Thermal Field-Flow Fractionation with MALS and Viscometer – Comprehensive Two-Dimensional Polymer Separation with Advanced Detection

General Information **ID0060**

Application Polymer
Technology TF3-MALS-VISCO-ELSD
Info Postnova TF2000 Thermal FFF, PN3310 Viscometer, PN3621 MALS, PN3510 ELSD
Keywords TF3, MALS, Viscometer, Polymer Analysis, Molecular Weight, Molecular Structure, Degree of Branching

Introduction

Thermal Field-Flow Fractionation (TF3) is one of the preferred methods to determine the molecular weight and molecular weight distribution of large or complex polymer samples [1]. This is because, in contrast to the better-known GPC/SEC technology, TF3 does not use a packed column but separates the polymer in an empty channel. This results in very low shear forces during separation and a much higher molecular weight separation limit. TF3 can separate samples with molar masses from few kilodaltons up to many megadaltons (approx. 10 kDa - 100 MDa). The other advantage is that TF3 separates a sample by both hydrodynamic size and thermal diffusion coefficient, so it can be considered a two-dimensional separation within one single instrument.

Maximizing the Amount of Information From a Single Separation Experiment

The amount of information collected from a single TF3 experiment can be maximized using a suitable set of detectors [2]. Multi Angle Static Light Scattering (MALS) provides absolute molar mass of a sample [3] while online viscosity detection adds the intrinsic viscosity of a sample. By plotting the intrinsic viscosity of a sample against its molar mass in a double logarithmic scale, the Mark-Houwink plot can be generated. The Mark-Houwink plot is the most important structure plot in polymer analysis as it clearly shows any structural difference between polymer samples. A polymer with a linear structure will yield a linear Mark-Houwink plot, while a branched polymer will yield a non-linear plot. Using the Zimm-Stockmayer theory, an absolute number of branches for a star-branched or randomly branched polymer sample can then be calculated [4].

Thermal Field-Flow Fractionation

In TF3, separation is based on the application of a temperature gradient between an upper hot plate and a lower cold plate of the separation channel. By this means, a temperature gradient of up to 120 °C across the separation channel can be achieved (Fig. 1). Within this temperature gradient field, sample constituents are separated during elution not only because of their different hydrodynamic sizes but also with respect to their different thermal diffusion coefficients.

TF3 is an excellent method for separating synthetic polymers in organic solvents. A typical application example is the separation and characterization of synthetic and natural rubber samples in THF.

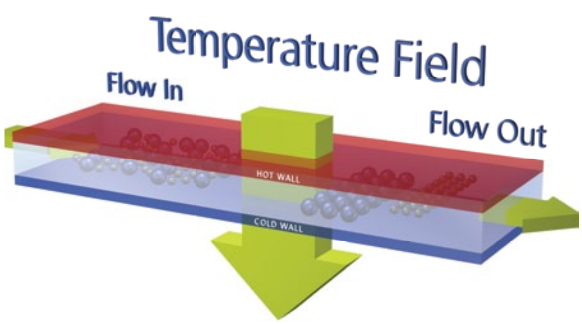

Fig. 1: Principle of Thermal Field-Flow Fractionation.

Fig. 2: Postnova TF2000 Thermal Field-Flow Fractionation System.

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Multi Angle Light Scattering

The MALS detector measures the scattered light at 21 different scattering angles (Fig. 3) and the absolute molar mass of a polymer sample as well as its radius of gyration can be determined by plotting the scattered light versus the detection angles and extrapolating the data to the theoretical scattering angle of zero degrees.

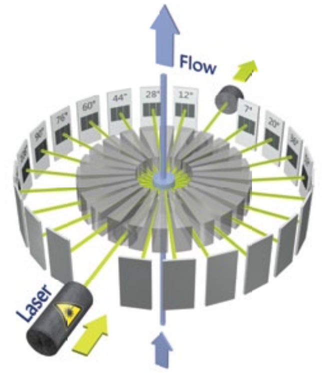

Fig. 3: Principle of MALS detection.

