Characterization of Rubber Polymers by Flow FFF

Markus J. Spallek, Evelin Moldenhauer, Soheyl Tadjiki, Rainer Jünger, Thorsten Klein*
www.postnova.com

POSTNOVA
Leading in FFF

Introduction

Based on chromatographic principles Field-Flow Fractionation (FFF) has emerged to a unique and powerful method for analysis of particles, polymers and biomolecules. By using a separation channel without stationary phase common drawbacks of packed columns (phase interaction) are overcome. Separation is acchieved by application of Flow (AF4), Thermal (TF3), Centrifugal (CF3) or Gravitational (GF3) forces counteracting on sample diffusion (Brownian Motion). A platform of FFF technologies is generated, each having additional separation parameters complementing one another. This renders the FFF-Platform highly valuable enabling the user to choose the most appropriate technique for a given application to obtain best performance only!

Separation Principle

- Application of various separation fields
- Particles are forced towards channel bottom (accumulation wall)
- Laminar flow (parabolic flow profile) inside the channel
- Diffusion of particles leads to arrangement in layers (different flow velocity)

Separation according to molar mass and size: Flow FFF (AF4)
- and chemical composition (Thermal FFF), TF3
- and density (Centrifugal and Gravitational FFF), CF3 and GF3

FFF-Techniques - A schematic overview

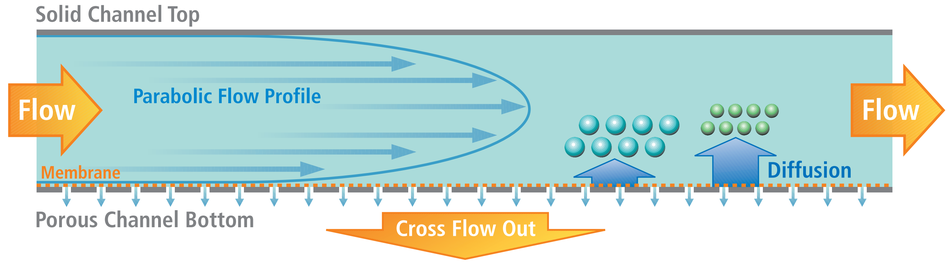


Figure 1: Flow Field-Flow Fractionation (AF4) channel cross section

Parameters to choose from: flow rate, separation force and gradient, temperature, focus & outlet splitting technology, fraction collection, pre-purification and up-concentration.

AF4-MALS Size Determination, Distribution and Fractal Dimension of Synthetic Rubber Samples (dissolved in THF):

Identification of best processing procedures for nature-like rubber materials by AF4-MALS (92°)

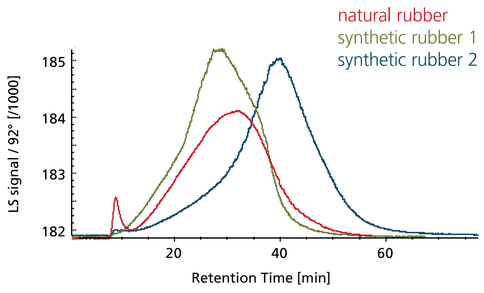


Figure 2: Analysis of rubber samples by AF4-MALS

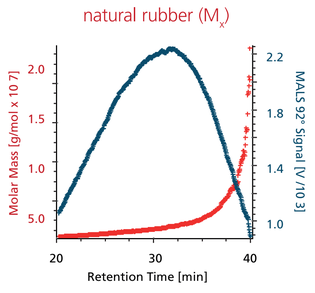


Figure 3: Molecular mass of natural rubber

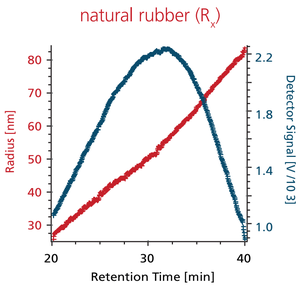


Figure 4: Calcl. radii of natural rubber

➡ Larger polymer material present within synthetic rubber 2 (blue line).

