Application of Flow and Thermal Field-Flow Fractionation for optimized Separation of various Polymer Systems

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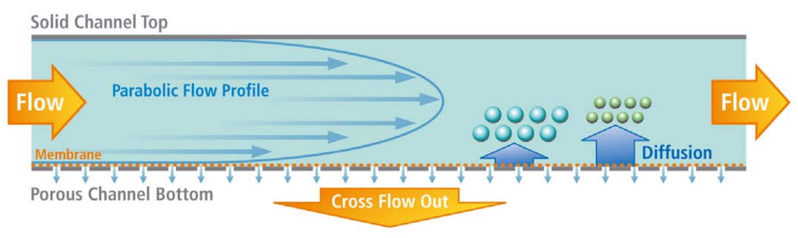
Introduction

Recently, the analysis of polymer materials was mostly done by size exclusion chromatography (SEC) connected to mass-sensitive detectors, like e.g. Multi-Angle Laser Light Scattering (MALLS). However, SEC is very limited in its applicability for polymers of high molar mass with pronounced chain branching or even gel content. Shear degradation, filtration, abnormal elution and partially low resolution are falsifying the results [1-3]. In addition, no information about the chemical polydispersity of the samples can be obtained with traditional SEC, while HPLC often requires laborious method development [4]. Asymmetrical Flow and Thermal Field-Flow Fractionation (AF4, TF3) are not prone to the above listed problems because no stationary phase is involved in the separation process [5]. The cross-flow field of AF4 is used for separation according to the Hydrodynamic Volume. In addition, a ceramic membrane with low cut-off makes the advantages of AF4 now available also for high temperature applications like e.g. polyolefin analysis. Complementary to AF4, the thermal gradient of TF3 can be used for additional separation according to chemical composition.

There are two major FFF Versions for Polymer Separation

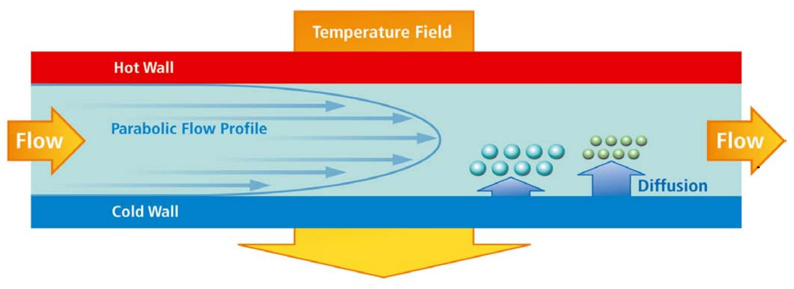
Flow FFF (AF4)

- Separation Field: Asymmetric Cross-Flow
- Separation based on Diff. Coefficient D (~1/R_h)
- Usable at temperatures up to 200°C → HT-AF4 (e.g. for polyolefin characterization)



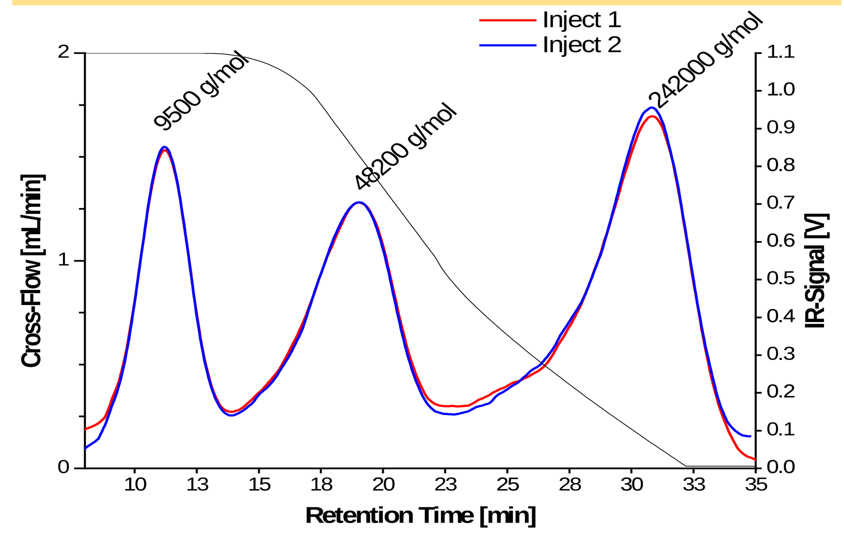
Thermal FFF (TF3)

