

Springer Laboratory
Manuals in Polymer Science

Guillaume Greyling
Harald Pasch

Thermal Field-Flow Fractionation of Polymers



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Preface

Liquid chromatography is one of the workhorses in the analysis of polymers when it comes to addressing the challenges associated with characterising their complex molecular structure. The gold standard for molar mass determination is size exclusion chromatography (SEC) as it not only provides reliable and accurate information but also has a well-developed theoretical foundation from which to predict and explain the retention behaviour of polymers.

However, SEC separates polymers according to their size in solution and not according to their molar mass. The correlation between hydrodynamic size and molar mass is obtained through SEC calibration or the use of molar mass sensitive detectors. SEC also has limitations when it comes to complex or high molar mass samples (such as block copolymers, polyelectrolytes and polymer self-assemblies) as these can undergo shear degradation or even adsorption onto the stationary phase. Moreover, since SEC separates only according to size, multidimensional techniques (such as two-dimensional liquid chromatography) need to be developed in order to obtain more than just molar mass data. However, these techniques can be tedious and experimentally iterative.

To address the limitations inherent to column-based fractionation techniques, channel-based fractionation techniques, such as field-flow fractionation, have become important alternative fractionation platforms to separate and characterise not only polymers but also other complex analytes such as polymer self-assemblies. One of the most prominent subtechniques of field-flow fractionation for polymer characterisation is thermal field-flow fractionation (ThFFF) as it can separate polymers based on not only their size in solution (or molar mass) but also according to their chemical composition in a single analysis. Over the last few years, both the development of ThFFF theory and the application of the technique to characterise complex analytes have shown tremendous growth and as a result have started to gain increased attention from the polymer community.

In this textbook, we address the theoretical and experimental aspects of ThFFF and demonstrate its remarkable fractionating capabilities through various examples and experiments. This book is written for beginners as well as for experienced separation scientists and will enable not only polymer chemists but also physicists, material scientists as well as students of polymer and analytical sciences to optimise

experimental conditions for a specific fractionation problem and solve various problems that can arise during the operation of the instrument.

This book is dedicated to friends and colleagues who contributed (directly or indirectly) to this book by their perseverance and dedication to developing not only the fundamental understanding of the thermal diffusion of polymers but also pioneering the characterisation of complex polymers and other nanosized materials. Amongst others, Kim R. Williams (USA), Alben Lederer (Germany), Michel Martin (France), Wim Kok (Amsterdam), Edwin Mes (Netherlands), Martin Schimpf (USA), Frédéric Violleau (France) and their graduate students are gratefully acknowledged.

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Symbols and Abbreviations

ACN	Acetonitrile
AF4	Asymmetrical flow field-flow fractionation
AFM	Atomic force microscopy
A_2	Second virial coefficient
BCP	Block copolymer
tBuMA	Poly(t-butyl methacrylate)
nBuMA	Poly(n-butyl methacrylate)
c^*	Critical overlap concentration
c	Polymer concentration in solution
c_0	Analyte concentration at the accumulation wall
CCD	Chemical composition distribution
CF	Chloroform
CH	Cyclohexane
δ	Hildebrand solubility parameter
D	Normal or translational diffusion coefficient
\bar{D}	Dispersity
DCM	Dichloromethane
D_h	Hydrodynamic diameter
DLS	Dynamic light scattering
DMA	Dimethylacetamide
DMF	Dimethylformamide
DOX	Dioxane
dRI	Differential refractive index
D_T	Thermal diffusion coefficient
dn/dc	Refractive index increment
dT/dx	Temperature gradient
F	Force
f	Friction coefficient
FFF	Field-flow fractionation
FIFFF	Flow field-flow fractionation
FTIR	Fourier-transform infrared spectroscopy
G	Centrifugal acceleration
ΔG	Gibbs free energy