	Mol. Mass (M_x)	Calc. Radii (R_x)
n-avverage	M_n = 1.11 x 10^6 g/mol	37 nm
w-average	M_w = 1.61 x 10^6 g/mol	44 nm
z-average	M_z = 2.97 x 10^6 g/mol	54 nm

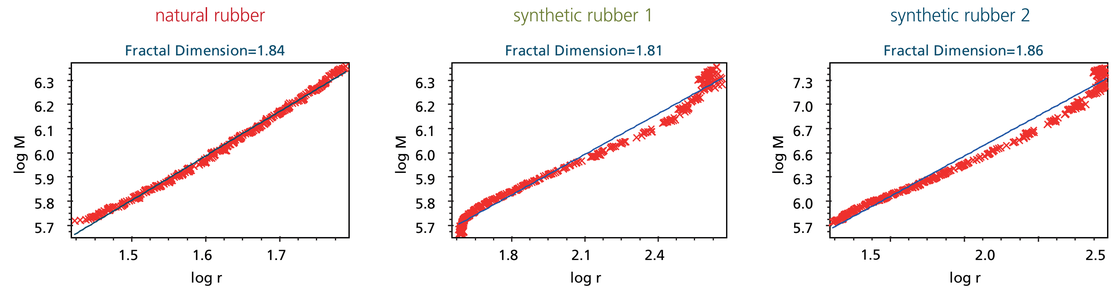


Figure 5: Conformation plots to determine fractal dimension for natural and synthetic rubber samples

➡ Equal fractal dimensions indicating comparable polymerization properties also for higher molecular weight polymers (polymerization degree).

Field-Flow Fractionation Benefits

- Determination of molecular weight parameters giving information about polymer properties (tensile strenght, flexibility and plasticity, glass temperature)
- Identification of polymer changes during processing
- Investigation and optimization of polymerization procedures
- Applicable for detection of polymer origin
- Quality control of starting materials from varying supply areas

Conclusions

The FFF technology coupled to suitable detector combinations (MALS, RI/ UV) enables the user to easily determine molecular weight and size distributions of macromolecules, which are impotant measures for polymer properties. Two synthetic rubber samples were analyzed and compared to a natural rubber sample. Results showed that the synthesis process of rubber is capable of producing higher molecular weight material without changing of the polymer structure during the polymerization process (comparable fractal dimension).

Polymer Characterization using Thermal FFF

Markus J. Spallek, Evelin Moldenhauer, Soheyl Tadjiki, Rainer Jünger, Thorsten Klein*
www.postnova.com

POSTNOVA
Leading in FFF

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

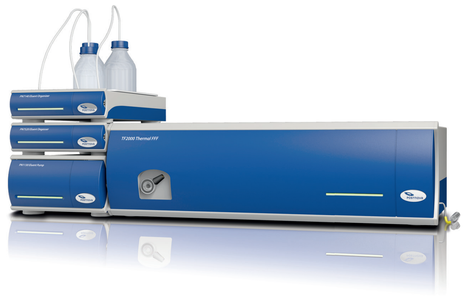


Figure 1: TF2000 Thermal FFF (member of the FFF-Platform)

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)

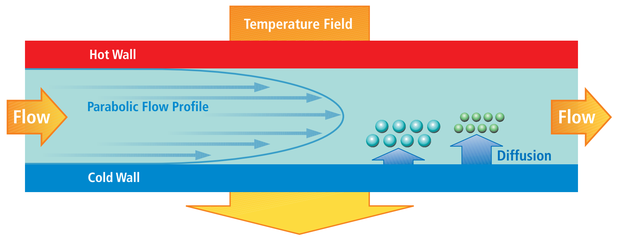


Figure 2: Thermal FFF principle (cross section shown)

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.

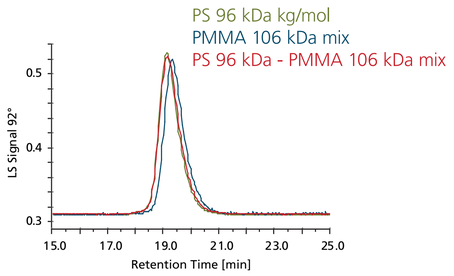


Figure 3: SEC Elugram of PS, PMMA and a mixture

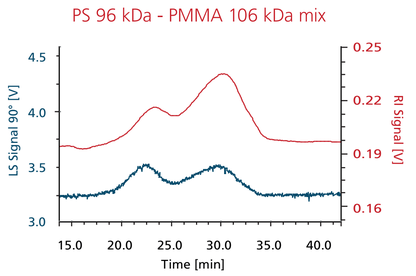


Figure 4: TF3 Fractogram showing **RI** and **LS** Signal of mixed PS-PMMA standards (Δ T = 115 K).

