Polymer Characterization using Thermal FFF

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Introduction

Currently characterization of synthetic or natural macromolecules is mostly performed by Size Exclusion Chromatography (SEC), which is ideal for small to medium molar mass polymers. Unfortunately, SEC can be limited in its applicability for larger molecular weight, cross-linked and branched polymer material. Shear degradation, unwanted interaction between sample and stationary phase and the low separation power in high molar mass regions often prevent the correct determination of the molar mass distribution or branching information. Thermal Field-Flow Fractionation (TF3) is a powerful separation technique applicable for polymers of even ultra-high molecular weight as well as cross-linked material and gels. As a result, the limitations of traditional techniques such as SEC are overcome and additional information can be obtained.

Thermal Field-Flow Fractionation (TF3)

Application of a thermal field between a hot and cold plate generates a temperature gradient perpendicular to the separation channel. Additionally to diffusion by Brownian Motion a temperature driven diffusion process (Thermal Diffusion) takes place.

Thermal gradient up to Δ120°C
Separation range 1 kDa up to several MDa
Typ. analysis time 10 - 60 min

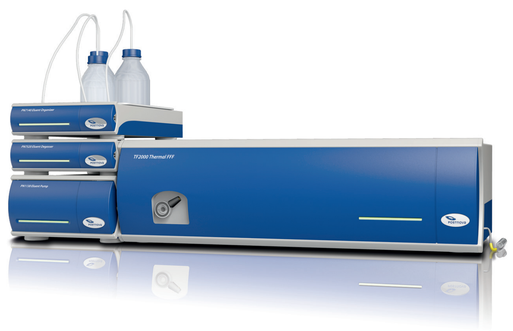

Figure 1: TF2000 Thermal FFF (member of the FFF-Platform)

Channel Design for Thermal FFF

The sample components are affected by two diffusion processes. This unique feature enables the TF3 to separate by:

- Hydrodynamic volume (diffusion by Brownian Motion)
- Separation according to size & chemical composition (Thermal Diffusion)

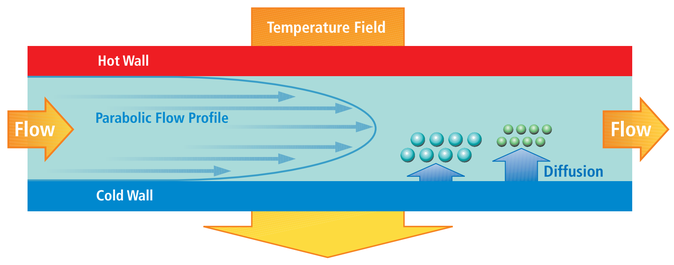

Figure 2: Thermal FFF principle (cross section shown)

Analysis of PS and PMMA by SEC and Thermal FFF

PS, PMMA and a mixture of both standards in THF. Taking advantage of the separation by chemical composition in TF3.

PS 96 kDa kg/mol
PMMA 106 kDa mix
PS 96 kDa - PMMA 106 kDa mix

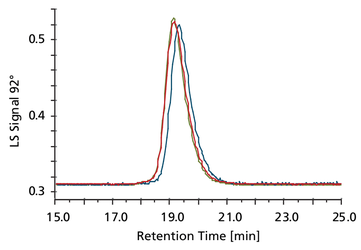

Figure 3: SEC Elugram of PS, PMMA and a mixture

PS 96 kDa - PMMA 106 kDa mix

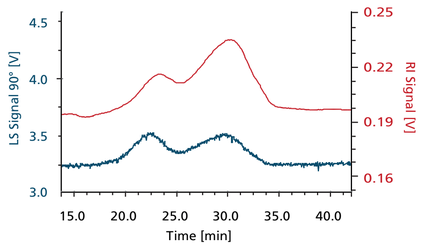

Figure 4: TF3 Fractogram showing **RI** and **LS** Signal of mixed PS-PMMA standards.(Δ T = 115 K).

Component	Retention Time (R_T)	Molecular Mass (M_W)
PS	19.1 - 24.7 min	95.7
PMMA	26.2 - 34.5 min	104.4

PS 226 kDa kg/mol
PMMA 242 kDa mix
PS 226 kDa - PMMA 242 kDa mix

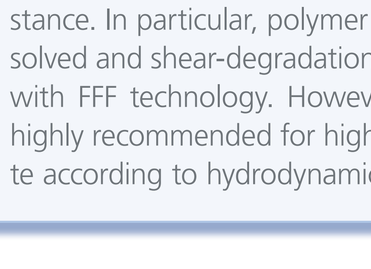

Figure 5: SEC Elugram of PS, PMMA and a mixture

PS 226 kDa - PMMA 242 kDa mix

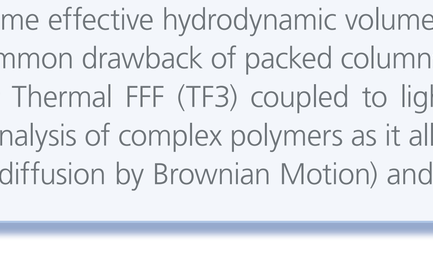

Figure 6: TF3 Fractogram showing **RI** and.**LS** Signal of mixed PS-PMMA standards.(Δ T = 90 K).

