Live Webinar Q&A Sheet:

SEC-MALS Characterization of Block Polymers

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.

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

SEC-MALS

Q: *How can I determine polymer radius or radius distributions when R_g is below 10 nm?*

A: While it can readily measure the molar mass of small polymers, MALS cannot generally measure the rms radius below 10 nm. There are a few strategies to accomplish this in the context of SEC-MALS.

In-line techniques such as dynamic light scattering (using a WyattQELS™ module embedded in the DAWN® MALS instrument) or viscometry (by adding a ViscoStar® differential viscometer to the SEC-MALS system) can determine hydrodynamic radius down to about half a nanometer.

Additionally, if you have good chromatography with a distribution of radius values, and a sizeable fraction is above 10 nm where MALS can measure the radius, you can use *Results Fitting* in the ASTRA® software. This method extrapolates the radius from the portion of the chromatogram containing the larger polymers by fitting a function of radius versus elution time.

Q: *How does the DAWN work in high temperature experiments? What kind of ovens are compatible with Wyatt's Ultra-High-Temperature DAWN?*

A: High-temperature operation is often needed to keep samples dissolved and the mobile phase at low viscosity. For such applications, we offer an ultra-high temperature version of the DAWN that can regulate temperature from ambient up to 210 °C, both in the flow cell and in the tubing going into and out of the flow cell. The heated line may be coupled to many ovens, like PolymerChar systems, Agilent Polymer Labs GPC-220 and Infinity II Ovens, and Tosoh EcoSEC ovens. When temperature regulation is required but not at such high temperatures, the heated/cooled DAWN can be stabilized from -15 to +150 °C.

Q: *What are the advantages/disadvantages of UHPLC vs HPLC for polymer characterization?*

A: The advantage of UHPLC technology is the ability to deliver uniform and consistent flow through columns with smaller, more tightly packed beads than traditional SEC columns, resulting in more

efficient separation. A disadvantage is that UHPLC columns must operate at much higher pressures than traditional HPLCs. However, having overcome the pressure issues, the net result is faster run times, lower sample loading, and higher resolution. In order to take advantage of the benefits of UHPLC, we developed UHPLC-compatible detectors like the microDAWN®, microViscoStar® and microOptilab® that have lower dispersion and higher acquisition rates than our standard HPLC detectors, as well as operating parameters optimized for UHPLC.

Q: *Can solvent mixtures be used when characterizing polymers via SEC-MALS?*

A: For isocratic chromatography, pre-mixed solvent mixtures are not problem. It's important to note that both the normalization coefficients and *dn/dc* depend on the refractive index of the solvent—so if, for example, you switch from 100% THF to a mixture of THF and chloroform, you would need to re-measure the normalization coefficients and determine *dn/dc* of your sample in that mixture.

Gradient chromatography such as reverse phase chromatography, where the solvent composition varies over the course of the elution, is more challenging, because the refractive index (and hence *dn/dc* as well) is also changing. For some solvent pairs you can find a range of mixtures where the refractive index is relatively constant, in particular acetonitrile/water over 20% – 60% acetonitrile.

Q: *How can we diagnose the SEC results to determine if the polymer is interacting with the column (slide 29) or if we have residual macroinitiator?*

A: If it is interaction, the molar mass should stay roughly constant across the tail; if it is residual macroinitiator, then the value of molar mass should be what you expect. It is often helpful to overlay the SEC-MALS trace of the macroinitiator on the trace from the copolymer.

Determination of dn/dc

Q: *If the intercept of your dn/dc concentration series is not exactly 0.0, what does that tell you?*

A: Usually that is an indication of an error in sample preparation (the concentrations are not what you thought they were) or a problem with the measurements. Sample concentration errors can be avoided with an automated diluter.

Q: *What is the typical accuracy of dn/dc values from literature? Where do we need to be careful?*

A: Usually *dn/dc* can be measured to within 1-2%. However, with literature values you have to be sure to check what wavelength and temperature were used; these affect the values, especially the former.