Viscosity Detector

A viscometer detector measures the absolute intrinsic viscosity (IV) of a polymer sample as it elutes from the TF3 system. It does this by using a balanced four capillary flow network based on the Wheatstone bridge principle which provides a differential measurement of the viscosity of the sample stream compared to a reference stream (Fig. 5).

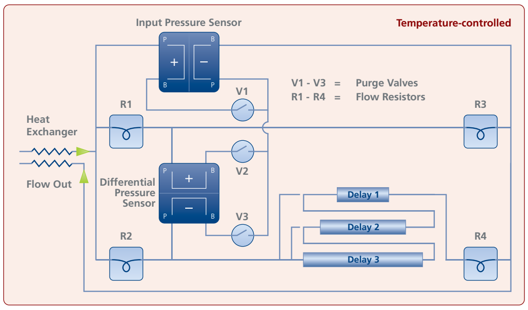

Fig. 4: Principle of Viscosity Detection.

Results

The MALS and Viscometer detectors provide the absolute molar mass distribution and the absolute intrinsic viscosity distribution of a polymer sample respectively. In addition to these two detectors, one or more concentration detectors, typically a refractive index detector (RI), a UV-detector or an evaporative light scattering detector (ELSD), are used to measure the concentration of the polymer sample at each point of the elution volume. The concentration detector can also be used to calculate the recovery of a polymer sample. In this example, a multi-detector TF3-MALS-VISCO-ELSD setup was used to investigate the molecular structure of a natural rubber sample. Figure 5 shows the signals of the different detectors for a linear broad polystyrene sample with a weight average molar mass of 250.000 g/mol and a polydispersity index of 2.5. The branched structure of the natural rubber sample compared to the linear polystyrene sample is also shown (Fig. 6).

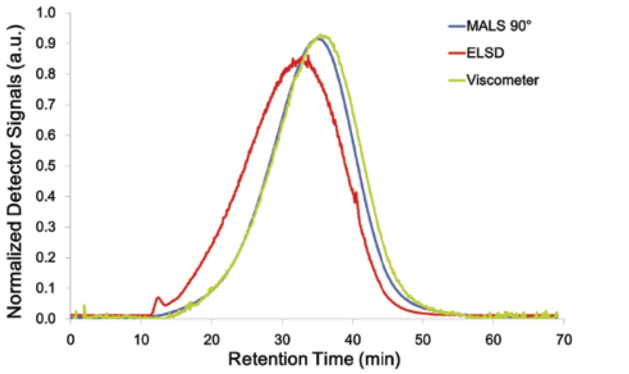

Fig. 5: TF3 Fractogram of a linear polystyrene sample with a broad distribution (blue: MALS, red: ELSD, green: Viscometer).

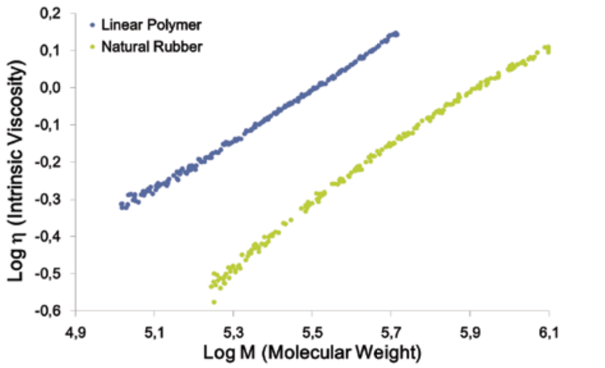

Fig. 6: Mark-Houwink-Plot of a linear polystyrene (blue line) and a slightly branched natural rubber sample (green line).

Conclusion

Thermal Field-Flow Fractionation (TF3) is a powerful technique for the separation of large or complex polymer samples. When used in conjunction with advanced detection systems such as Multi Angle Light Scattering and Viscosity it is an indispensable tool to gain deeper insight into the nature of these complex polymer samples.

References

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