – often over one or more orders of magnitude – and have wide-ranging charge properties and molecular architectures such as short-chain branching, long-chain branching, hyperbranching, etc., and in many cases are not even soluble in aqueous solutions, so SDS-PAGE is not applicable.