High temperature multidimensional chromatography of complex and functionalized polyolefins

by

Anthony Ndiripo

Thesis presented in partial fulfilment of the degree of
Doctor of Philosophy (PhD) in Polymer Science

at the
University of Stellenbosch

Supervisor: **Professor Harald Pasch** **December 2018**

Declaration for dissertation

By submitting this thesis electronically, I declare that the entirety of the work contained therein is my own, original work, that I am the sole author thereof (save to the extent explicitly otherwise stated), that reproduction and publication thereof by Stellenbosch University will not infringe any third party rights and that I have not previously in its entirety or in part submitted it for obtaining any qualification.

Anthony Ndiripo December 2018

Declaration for publications

I, Anthony Ndiripo further declare that the research papers titled:

1. A Multidimensional Fractionation Protocol for the Oligomer Analysis of Oxidized Waxes (Ndiripo, A.; Pasch, H. *Anal. Chim. Acta* **2018**, *1027*, 137–148.),
2. Comprehensive Analysis of Oxidized Waxes by Solvent and Thermal Gradient Interaction Chromatography and Two-Dimensional Liquid Chromatography (Ndiripo, A.; Pasch, H. *Anal. Chem.* **2018**, *90*, 7626–7634.) and
3. Chemical Composition Fractionation of Olefin Plastomers/Elastomers by Solvent and Thermal Gradient Interaction Chromatography (Ndiripo, A.; Albrecht, A.; Monrabal, B.; Wang, J.; Pasch, H. *Macromol. Rapid Commun.* **2018**, *39*, 1700703.)

submitted in this dissertation is based on actual and original work carried out by me. I further certify that these research papers have not been submitted and will not be submitted for obtaining any other qualification.

The author and co-authors listed in the manuscripts submitted in this dissertation made the following contributions:

Name	Email address	Nature of contribution	Contribution (%)
Candidate			
Anthony Ndiripo	[redacted]	Experimental work Data Analysis Discussion of result Write-up of the manuscripts Addressing reviewers comments	80
Co-author			
Andreas Albrecht	[redacted]	Provided copolymer samples	4
Benjamin Monrabal	[redacted]	Experimental work	2
Elena Pomakhina	[redacted]	Experimental work	2
Jingbo Wang	[redacted]	Provided copolymer samples	2
Harald Pasch	[redacted]	Supervision and mentoring Revision and correction of manuscripts	10

Signature of candidate:……

Date:……./2018

Declaration by co-authors:

1. The declaration above accurately reflects the nature and extent of the contributions of the candidate and co-authors to the four manuscripts in this dissertation,
2. No other authors contributed to the manuscripts in the dissertation besides those specified above, and
3. Potential conflicts of interest have been revealed to all interested parties and that the necessary arrangements have been made to use the materials in the four manuscripts in this dissertation.

Signature	Institutional/Industrial affiliation	Date
Declaration with signature in possession of candidate and supervisor	Borealis Group	30 July 2018
Declaration with signature in possession of candidate and supervisor	Polymer Char	30 July 2018
Declaration with signature in possession of candidate and supervisor	Stellenbosch University	30 July 2018

Abstract

Polyolefins like all other synthetic polymers have complex microstructures that must be understood in order to predict product performance and adjust catalyst and reactor technologies. Between synthesis and polymer application, characterization techniques act as the visual aid for polymer microstructure. In further conversion processes, products can be modified e.g. via oxidation or grafting which introduces functionality and functionality type distributions (FTD), in addition to the molar mass and chemical composition distributions (MMD and CCD, respectively). Furthermore, the use of multiple reactor and catalyst technologies to produce a given product results in complex mixtures or alloys of polymers with superior properties, but very complex microstructures. These microstructural properties must be defined and if possible, libraries of microstructural data and suitable comprehensive techniques should be established for each type of material.