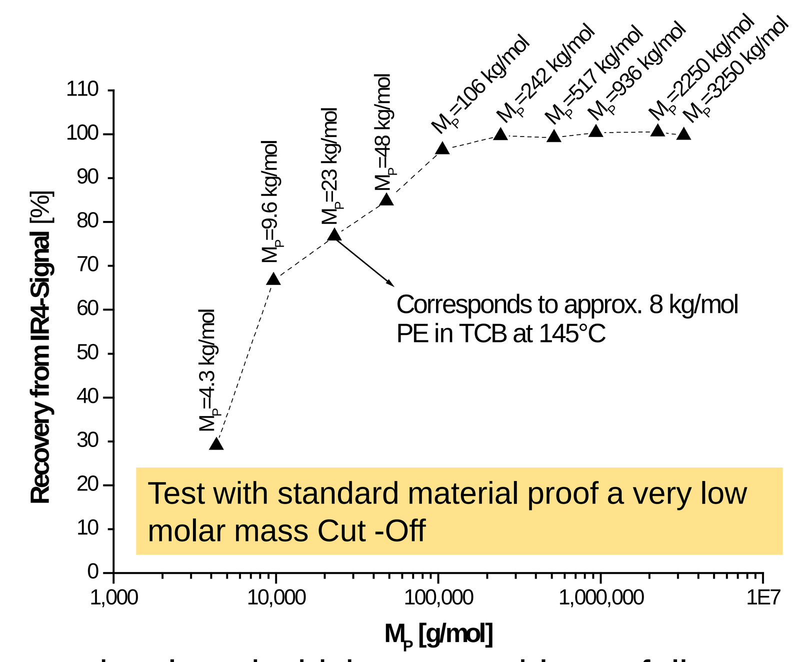
- Separation Field: Temp.gradient ΔT up to 120K
- Separation according to Diffusion Coefficient D (D~1/R_h) <u>and</u> Thermal Diffusion Coefficient D_T
- D_T depends on chemical composition!



New HT-AF4 Membrane with low Cut-Off

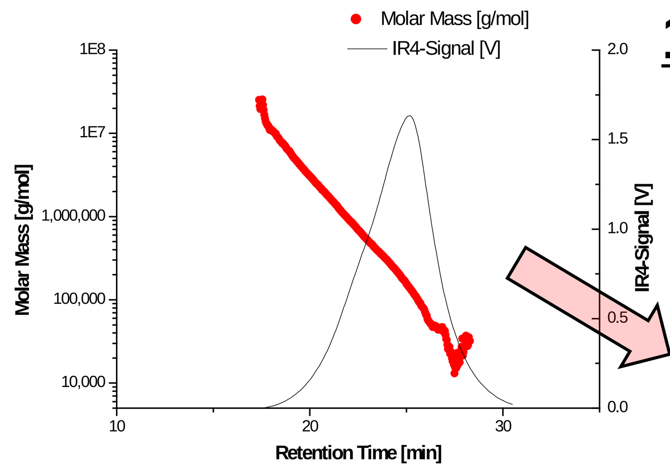
- Narrow distributed PMMA standards were separated with HT-AF4-IR4 in TCB at 145°C
- Recovery was calculated from the area of the IR4 signal

