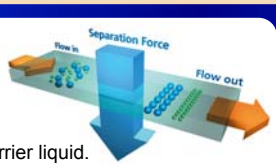
Advanced Characterization of Polymers using different FFF-Techniques

Tino Otte, Michel Palu, Thorsten Klein, Postnova Analytics GmbH, Max-Planck-Str. 14, 86899 Landsberg/Lech, Germany
info@postnova.com, www.postnova.com

Introduction

Until now, the characterization of synthetic or natural polymer material is mostly performed by Size Exclusion Chromatography (SEC) combined with Multi-Angle Light Scattering (MALS) detection. Unfortunately, SEC is very limited in its applicability for polymer material. Shear degradation, unwanted interaction between sample and stationary phase and the low separation power for high molar mass material often prevent the correct determination of the molar mass distribution or branching information. Field-Flow Fractionation (FFF) is a powerful new separation technique for the separation of polymers and particles up to a size of several micrometers inside an empty flow channel without any stationary phase. As a result, the limitations of old techniques such as SEC are eliminated and additional information can be obtained.

Separation Principle

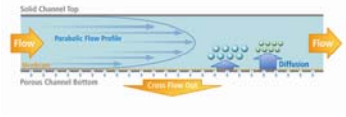


- Parabolic flow profile of the carrier liquid inside the channel (laminar Newtonian flow)
- External field is applied perpendicular to the carrier liquid.
- Interaction with the external field concentrates the analytes at the accumulation wall.
- Resulting concentration gradient causes a diffusion force in reverse direction.
- Dynamic equilibrium between external field and diffusion force is established.
- Larger analytes remain closer to the accumulation wall and elute later than smaller ones.

There are two major FFF methods for polymer separation:

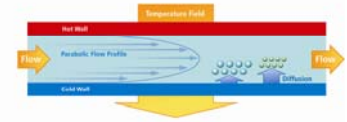
Asymmetric Flow FFF (AF4)

- Separation field: asymmetric Cross-Flow
- Separation based on Diff. Coefficient D (~1/R_h)
- Usable at temperatures up to 200°C (e.g. for polyolefin characterization)



Thermal FFF (TF3)

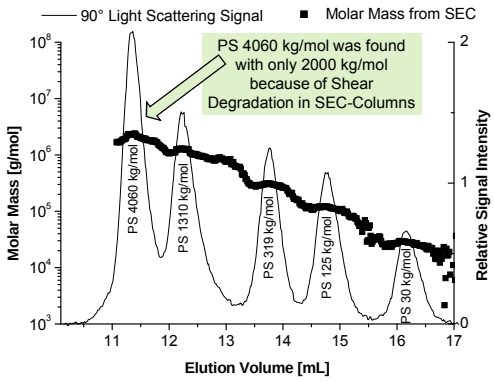
- Separation Field: Temp. gradient ΔT up to 120
- Separation according to Diffusion Coefficient D (D~1/R_h) and Thermal Diffusion Coefficient D_T
- D_T depends on chemical composition!



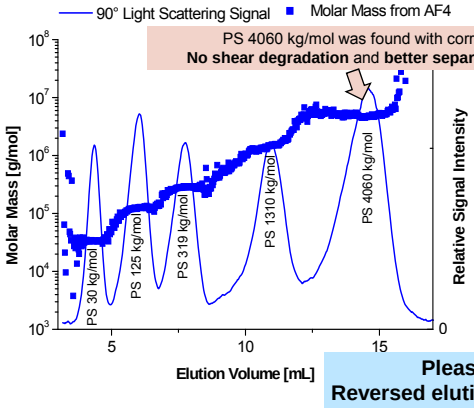
Comparison FFF vs. SEC

A mixture of PS standards was separated with FFF- and SEC-MALS to compare the performance of both methods.