High-temperature chromatographic techniques have emerged as fast and reliable techniques for polyolefin characterization. High-temperature liquid chromatography (HT-LC) which can be operated using solvent gradient and thermal gradient interaction modes (SGIC and TGIC, respectively) provides interesting alternatives to gas chromatography (GC) for the analysis of low molar mass oxidized waxes. In addition, non-crystallizing elastomers that cannot be characterized using crystallization-based methods such as temperature rising elution fractionation (TREF) and crystallization analysis fractionation (CRYSTAF) can be analysed using the mentioned modes of HT-LC. Polyolefin characterization is enhanced by the hyphenation of multiple techniques as no one method is able to fully define the multiple microstructural distributions. Preparative fractionation has emerged as an indispensable tool that, when coupled to other separation and fractionation techniques, yields a wealth of information on polyolefin microstructure.

The aim of the thesis is to utilize comprehensive HT-LC methods for the separation of complex polyolefin materials such low molar mass oxidized waxes, elastomers, and bimodal high density polyethylene (HDPE). Each type of selected polyolefin material presents a set of specific characterization challenges that must be addressed by HT-LC and/or hyphenation to a suitable preparative fraction technique.

Work presented in this study demonstrates the separation of oligomers on porous graphitic carbon (PGC) of oxidized waxes under tailored HT-LC conditions irrespective of oxidation level. However, oxidation levels are shown to affect detector response. As a preparative fractionation technique, solution crystallization fractionation (SCF) is also shown to enhance the separation and identification of smaller oligomers. For the first time, the separation according to polarity of oxidized low molar mass waxes using HT-SGIC and HT-TGIC on silica as the stationary phase is demonstrated under tailored conditions. In addition, the oxidation level is shown to influence the quantities of retained fractions.

Using a set of propylene-ethylene copolymers with increasing comonomer contents, the separation ranges of HT-SGIC and HT-TGIC are compared. In HT-SGIC a linear dependency of elution volume on the ethylene content is obtained for the entire average chemical composition (ethylene content) range. However, with HT-TGIC a linear dependency only is obtained within certain ethylene content limits. From this set of samples, it is also shown that HT-SGIC has a greater separation range (26.8 – 100 mol% ethylene) as compared to that of HT-TGIC (50 – 100 mol% ethylene).

Lastly, preparative TREF is coupled offline to HT-SGIC for the characterization of bimodal ethylene-1-hexene HDPEs. Two model bimodal HDPE samples with similar comonomer contents are compared to a HDPE homopolymer produced with the same catalyst technology. The presence of copolymer fractions in the two samples introduces complexity in the microstructure of the bimodal HDPE. For a detailed analysis of the resins, the use of multiple techniques is shown to provide more information on the bimodal HDPE microstructure. It is also shown that the separation and selectivity of HT-SGIC for the analysis of bimodal HDPEs improves when coupled to a preparative fractionation technique such p-TREF as using this approach the complexity of the materials is reduced. However, the co-elution of low molar mass PE with the copolymer remains an obstacle, which can be overcome.

Opsomming

Poliolefiene, soos alle ander sintetiese polimere, het 'n komplekse mikrostruktuur wat verstaan moet word om produkprestasie te voorspel en om katalisator- en reaktortegnologieë aan te pas. Tussen sintese en die toepassing van polimeer word karakteriseringstegnieke gebruik as visuele hulpmiddel vir die identifisering van polimeer mikrostruktuur. As 'n na-sintese-proses kan produkte deur middel van oksidasie of enting aangepas word. Hierdie prosesse beïnvloed nie net die funksionaliteit en funksionaliteitsverdelings (FTD) van ’n materiaal nie maar ook die molêre massa en chemiese samestellingverdelings (MMD en CCD onderskeidelik). Die gebruik van meervoudige reaktor- en katalisator-tegnologieë om 'n enkele produk te produseer lei dikwels na komplekse mengsels van polimere met superieure eienskappe en komplekse mikrostrukture. Hierdie ingewikkelde mikrostruktuur eienskappe moet gedefinieer word en, indien moontlik, moet biblioteke van mikrostruktuurdata en geskikte, omvattende tegnieke vir elke tipe materiaal opgestel word.