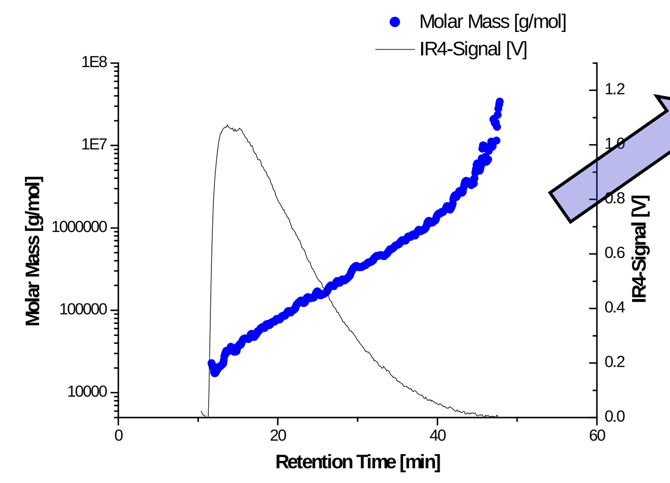


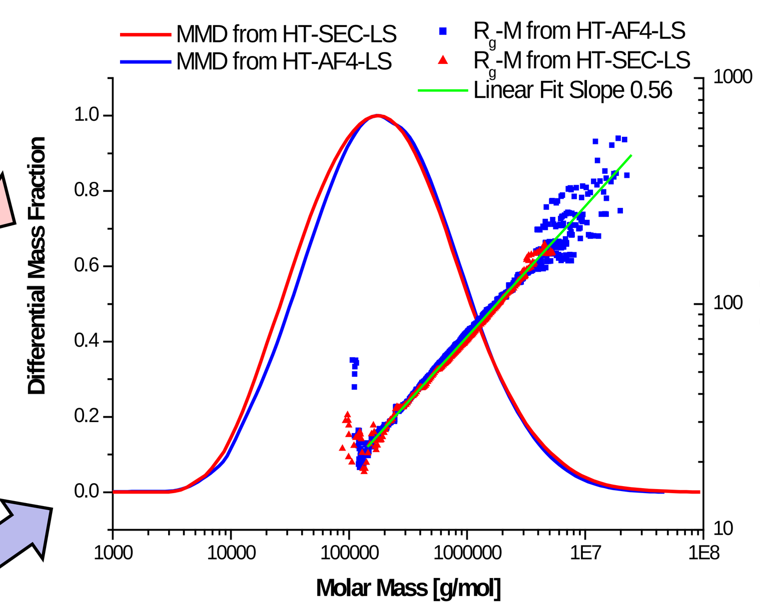


A new ceramic membrane with a low cut off in TCB was developed which now enables to fully characterize polyolefin samples without the loss of low M_w material!

HT-AF4 vs. HT-SEC of NIST 1496 (linear HDPE Reference)

