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Harald Pasch • Muhammad Imran Malik

Advanced Separation Techniques for Polyolefins

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Harald Pasch
Department of Chemistry and Polymer Science
University of Stellenbosch
Matieland
South Africa

Muhammad Imran Malik
International Center for Chemical and Biological Sciences (ICCBS)
H.E.J. Research Institute of Chemistry
University of Karachi
Karachi
Pakistan

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Preface

Polyolefins are the most widely used synthetic polymers and their production capacities are rapidly increasing. Polyolefins are produced from very simple monomers containing only carbon and hydrogen, yet they exhibit very complex molecular structures. As all other synthetic polymers, polyolefins are distributed regarding various molecular properties, including molar mass, chemical composition, microstructure and molecular topology.

One consequence of the complex structure of polyolefins is the need for advanced analytical methods that provide accurate and quantitative information on the different parameters of molecular heterogeneity. In addition to analysis of bulk properties by spectroscopic methods, emphasis is on the analysis of property distributions that require suitable fractionation methods. If the material is distributed in more than one molecular property, multidimensional fractionations or the combination of fractionation and spectroscopic analysis might be required. High temperature fractionation methods must be used because most polyolefins are semi-crystalline and do not dissolve in common solvents at ambient temperatures. Powerful and well established methods include high temperature size exclusion chromatography (HT-SEC) for molar mass analysis, temperature rising elution fractionation (TREF) and crystallization analysis fractionation (CRYSTAF) for the analysis of chemical composition and branching. Recently, a number of more advanced methods including high temperature two-dimensional liquid chromatography (HT-2D-LC), temperature gradient interaction chromatography (TGIC) and crystallization elution fractionation (CEF) have been developed.

The fractionation of polyolefins has been addressed in numerous original publications and review articles. The most recent reviews were published by Monrabal (Adv. Polym. Sci., 2013, 257:203–51) and the authors of this book (Adv. Polym. Sci., 2013, 251:77–140) in 2013. These reviews provide an excellent overview on the current status of polyolefin characterization. They do not, however, give any detailed information on experimental protocols and procedures. To date, no textbook has been published that addresses the experimental background of different polyolefin fractionation techniques in great detail. This challenge is now addressed in the present textbook.

Similar to the previous textbooks in the Springer Laboratory Series, this laboratory manual is written for beginners as well as for experienced scientists. The subject of the book is the description of the experimental approach for the analysis

of complex polyolefins. It summarizes important applications in all major fractionation methods with emphasis on multidimensional analytical approaches. The theoretical background, equipment, experimental procedures and applications are discussed for each fractionation technique. It will enable polymer chemists, physicists and material scientists, as well as students of polymer and analytical sciences, to optimize experimental conditions for specific fractionation problems. The main benefit for the reader is that a great variety in instrumentation, separation procedures and applications is given, making it possible to solve simple as well as sophisticated separation tasks.

The book is structured in a similar fashion to the review article of the authors. It commences with a short introduction to the molecular complexity of polyolefins. This is followed by a discussion of crystallization-based fractionation techniques, including TREF, CRYSTAF and CEF. The major part addresses column chromatographic techniques for molar mass, chemical composition and microstructure, and the combination of different fractionations in multidimensional experimental set-ups. Finally, some first information on the application of field-flow fractionation is presented.

This textbook is dedicated to friends and colleagues that contributed (directly or indirectly) to this book by pioneering high temperature fractionation using HPLC, TREF, CRYSTAF, CEF and multidimensional chromatography, most prominently Tibor Macko (Germany) and, among others, Benjamin Monrabal (Spain), Freddy van Damme (The Netherlands), Yefim Brun, Colin Li Pi Shan and Rongjuan Cong (USA), Wolf Hiller, Robert Bruell, Dieter Lilge, Volker Dolle and Peter Montag (Germany), Joao Soares (Canada), Albert van Reenen (South Africa) and a number of former graduate students including Lars-Christian Heinz, Andreas Albrecht, Nyambeni Luruli, Pritish Sinha, Tino Otte, Anton Ginzburg, Stefan de Goede, Elana de Goede and Sadiqali Cheruthazhekatt.