Hoëtemperatuur-chromatografiese tegnieke het vinnige bekend geword as betroubare tegnieke vir die karakterisering van poliolefien. Hoë-temperatuur vloeistof chromatografie (HT-LC), wat gebruik kan word in die oplosmiddel-gradiënt en temperatuur-gradiënt interaksie modes (SGIC en TGIC onderskeidelik), bied interessante alternatiewe vir gaschromatografie (GC) vir die analise van lae molêre massa geoksideerde wasse. Boonop kan nie-gekristalliseerde elastomere, wat nie gekarakteriseer kan word deur kristallisasie-gebaseerde metodes soos temperatuurstygingseluksiefraksionering (TREF) en kristallisasie analise fraksionering (CRYSTAF) nie, gekarakteriseer word met behulp van die genoemde modi van HT-LC. Poliolefien karakterisering word verder versterk deur die inkorporering van verskeie tegnieke aangesien geen enkele metode die volledige mikrostruktuurverdelings volledig kan definieer nie. Preparatiewe fraksionering het ook na vore gekom as 'n noodsaaklik hulpmiddel wat, wanneer gekoppel aan ander skeiding en fraksioneringstegnieke, 'n rykdom van inligting oor poliolefienmikrostruktuur lewer.

Die doel van hierdie proefskrif is om omvattende HT-LC metodes te gebruik vir die skeiding van komplekse poliolefienmateriale soos lae molêre massa geoksideerde wasse, elastomere en bimodale hoëdigtheid poliëtileen (HDPE). Elke tipe geselekteerde poliolefienmateriaal bied 'n stel

spesifieke karakteriseringsuitdagings wat aangepak moet word deur HT-LC en / of die koppeling aan 'n geskikte preparatiewe fraksioneringstegniek.

Werk wat in hierdie proefskrif aangebied word, wys die skeiding van oligomere op poreuse grafitiese koolstof (PGC) van geoksideerde wasse onder geselekteerde HT-LC toestande, ongeag oksidasievlak. Dit word ook gewys dat oksidasievlakke wel die detektorreaksie beïnvloed.

As 'n preparatiewe fraksioneringstegniek word kristallisasie-fractionasie (SCF) ook gebruik om die skeiding en identifikasie van kleiner oligomere te verbeter. Vir die eerste keer word die skeiding van geoksideerde lae molêre massa wasse volgens polariteit gedemonstreer deur middel van HT-SGIC en HT-TGIC met silika as die stasionêre fase en geselekteerde toestande te gebruik. Dit word ook gedemonstreer dat die oksidasie-vlak beïnvloed die hoeveelheid materiaal in elke fraksie.

Met behulp van 'n stel etileen-propileen kopolimere, met toenemende komonomer inhoud, word die skeidingsgrense van HT-SGIC en HT-TGIC vergelyk. In HT-SGIC word 'n lineêre afhanklikheid van die elusie-volume op die etileeninhoud verkry vir die totale gemiddelde chemiese samestelling (etileeninhoud) van die reeks. By HT-TGIC word egter slegs lineêre afhanklikheid binne sekere grense van etileeninhoud verkry. Uit hierdie stel monsters word ook getoon dat HT-SGIC 'n groter skeidingsgrens het (26.8 - 100 mol% etileen) in vergelyking met HT-TGIC (50 – 100% etileen).

Ten slotte word preparatiewe TREF gekoppel aan HT-SGIC vir die karakterisering van bimodale etileen-1-heseen HDPE. Twee model bimodale HDPE monsters met soortgelyke komonomer inhoud word vergelyk met 'n HDPE homopolymeer wat met dieselfde katalisatortegnologie vervaardig was. Die teenwoordigheid van kopolimeer fraksies in die twee monsters verhoog die kompleksiteit in die mikrostruktuur van die bimodale HDPE. Vir 'n gedetailleerde analise van die harse, word die gebruik van verskeie tegnieke getoon om meer inligting oor die bimodale HDPE mikrostruktuur te verkry. Daar word ook getoon dat die skeiding en selektiwiteit van HT-SGIC vir die analise van bimodale HDPE verbeter wanneer dit gekoppel word aan 'n preparatiewe fraksioneringstegniek soos p-TREF aangesien die kompleksiteit van die materiale verminder word. Die ko-elusie van lae molêre massa PE met die kopolimeer bly egter 'n hindernis, maar dit kan oorkom word.