$g_1(\tau)$	Normalised first-order correlation function
ΔH	Enthalpy
$^1\text{H NMR}$	Proton nuclear magnetic resonance spectroscopy
k	Boltzmann's constant
K^*	Optical constant
λ	Retention parameter
λ_i	Wavelength of the incident light
l	Average distance of the analyte cloud from the accumulation wall
LAC	Liquid absorption chromatography
LCCC	Liquid chromatography at the critical conditions
m'	Effective particle mass
M_i	Mass fraction
M_n	Number-average molar mass
M_w	Weight-average molar mass
MALLS	Multiangle laser light scattering
MEK	Methyl ethyl ketone
MMD	Molar mass distribution
n_i	Mole fraction
n	Refractive index of carrier liquid
η	Viscosity of the carrier liquid
NMR	Nuclear magnetic resonance spectroscopy
$P(\theta)$	Particle scattering factor
$\Delta\rho$	Difference in density between the carrier liquid and analyte
PB	Polybutadiene
1,2-PB	1,2-polybutadiene isomer
1,4-PB	1,4-polybutadiene isomer
PB-PS	Polybutadiene-polystyrene block copolymer
1,4-PB-PS	1,4-Polybutadiene-Polystyrene block copolymer micelles
1,2-PB-PS	1,2-Polybutadiene-Polystyrene block copolymer micelles
PBA	Poly(butyl acrylate)
PtBA	Poly(t-butyl acrylate)
PI	Polyisoprene
1,4-PI	1,4-polyisoprene isomer
3,4-PI	3,4-polyisoprene isomer
PMMA	Poly(methyl methacrylate)
PMMA-PS	Poly(methyl methacrylate)-polystyrene block copolymer
PMAA	Poly(methacrylic acid)
PS	Polystyrene
PS-PEO	Polystyrene-polyethylene oxide block copolymer
PSD	Particle size distribution
PS-PBA	Polystyrene-poly(butyl acrylate) block copolymer
PS-PMA	Polystyrene-poly(methacrylate) block copolymer
PVP	Poly(vinyl pyridine)
P2VP	Poly(2-vinyl pyridine)
P4VP	Poly(4-vinyl pyridine)

PVP-PS	Poly(vinyl pyridine)-polystyrene block copolymer
P2VP-PS	Poly(2-vinyl pyridine)-polystyrene block copolymer
P4VP-PS	Poly(4-vinyl pyridine)-polystyrene block copolymer
PVCH	Poly(vinyl cyclohexane)
q	Scattering vector
R	Retention ratio
R_g	Radius of gyration
R_g/R_h	Shape factor
R_h	Hydrodynamic radius
RI	Refractive index
R_0	Rayleigh ratio
θ	Scattering angle
ΔS	Entropy change
S_T	Soret coefficient
SdFFF	Centrifugal field-flow fractionation
SEC	Size exclusion chromatography
SEM	Scanning electron microscope
SLS	Static light scattering
T	Absolute temperature
t_r	Retention time of analyte
t^0	Retention time of unretained analyte
TEM	Transmission electron microscopy
T_g	Glass transition temperature
THF	Tetrahydrofuran
ThFFF	Thermal field-flow fractionation
TOL	Toluene
U	Migration velocity
w	Channel thickness
w_i	Weight fraction i
Z	Aggregation number



Abstract

Synthetic polymers are complex and multicomponent materials. Their development and further advancement is driven by the increasing demand for new functional materials with improved performance and tailored properties. Synthetic polymers are inherently complex materials as they can exhibit various distributions in properties such as molar mass (chain length), chemical composition, microstructure as well as molecular architecture and topology. As property distributions significantly influence the physical properties and end-use applications, proper monitoring and characterisation of distributions in key physical and physicochemical parameters is crucial for the improvement of polymer properties and performance. Most frequently, in order to characterise the various property distributions, a separation is required. As a result, fractionation techniques such as liquid chromatography and field-flow fractionation have become principal techniques for polymer characterisation.