Stellenbosch, South Africa — Harald Pasch
Karachi, Pakistan — Muhammad Imran Malik
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Symbols and Abbreviations

AF4, AFFFF	asymmetric flow field-flow fractionation
ATR	attenuated total reflectance
A-TREF	analytical temperature rising elution fractionation
BF	branch frequency
BHT	2,6-bis(1,1-dimethylethyl)-4-methylphenol
c	concentration
CCD	chemical composition distribution
CEF	crystallization elution fractionation
CRYSTAF	crystallization analysis fractionation
CSTR	continuous stirred tank reactor
D	diffusion coefficient
2D-LC	two-dimensional liquid chromatography
DLS	dynamic light scattering
DSC	differential scanning calorimetry
DVB	divinyl benzene
EA	ethylene–acrylate
EB	ethylene–butene
ED	ethylene-1-decene
EGMBE	ethyleneglycol monobutylether
EH	ethylene–hexene
ELSD	evaporative light scattering detector
EMA	ethylene–methyl acrylate
EMMA	ethylene–methyl methacrylate
EO	ethylene–octene
EP	ethylene–propylene
EPC	ethylene–propylene copolymer
EPDM	ethylene–propylene–diene rubber
EPR	ethylene–propylene rubber
EVA	ethylene–vinylacetate copolymer
f	frictional drag
FFF	field-flow fractionation
FID	free induction decay
FTIR	Fourier transform infrared spectroscopy
ΔG	Gibbs free energy

ΔG_m	Gibbs free energy of mixing
GPC	gel permeation chromatography
ΔH	interaction enthalpy
ΔH_m	mixing enthalpy
ΔH_u	heat of fusion
HDPE	high density polyethylene
HPLC	high performance liquid chromatography
HT	high temperature
IC	interaction chromatography
i.d.	internal diameter
IPC	impact polypropylene copolymer
IR	infrared
J	net flux
K^*	optical constant in light scattering
K_d	distribution coefficient
l	mean layer thickness
LALLS	low angle laser light scattering
LALS	low angle light scattering
LAM	longitudinal acoustic mode
LC	liquid chromatography
LCB	long chain branching
LCCC	liquid chromatography at critical conditions
LDPE	low density polyethylene
LLDPE	linear low density polyethylene
LS	light scattering
M	molar mass
M_n	number-average molar mass
M_o	molar mass of repeat unit
M_v	viscosity-average molar mass
M_w	weight-average molar mass
MA	methyl acrylate
MALLS	multi-angle laser light scattering
MALS	multi-angle light scattering
MFI	melt flow index
MMA	methyl methacrylate
MMD	molar mass distribution
MT	medium temperature
m_i	mass of species i
n_i	number of species i
N_A	Avogadro's number
NMR	nuclear magnetic resonance
OBC	olefin block copolymer
ODCB	ortho-dichlorobenzene
P	degree of polymerization
$P(\Theta)$	scattered light angular dependence

PE	polyethylene
PMMA	poly(methyl methacrylate)
PP	polypropylene
aPP	atactic polypropylene
iPP	isotactic polypropylene
sPP	syndiotactic polypropylene
PS	polystyrene
P-TREF	preparative temperature rising elution fractionation
PVAc	poly(vinyl acetate)
R, R_g	radius of gyration
R_h	hydrodynamic radius
$R(\Theta)$	intensity of scattered light
RALLS	right angle laser light scattering
RI	refractive index
RT	retention time
ΔS	conformational entropy
SCB	short chain branching
SCBD	short chain branching distribution
SDV	styrene-divinylbenzene copolymer
SEC	size exclusion chromatography
SEM	scanning electron microscopy
SGIC	solvent gradient interaction chromatography
SNR	signal-to-noise ratio
SSA	successive self-nucleation annealing
SSF	successive solution fractionation
T	temperature
T_c	crystallization temperature
T_m	melting temperature
TCB	1,2,4-trichlorobenzene
ThF3	thermal field-flow fractionation
TGA	thermo-gravimetric analysis
TGIC	temperature gradient interaction chromatography
TREF	temperature rising elution fractionation
TriSEC	triple-detector SEC
U	applied force (in FFF)
UHM	ultrahigh molar mass
UV	ultraviolet
V_e	elution volume
V_i	interparticle volume
V_p	pore volume
V_R	retention volume
VA	vinyl acetate
Visco	viscometer
w_i	weight fraction
w%	weight percentage

WAXD	wide-angle X-ray diffraction
ZN	Ziegler-Natta
η	viscosity
$[\eta]$	intrinsic viscosity, Staudinger index
η_o	viscosity of a solvent
η_{rel}	relative viscosity
η_{sp}	specific viscosity
λ	wavelength
λ	retention parameter (in FFF)

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