Dedication

For my beloved mother, Stella, with whom I have to sit down and explain in detail this work. I don't know what her expectations are until they are not met.

Acknowledgements

My utmost gratitude goes to my supervisor Prof. Harald Pasch for the opportunity to study in his group, mentorship, motivation, guidance and financial support throughout the course of this study. It's pretty easy to succeed when you are supported and for that I am forever grateful. I undoubtedly have gained an enormous wealth of knowledge and experience from the numerous discussions we had over the course of my study at Stellenbosch University.

My most sincere thanks go to the following: Dr. Andreas Albrecht and Dr. Jingbo Wang (Borealis) for providing samples and for carrying out some of the analytical work; Dr. Elena Pomakhina (Borealis) for the NMR analyses; Dr. Benjamin Monrabal (Polymer Char) for some of the analytical work.

Prof. Albert J. van Reenen for the access to the olefins lab where the preparative fractionation work was carried out.

Dr. Guilaume H. Greyling for translating the abstract into Afrikaans.

All members and staff of the Department of Chemistry and Polymer Science, Mrs Erinda Cooper, Mrs Aneli Fourie, Mr Deon Koen, Mr Jim Motshweni and Mr Calvin Maart.

All members of the Pasch group past and present: for their contributions during our group meetings: Paul, Mawande, Douglas, Zanelle, Ndumiso, Upenyu Lucky, Clement, Guilaume, Helen.

Department of Applied Chemistry Staff at the National University of Science and Technology.

Good friends: Nusrat M. Begum and Sifiso Magagula.

National University of Science and Technology (NUST) and the National Research Foundation (NRF) for funding.

Table of contents

List of figures

From Chapter 2

From Chapter 3

From Chapter 4

List of tables

List of symbols

ΔG	Gibbs free energy
ΔH	Change in enthalpic contribution
ΔH_m	Melting enthalpy
ΔS	Change in entropic contribution
C_{MS}	Concentration of analyte in mobile phase
C_{SP}	Concentration of analyte on stationary phase
K_d	Partitioning coefficient
M_w	Weight-average molar mass
M_n	Number-average molar mass
M_p	Peak molar mass
M_v	Viscosity-average molar mass
M_z	Z-average molar mass
R	Gas constant
T	Temperature
T_c	Crystallisation temperature
T_m	Melting temperature
V_e	Elution volume
V_h	Hydrodynamic volume

List of abbreviations

2D-LC	Two-dimensional liquid chromatography
^{13}C-NMR	Carbon-13 nuclear magnetic resonance
ATR	Attenuated total reflectance
ATR-FTIR	Attenuated total reflectance-Fourier transform infrared
BHT	2,6-di-*tert*-butyl-4-methylphenol
CEF	Crystallisation elution fractionation
CFC	Chromatographic cross-fractionation
CRYSTAF	Crystallisation analysis fractionation
Đ	Dispersity
DSC	Differential scanning calorimetry
DRI	Differential refractive index
ELSD	Evaporative light scattering detector
EPC	Ethylene-propylene copolymer
EVA	Ethylene-co-vinyl acetate
FTIR	Fourier transform infrared spectroscopy
GPC	Gel permeation chromatography
HDPE	High density polyethylene
HPLC	High performance liquid chromatography
HT-2D-LC	High-temperature two-dimensional liquid chromatography
HT-HPLC	High-temperature liquid chromatography
HT-SEC	High-temperature size exclusion chromatography
HT-SGIC	High-temperature solvent gradient interaction chromatography
HPer DSC	High performance differential scanning calorimetry
IC	Interaction chromatography
IR	Infrared
LAC	Liquid adsorption chromatography
LC-CC	Liquid chromatography at critical conditions
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
LS	Light scattering
MALLS	Multi-angle laser light scattering
MM	Molar mass
MMD	Molar mass distribution
NMR	Nuclear magnetic resonance
o-DCB/ODCB	*ortho*-Dichlorobenzene
PE	Polyethylene
PGC	Porous graphitic carbon
PP	Polypropylene
PVC	Polyvinyl chloride
RI	Refractive index
SCB	Short chain branching
SCBD	Short chain branching distribution
SCF	Solution crystallization fractionation
SEC	Size exclusion chromatography
SEC-IR	Size exclusion chromatography with infrared detection