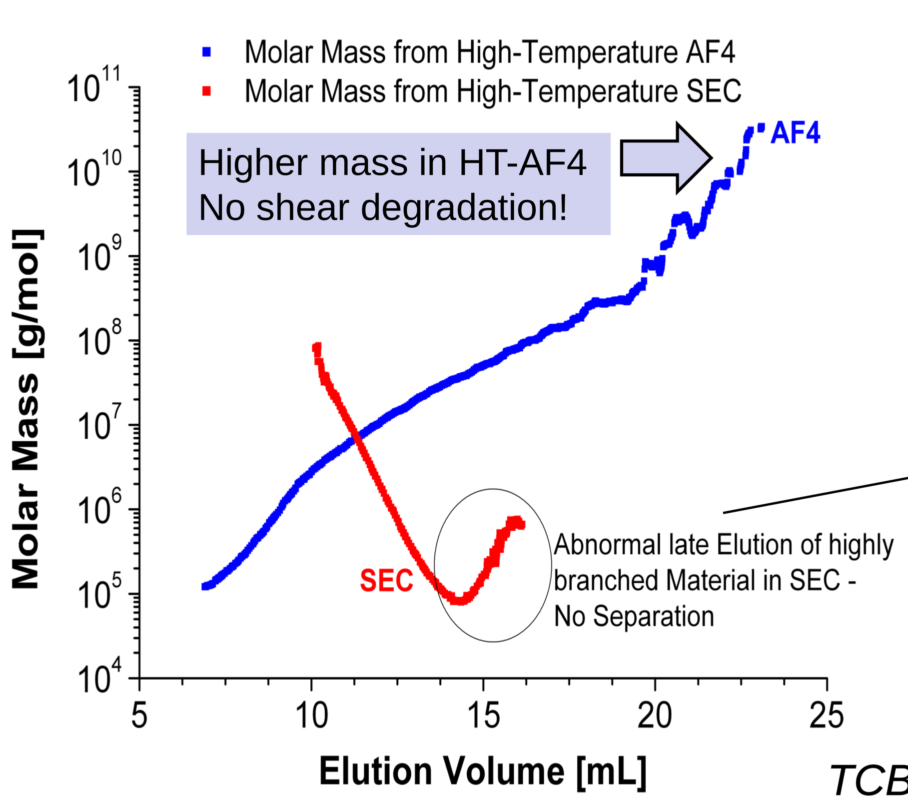


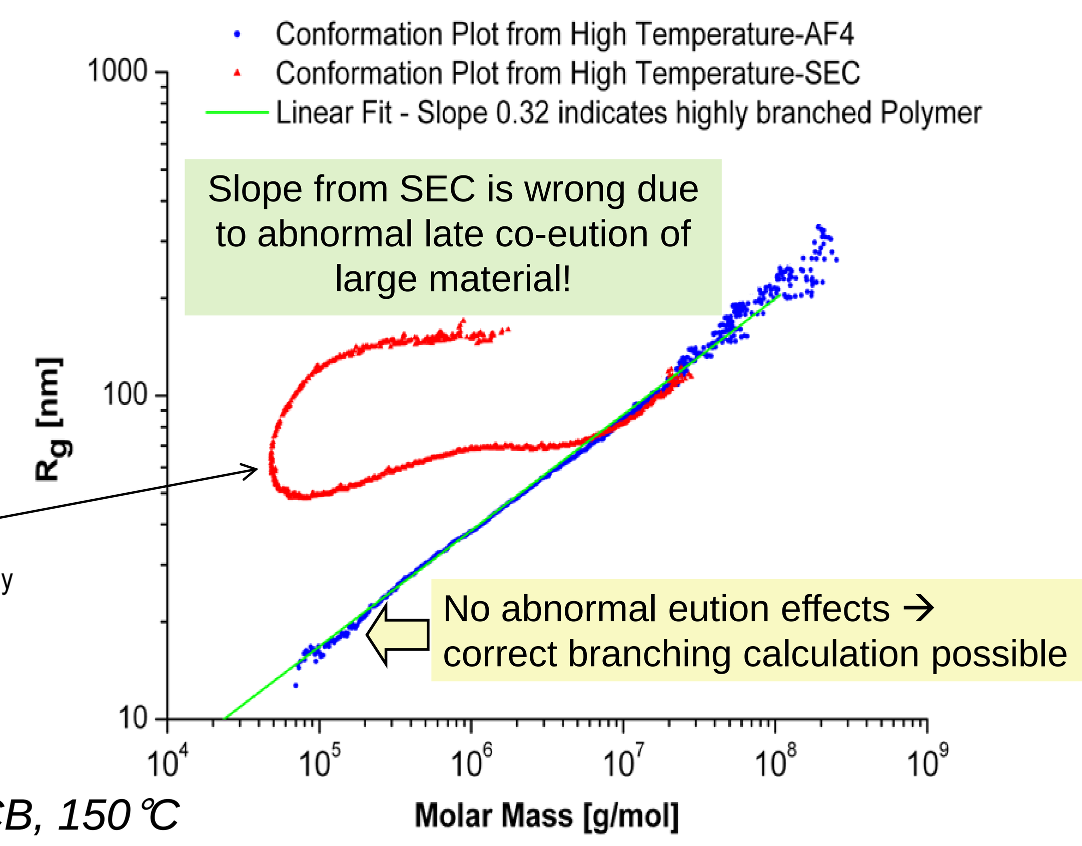




The same shape of both differential molar mass distributions (MMDs) from HT-AF4 and HT-SEC confirms negligible material loss for the NIST reference