Q: *Can molar masses of block co-polymers be measured accurately if the dn/dc values of the blocks differ significantly?*

A: There is no inevitable problem if this is the case. It does mean the "error" term in light scattering will be larger, all things being equal, but if the composition distribution is narrow, it won't matter much. The experimental test, which is tedious but revealing, would be to make the measurements in two solvents, thereby changing both dn/dc values. If your resulting value for molar mass is the same, then there is definitely no problem.

Q: *Is it possible to accurately measure dn/dc of a miktoarm star polymer (i.e., equal chain length for each block constituting the overall miktoarm star)?*

A: Yes. However, this will be an average over the entire sample. Individual polymers may have quite different values.

Q: *How can you analyze PLGA with different L/G ratio and molecular weight? How can you measure dn/dc for PLGA with different L/G ratio and molecular weight?*

A: L/G form reasonably "random" copolymers, and the dn/dc values of each component are not too different. This makes it straightforward to determine dn/dc of a given ratio and the determine accurate molar masses.

Block co-polymers – synthesis and properties

Q: *How does molar mass dispersity affect block polymer self-assembly?*

A: Self-assembly is, in some sense, an averaging process. Consequently, very well-defined nanostructures can be achieved with quite broad samples (dispersity of 1.5, for example). On the other hand, if the mean composition places the sample near a transition from one structure to another (as in the gyroid sample presented), then dispersity can tip the balance. There are also instances where certain kinds of designed dispersity can allow access to different phases altogether.

Q: *How much can a UV detector (or other species-selective concentration detector) help with block co-polymer characterization?*

A: With specific dual-component co-polymers, where the extinction coefficients of the homopolymers differ sufficiently from each other, ASTRA's *Copolymer Analysis* method characterizes the copolymer in each eluting volume by measuring both UV and dRI signals. The analysis takes into account the *dn/dc* value and extinctions coefficient of each component to determine the mass fraction of each constituent in the co-polymer. Further adding MALS data provides the overall co-polymer molar mass as well.

Q: *Why wouldn't you use the "macroinitiator" approach, even if direct sequential monomer addition is possible, in order to improve characterization of the final product?*

A: It is possible that "sampling" the reactor after preparing the first block will lead to some unintended termination (especially for anionic polymerization).

Q: *Why are typical block co-polymers smaller than 200,000 g/mol?*

A: As a general rule, polymers should be large enough to achieve desired properties, but no larger, since higher molar mass makes both synthesis and processing more challenging. With block copolymers, sufficient molar mass to achieve self-assembly (or "microphase separation") depends on the interaction parameter between the two blocks, but typically 10,000 to 50,000 is enough in the bulk. Similarly, micellization is driven by the solvent selectivity, and even low molar mass surfactants self-assemble in the right solvent.

Q: *Are you telling us that a narrow SEC peak (say, dispersity < 1.02) is no guarantee of a clean block polymer product?*

A: Correct. The narrow peak indicates a narrow size distribution. If it is a linear polymer, then the molar mass distribution is also narrow. However, narrowness of the peak says nothing about compositional heterogeneity. In addition, if the polymer is branched, the narrow peak may conceal many different structures.

Q: *What is the recommendation for characterizing ionic-amphiphilic co-polymers, as their radius of gyration can vary with composition?*

A: It's important to keep in mind that MALS measures molar mass and radius from first principles, absolutely and irrespective of calibration kits or other relative comparisons. So as you explore your co-polymers, and if they are of sufficient size, you can correlate the composition to the radius information from MALS. If they are too small, you can perform a similar correlation with intrinsic viscosity or DLS.

Taking your analysis one step further, if you combine the size information from MALS, viscometry, and/or DLS with the molar mass information from MALS, you can further understand conformation of the co-polymer. If you have several different compositions, you can then understand how the conformation changes with respect to those compositional changes.

Q: *In a SEC-MALS analysis of a RAFT homopolymer, ASTRA shows the polydispersity is 1.00. Is this reasonable? If not, what could be the reason?*

A: The Poisson distribution sets a lower limit for an achievable dispersity, and it must be greater than 1. For a very narrow polymer (say < 1.01), SEC-MALS can actually report a dispersity that is too small, because the peak broadening puts some of every polymer into every slice. It's

important to ensure that you have determined ASTRA's interdetector alignment parameter based on a monodisperse polymer in order to avoid erroneous underestimates of polydispersity.