SF	Soluble fraction
SGIC	Solvent gradient interaction chromatography
TCB	1,2,4-trichlorobenzene
TCE-d2	Deuterated 1,1,2,2-tetrachloroethane
TGIC	Thermal gradient interaction chromatography
TREF	Temperature rising elution fractionation
ZN	Ziegler-Natta
ZN-LLDPE	Ziegler-Natta linear low density polyethylene

Chapter 1

General introduction and objectives

A general overview of the fundamental role of polyolefin characterisation and the various techniques is given. Low molar mass waxes, olefin elastomers and bimodal HDPE are discussed briefly, highlighting the knowledge gaps that exist in their characterization as far as analysis with chromatography is concerned. The work reported in this thesis is condensed into the main objectives. A layout of the thesis is also given.

1.1 Introduction

It is known that polymers in general are complex materials with respect to their microstructure. Polymer microstructure can be expressed as molar mass and chemical composition distribution.[1-3] Polymer microstructure is ultimately revealed in the physical and mechanical properties of the material. Therefore, for structure-property relationships to be established, the microstructure of the polymer must be comprehensively revealed and understood.

Polyolefins form a unique class of synthetic polymers and have become virtually indispensable due to their ease of fabrication, application and durability.[2,4] Polymerization of olefins produces statistical polymer chains and comonomer insertions which are dependent on the catalyst used and the reactor technology.[5] Furthermore, as a further conversion process, polyolefins can be functionalized via grafting or oxidation which makes the materials' microstructure more complex.[6,7] In addition, the ever changing landscape of polymer technology introduces new materials with complex microstructures that must be understood in order to predict end use properties.

A variety of characterization methods is available for the unravelling of the polyolefin microstructure. For molar mass characterization, high-temperature size exclusion chromatography (HT-SEC) is employed with thermodynamically good solvents such 1,2,4-trichlorobenzene (TCB) being employed as mobile phase.[8-13] The separation method can be coupled to several detectors which give chemical composition or branching information as a function of elution volume. However, SEC/HT-SEC only separates according to hydrodynamic volume which may result in the co-elution of branched and linear analogues or functionalized and non-functionalized polymer chains.[14-16]

Liquid chromatography separation according to chemical composition of polyolefins was only introduced in the early 2000s. The adaptation of equipment and stationary phases capable of handling high operating temperatures made it possible to study polyolefins since they have high dissolution temperatures due to their semi-crystalline nature. Since then, robust sample handling, thermostated column housing and sample detection instrumentation have been built and perfected. Although a lot of work with regard to high-temperature high performance liquid chromatography (HT-HPLC) has been done, a variety of new and established polyolefins are still to be characterized

using the technique. In addition, conditions have to be tailored to obtain the most relevant information regarding specific polyolefin materials. Niche products such as oxidized waxes, functionalized polyethylene copolymers, high comonomer content polyolefin copolymers (elastomers) and bimodal high density polyethylene (HDPE) are complex materials whose microstructure is yet to be fully explored via HT-HPLC.