HT-AF4-MALLS Separation of highly branched LDPE



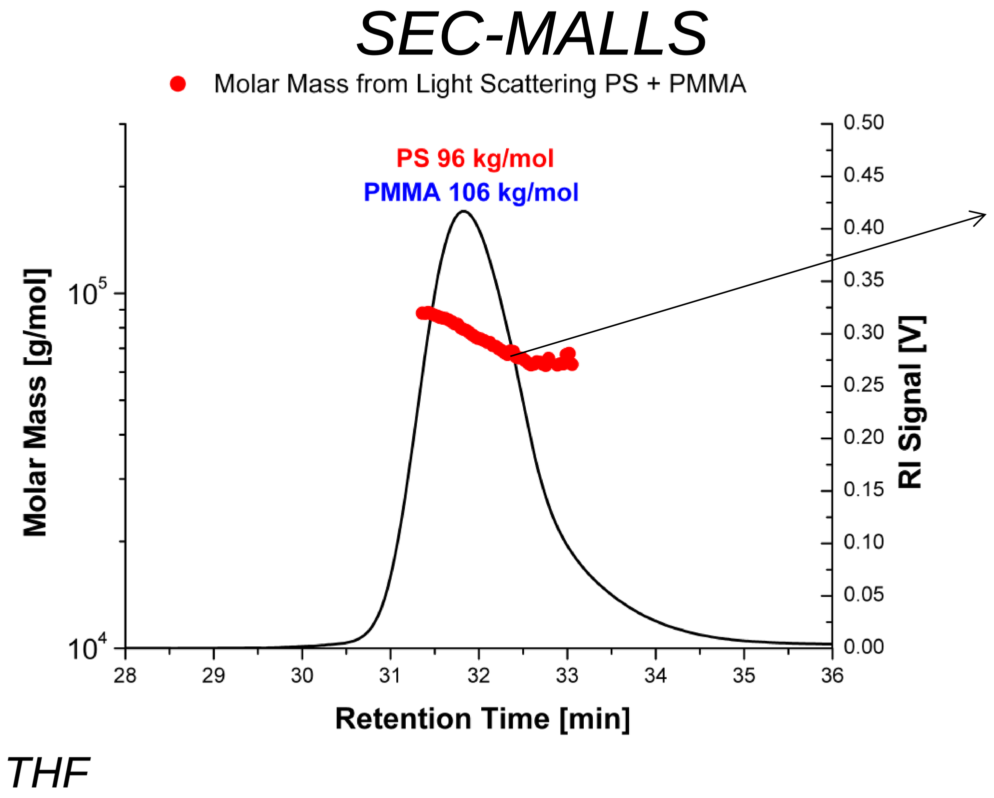


TCB, 150 ℃

HT-AF4 delivers complete structure/size information of various polyolefin samples!

