WINGPC Applications

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Application # 19

applicable for: PSS WINGPC Version 4 and higher

Structure Elucidation with GPC Coupled with Molar Mass Sensitive Detectors

GPC coupled with molar mass sensitive detectors is a powerful method to investigate polymer structures and branching. On-line multi angle light scattering detectors and on-line viscometers are typical molar mass sensitive detectors.

Besides the molar mass distribution on-line viscometers measure the slice intrinsic viscosity while multi angle light scattering detectors measure the slice radius of gyration. Those values and the values of a linear sample can be used to get the branching coefficients g' and g, respectively.

$$g' = \left(\frac{[\eta]_{branched}}{[\eta]_{linear}} \right)_M \qquad g = \left(\frac{[R_g]_{branched}}{[R_g]_{linear}} \right)_M$$

M indicates here, that the intrinsic viscosity/the radius of gyration at the same molecular weight are compared.

The intrinsic viscosity /the radius of gyration is for a branched sample always smaller than for a linear one of the same molecular weight. This results in:
$g', g < 1$.

A lot of information can be already drawn from the quantitative analysis. Fig. 1 shows the specific and intrinsic viscosity of a linear sample compared to the specific and intrinsic viscosity of a branched sample. The low intrinsic viscosity (at the same molecular weight) shows at one glance that the sample is really branched.
The slope of the plot of log molar mass versus log [η] gives information about the structure of the polymer in solution. WINGPC fits the data

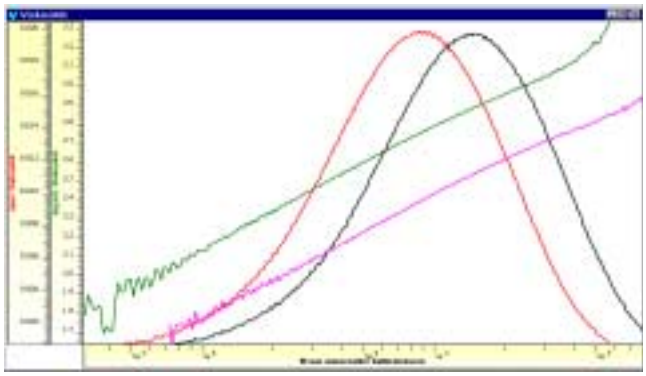

***Figure 1**: Plot log molar mass versus log [•] (= Mark-Houwink Plot) in the WINGPC viscosity window*

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automatically and calculates as one of the many results the Mark-Houwink exponent a.
It is: a (sphere) = 0 a (coil) = 0,5-0,8 a (rigid rod) = 2

A sign for a change in structure within the polymer is if the slope a changes with the molecular weight. This is for example the case for long chain branching.

WINGPC also determines the structure coefficients when the K and a values for the linear sample are known. The coefficients can be displayed versus the molecular weight or versus the elution volume. Therefore you have to select e.g. [Options][Branching g'] in the menu of the viscosity window. The Mark-Houwink coefficients of the linear sample can be entered using [Viscosity] [MH-Coeff. branching].

Hints:
g and g' are related via $g' = g^{\varepsilon}$. There are several theories predicting values for ε, but not many experimental date.

Which detector is more useful for the characterization of branched polymers depends on polymer type, molecular weight range, dispersity and many other parameters. PSS can assist you with the decision due to its long experience with molar mass sensitive detection - please contact us if you need consultation!

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