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

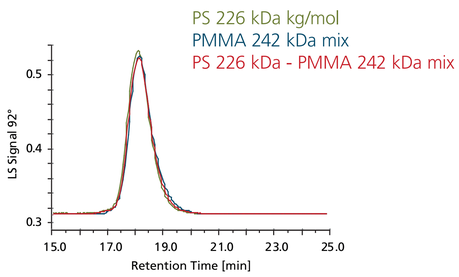


Figure 5: SEC Elugram of PS, PMMA and a mixture

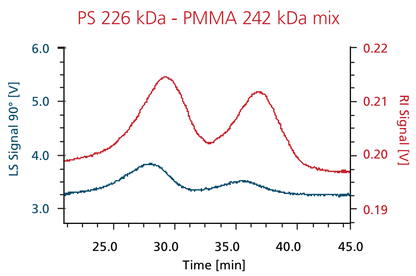


Figure 6: TF3 Fractogram showing **RI** and **LS** Signal of mixed PS-PMMA standards (Δ T = 90 K).

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

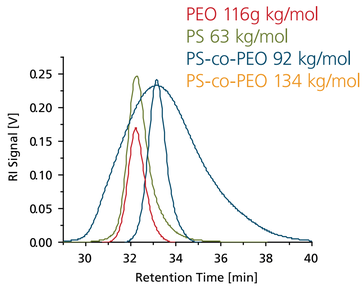


Figure 7: SEC Elugram of PEO, PS and PS-co-PEO polymer standards of comparable random coil volume

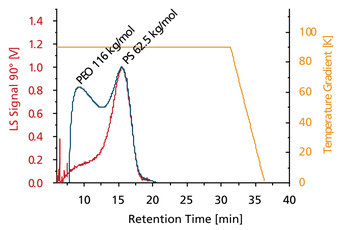


Figure 8: TF3 Fractogram of PS and PEO with partial peak separation

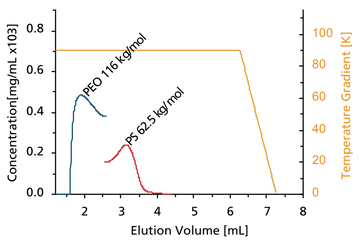


Figure 9: Concentration determination of homopolymer standards by RI using specific dn/dc values

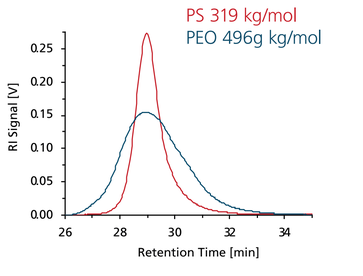


Figure 10: SEC Elugram of PS and PEO showing no separation

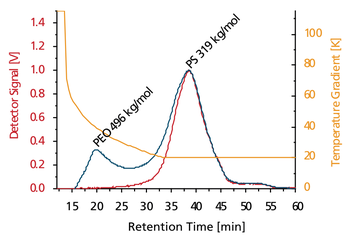


Figure 11: TF3 Fractogram of PS and PEO with partial peak separation

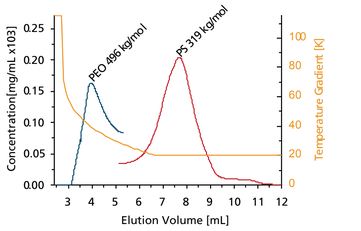


Figure 12: Concentration determination of homopolymer standards by RI using specific dn/dc values

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.

Latex Nanoparticle Analysis by Flow FFF - DLS coupling

Markus J. Spallek, Evelin Moldenhauer, Soheyl Tadjiki, Rainer Jünger, Thorsten Klein*
www.postnova.com

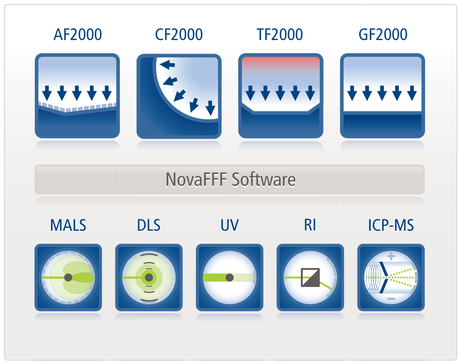
POSTNOVA
Leading in FFF

Introduction

Field-Flow Fractionation (FFF) technology has developed to a powerful separation technique capable for the analysis of various nano- and macro-sized sample types. Depending on the technique applied, FFF covers an entirely sample size range between 1 nm up to several microns. This enables the scientist to analyze particles, polymers and biomacromolecules, determine size- and molecular weight distributions of several magnitudes (10^3 Da - 10^{12} kDa, 1 nm - 100 µm, respectively). In particular, Flow FFF (AF4) and Centrifugal FFF (CF3) have become the state-of-the-art technique perfectly fitting to light scattering detection. Consequently, FFF online-coupling of suitable light scattering detectors (DLS, MALS) features integration of real-time separation and analysis. This is highly recommended for any scientist interested in highest resolution and reproducibility.