Separation of PS and PMMA of same Rh

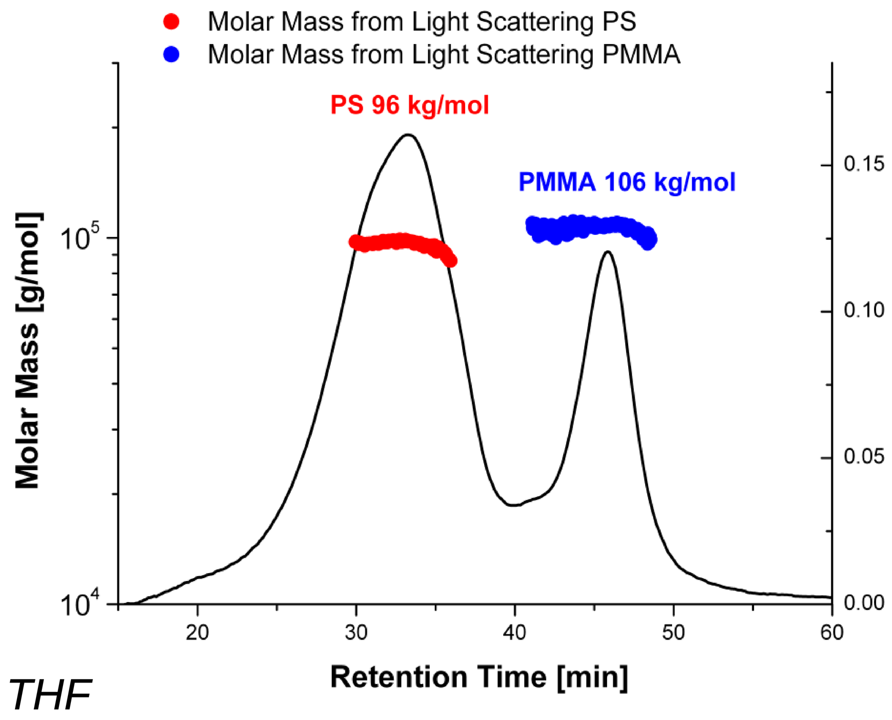
SEC-MALLS



Decay of molar mass is caused by different dn/dc of both co-eluting materials

in THF

TF3-MALLS



High selectivity due to different D_T of both materials

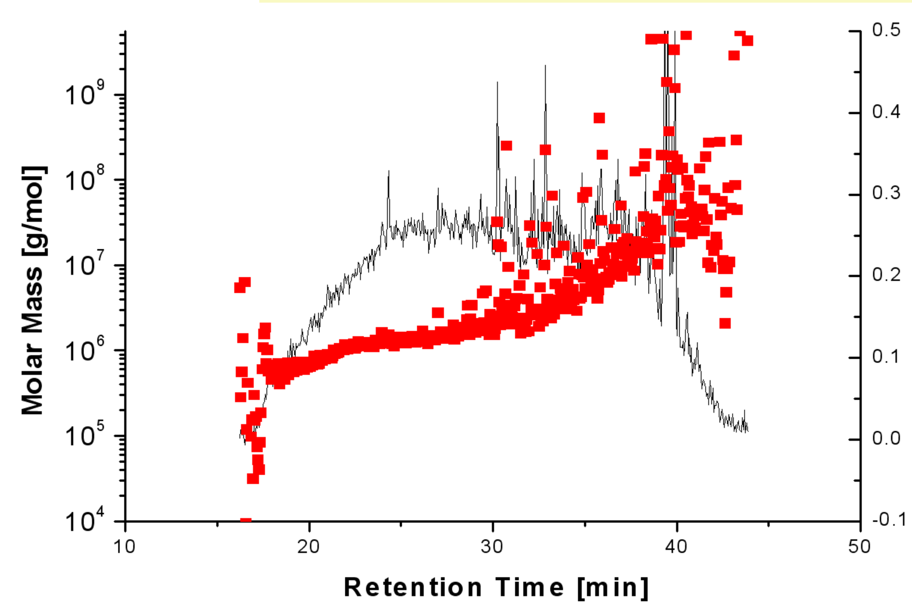
Thermal FFF separates both samples despite the similar size