Component	Retention Time (R_T)	Molecular Mass (M_W)
PS	23.5 - 30.5 min	225.9
PMMA	31.0 - 39.5 min	259.4

➡ Successful separation of both PS-PMMA samples of comparable hydrodynamic volume by TF3 technology.

Investigation of PEO-PS homopolymer mix by Thermal FFF

PEO 116g kg/mol
PS 63 kg/mol
PS-co-PEO 92 kg/mol
PS-co-PEO 134 kg/mol

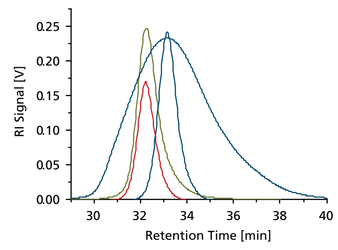

Figure 7: SEC Elugram of PEO, PS and PS-co-PEO polymer standards of comparable random coil volume

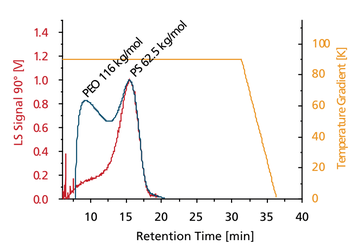

Figure 8: TF3 Fractogram of PS and PEO with partial peak separation

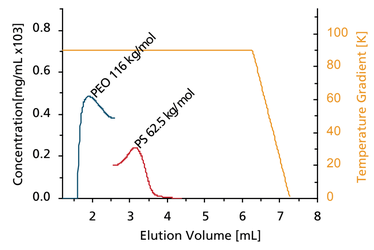

Figure 9: Concentration determination of homopolymer standards by RI using specific dn/dc values

PS 319 kg/mol
PEO 496g kg/mol

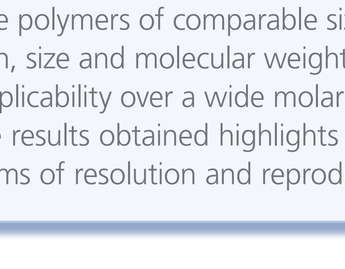

Figure 10: SEC Elugram of PS and PEO showing no separation

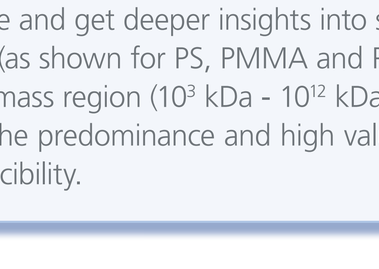

Figure 11: TF3 Fractogram of PS and PEO with partial peak separation

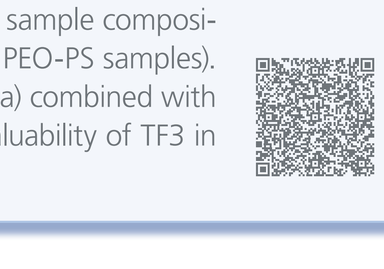

Figure 12: Concentration determination of homopolymer standards by RI using specific dn/dc values

dn/dc_{PEO} = 0.068 mL/g
dn/dc_{PS} = 0.165 mL/g

➡ Partial resolution of both PEO-PS homopolymer samples of comparable hydrodynamic volume acchieved by TF3.

Conclusions

Packed-column chromatography separates according to hydrodynamic radii in the first instance. In particular, polymer species of same effective hydrodynamic volume will not be resolved and shear-degradation, another common drawback of packed columns are overcome with FFF technology. However, especially Thermal FFF (TF3) coupled to light scattering is highly recommended for high resolution analysis of complex polymers as it allows to separate according to hydrodynamic properties (diffusion by Brownian Motion) and additionally to chemical composition (by Thermal Diffusion). This unique feature allows the scientist to separate polymers of comparable size and get deeper insights into sample composition, size and molecular weight (as shown for PS, PMMA and PEO-PS samples). Applicability over a wide molar mass region (10^3 kDa - 10^{12} kDa) combined with the results obtained highlights the predominance and high valuability of TF3 in terms of resolution and reproducibility.