The FFF Platform

- Asym. Field-Flow Fractionation (AF2000)
- Centrifugal Field-Flow Fractionation (CF2000)
- Thermal Field-Flow Fractionation (TF2000)
- Gravitational Field-Flow Fractionation (GF2000)



FFF-Application range

Analyte Size and Weight

Analysis of nano- and micro sized particles, oligomers, high- and ultra high molecular weight polymers with state-of-the-art FFF-Technologies.

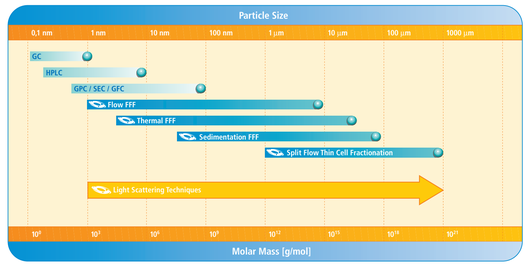


Figure 1: FFF-Platform and esteablished chromatographic techologies

Investigation of Latex Nanoparticle Standards

Online-coupling of AF4 and DLS for real-time resolved analysis

Flow FFF (AF2000)

Malvern Zetasizer Nano ZS®

Replacement of cell for change between online and batch DLS analysis mode

Centrifugal FFF (CF2000)

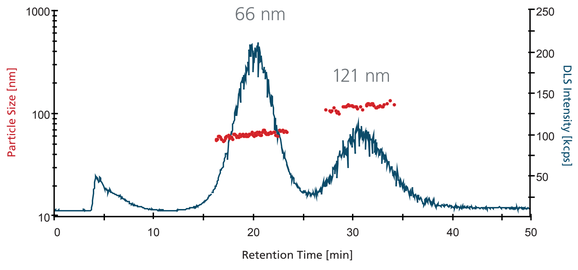


Figure 2: AF4 Fractogram and size of latex particle mix using monodisperse standards

Retention Time (R_T)	Hydrodynamic Diameter (D_h)
16.5 - 24.1 min	66 nm ± 4 nm
27.5 - 34.5 min	121 nm ± 5 nm

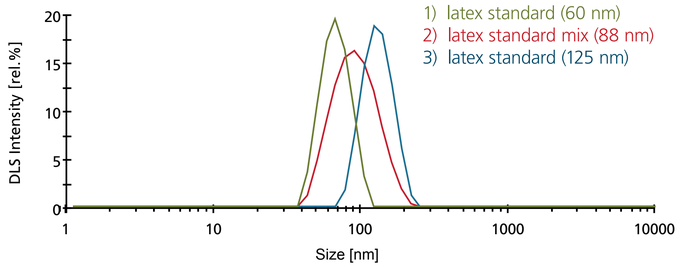


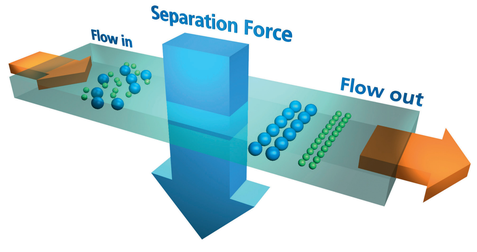
Figure 3: Traditional batch DLS measurements of monodisperse and mixed latex standards

#	Hydrodynamic Diameter (D_h)	Polydispersity Index (PDI)
1	66 nm	0.008
2	88 nm	0.113
3	125 nm	0.024

- Traditional batch measurements provide accurate data for monodisperse standards
- Batch mode is not applicable for sample analysis of polydisperse and broad samples due to:
  - Calculation of average size distributions
  - Discrimination of small particles due to strong scattering caused by large particles
  - limited DLS resolution

Field-Flow Fractionation - DLS Benefits

- Total sample characterization using different FFF variants
- Integration of Separation and Detection by FFF-DLS online-coupling within a single run
- Highest reproducibility and resolution by real-time resolved measurements („true“ size distribution, no averaging effect, no small particle discrimination)
- The FFF-Platform allows selection of the most appropriate FFF-technique coupled to various detectors of choice, e.g. MALS, DLS, UV, RI, MS
- Large size range of sample (10^3 Da - 10^{12} kDa, resp. 1 nm - 100 µm)



Conclusions

The FFF-Platform using different FFF variants in combination with appropriate detectors, such as DLS or MALS is a highly valuable tool for accurate analysis and reliable results. It was shown that FFF-DLS online-coupling is a powerful tool for analysis of mixed latex nanoparticles as traditional batch DLS measurements suffer from a „size-averaging“ effect generating missleading data! Therefore, the integration of separation and detection shown here represents the method of choice for any scientist to obtain best results for mixed, polydisperse and broad distributed nano-sized samples.