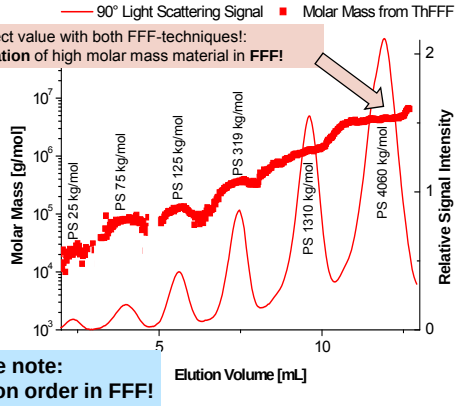
SEC *(2 SDV columns, PL mixed B)*



Asymmetric Flow FFF (AF4)

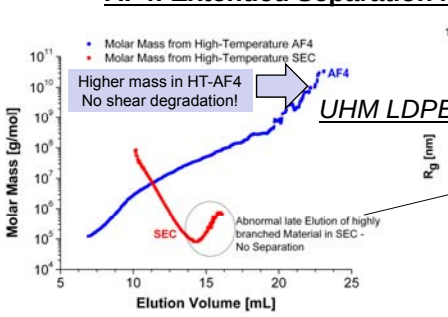


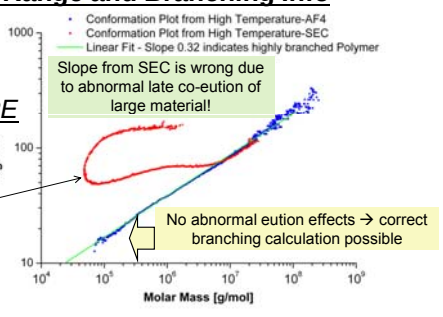
Thermal FFF (TF3)

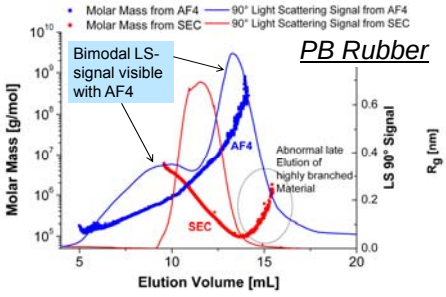


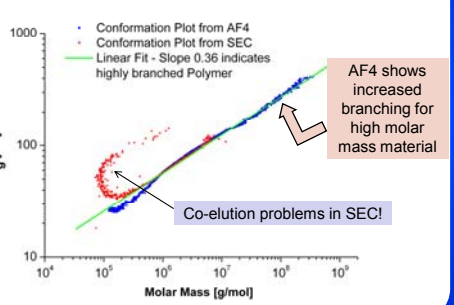
Please note: Reversed elution order in FFF!

AF4: Extended Separation Range and Branching Info

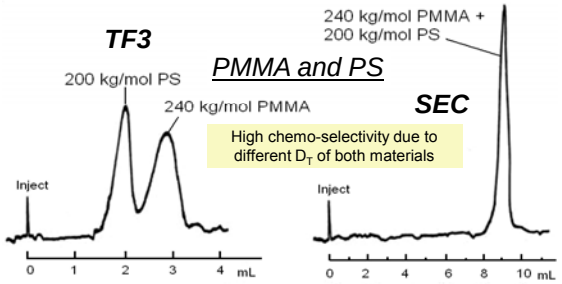






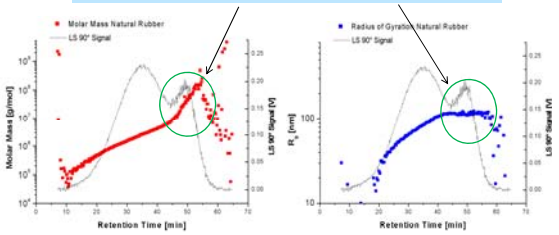


TF3: Additional Chemical Composition Info



Separation of Natural Rubber with TF3

High molar mass gel-structures of similar size are separated due to their different D_T



Conclusions

It was demonstrated that SEC coupled to a light scattering detector is not sufficient for analyzing ultra high molar mass or strongly branched polymer samples. Shear-degradation and a curvature in the calibration curves occur. As a result the mass data and information on branching from SEC separations are extremely falsified. Asymmetric Flow FFF (AF4) and Thermal FFF (TF3) enable to analyze such complex polymer materials as well as standards without irregular co-elution effects or degradation over a wide size range. New information on size and structure can be obtained for various samples. In addition, TF3 separates according to diffusion ability and differences in the actual chemical composition or structure which allows to separate components with similar hydrodynamic properties. The multiple applications and various advantages of FFF clearly illustrate the enormous potential of this technique for an significant improvement of polymer characterization in the near future.