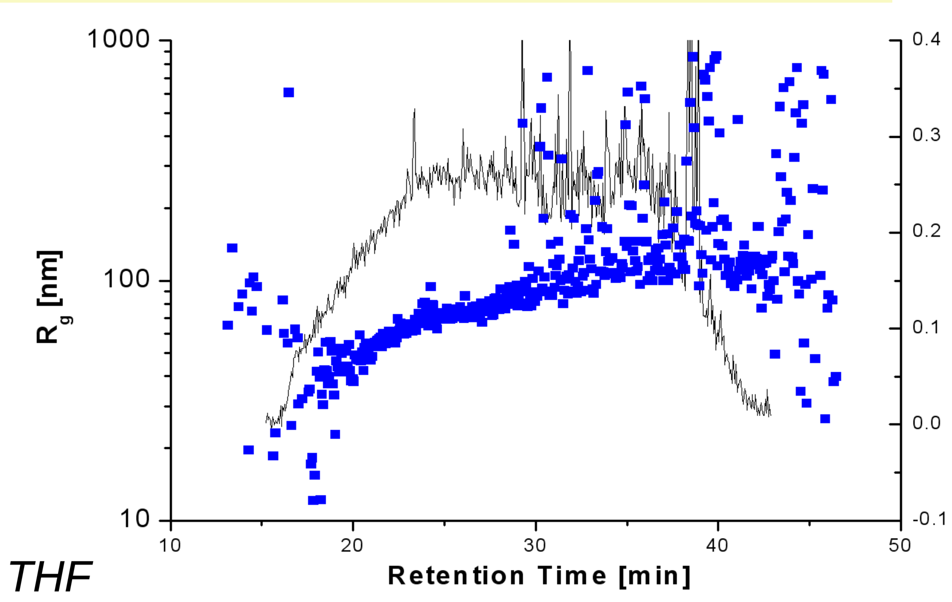
in THF

AF4 vs. TF3

AF4 Separation of Natural Rubber: t_R ~ 1/D ~ R_h

AF4 cannot separate impurities because of same Hydrodynamic Volume





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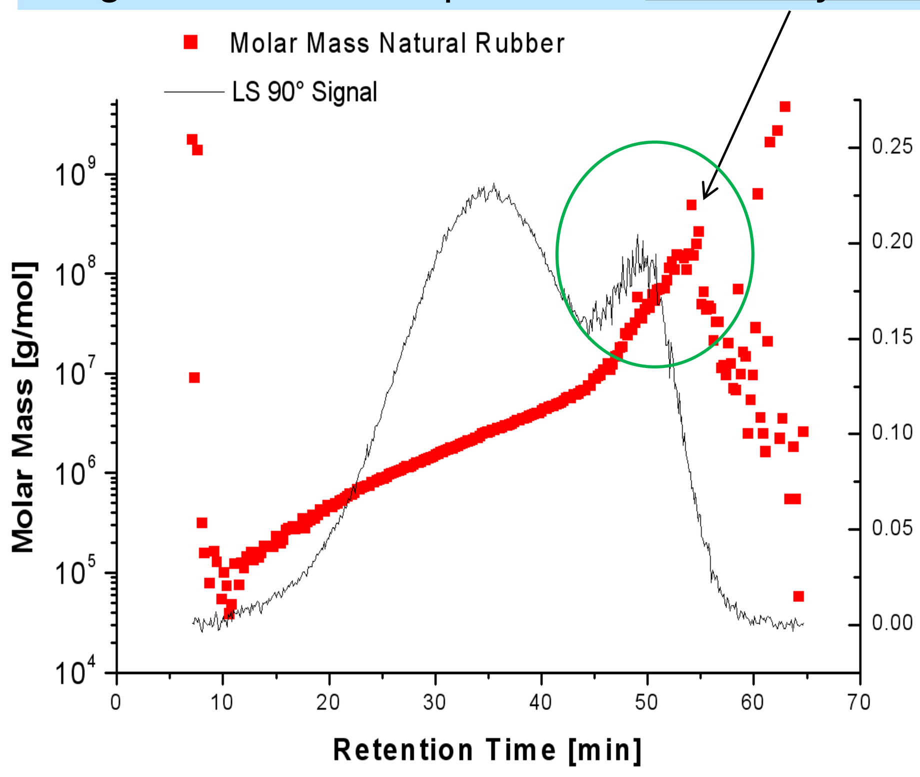
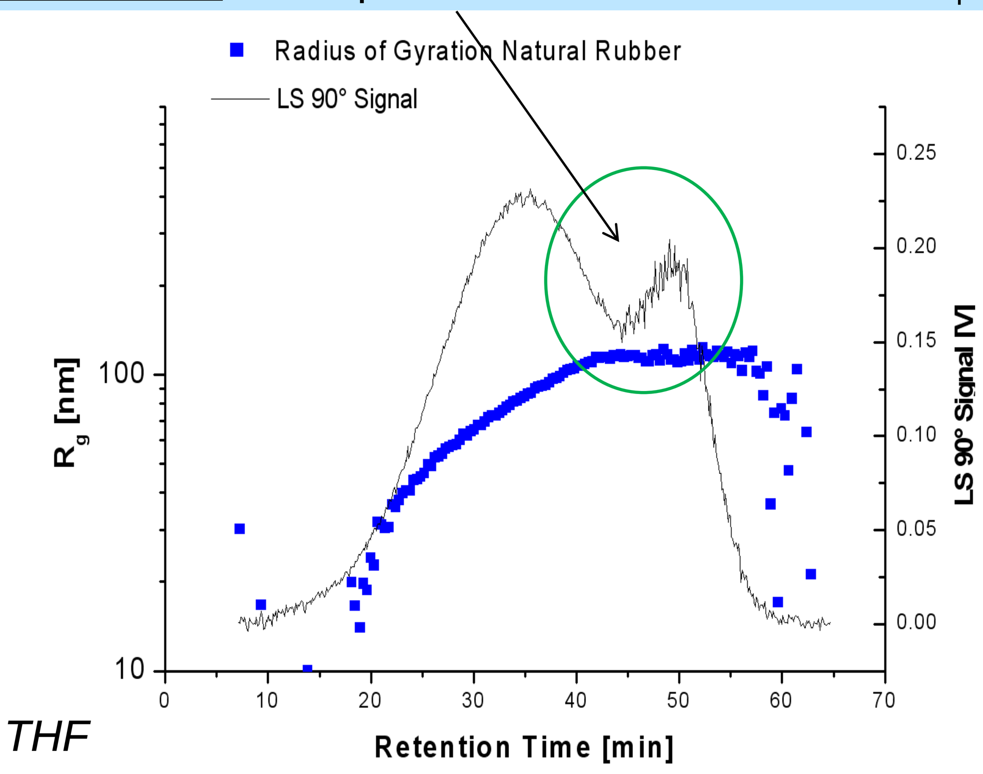
Thermal FFF Separation of Natural Rubber: t_R ~ D_TΔT/D

High molar mass impurities of <u>similar Hydrodynamic Volume</u> are separated due to their different D_T





in THF

References:

[1] M. Parth, N. Aust, K. Lederer, Int. J. Polym. Anal. Charact. 8 (2003) 175.
[2] N. Aust, J. Biochem. Biophys. Meth. 56 (2003) 323.
[3] E. Mes, H.deJonge, T. Klein, R. Welz, D.Gillespie, J.Chrom.A 1154 (2007)319.
[4] J. Raust, A. Brüll, C. Moire, C. Farcet, H. Pasch, J.Chrom.A 1203 (2008) 207.
[5] F. A. Messaud, R. D. Sanderson, J. R. Runyon, T. Otte, H. Pasch, S. K. R. Williams, Prog. Polym. Sci. 34 (2009) 351.

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. A complete analysis of branched LDPE with HT-AF4 was shown and the correct separation was confirmed with NIST reference material. The high potential of Thermal FFF was proved by separation of different mixtures of components with similar hydrodynamic volume but different composition. A combination of the size information from AF4 with the composition selective separation of TF3 may allows a HPLC-like analysis of e.g. co-polymer systems without the drawbacks of chromatographic methods in the near future.