With regard to oxidized waxes or functionalized polyethylene, polymers are produced that contain various types of functional groups, i.e. carboxylic, carbonyl, hydroxyl, and other oxygen functionalities.[17-19] As the properties of a material depend strongly on the chemical composition distribution (CCD) and its correlation to molar mass distribution (MMD), reliable methods are required to characterize the functional groups along the polymer chains. In general, functional group quantification of oxidized waxes can be done by acid number determination, infrared spectroscopy (IR) as well as proton and carbon-thirteen nuclear magnetic resonance spectroscopy (^{1}H NMR, ^{13}C NMR). These methods, however, provide only average functional group concentrations. Column-based separation methods including gas chromatography (GC)[20-24] and high temperature liquid chromatography (HT-LC) are powerful methods for the separation of polyolefin oligomers and polymers according to chain length or according to the distribution of functional groups.[25,26]

The use of GC methods has some limitations concerning the carbon range (up to C30) and concerning the analysis of compounds containing multiple carboxylic acid groups or high molar mass acids. This is due to the fact that the boiling points of these components are higher than the operating temperature of the GC. Accordingly, these compounds cannot be eluted from the GC column since they do not evaporate and move to the gas phase. The use of even higher temperatures in GC may result in the degradation of the waxes. To overcome these limitations, HT-LC seems to be an alternative method for the separation of functionalized waxes. There is promise that HT-LC is capable of separating these materials with regard to the distribution of functional groups along polymer chains.

High molar mass functionalized/polar polyolefins have been extensively studied by Albrecht and Pasch, as well as other groups.[25,27-29] Methods of adding polar groups to polyolefin backbones include copolymerizing ethylene with a suitable comonomer using Ziegler-Natta or metallocene catalysts and grafting polar units onto the polyethylene backbone.[6,30] Several types of oxygen

containing groups can be added onto the polyolefin backbone. These include maleic anhydride, vinyl acetate, ethyl acrylate, maleic acid, acrylic acid and many others. However, low molar mass waxes have not yet been analyzed using liquid adsorption chromatography at high temperatures. The low oxidation levels/comonomer contents and long crystallizable ethylene sequences prevent the dissolution of functionalized waxes at ambient temperatures in common polar solvents. High temperatures are, therefore, required for the separation and characterization of these materials according to the degree of insertion of polar groups onto the polyethylene backbone.

Due to the fact that HT-HPLC does not rely on the crystallizability of polyolefin materials for separation, but on the interactive forces between analyte and stationary phase, it offers an interesting alternative for the analysis of elastomers/plastomers.[31,32] Owing to the high comonomer contents of elastomers, these materials are difficult to characterize using crystallization-based techniques. The high comonomer contents result in lack of detectable crystallizable sequences in melt and high solubility in solution. As a result, melting and crystallization events cannot be detected by differential scanning calorimetry (DSC). In solution, the elastomers either fail to crystallize or co-elute at ambient temperatures when crystallization analysis fractionation (CRYSTAF) or temperature rising elution fractionation (TREF) are used.

HT-HPLC offers an alternative since separation on porous graphitic carbon (PGC) occurs due to interactive forces which are influenced by methylene sequence length rather than sample crystallinity. High-temperature solvent gradient interaction chromatography (HT-SGIC) and high-temperature thermal gradient interaction chromatography (HT-TGIC)[33] are two techniques which utilize different approaches for the chemical composition separation of polyolefin samples. HT-SGIC has been extensively employed for the separation and characterization of a variety of polyolefin materials.[34-38] However, HT-TGIC is relatively unexplored for polyolefins since its introduction, hence its separation range is rather ambiguous.

Another commercially important and unique material is bimodal high density polyethylene. The resin is produced commercially by combing the microstructural attributes of low molar mass polyethylene (PE) as well as low and high comonomer content high molar mass poly (ethylene-1-alkene) copolymers. State-of-the-art multimodal proprietary technologies are used to produce these bimodal PE resins in a cascade of reactors.[5,39,40] These materials have high environmental stress-cracking resistance (ESCR), long-term creep/burst resistance and uniquely high stiffness/impact

balance.[41,42] Bulk sample analyses do not provide much information regarding minute differences in the microstructure of these resins especially when the resins have comparable average chemical compositions or are produced batchwise for the same product. Therefore, preparative techniques in combination with advanced analytical techniques are used to probe the composition of selected resins with similar/dissimilar average comonomer contents.

1.2 Research hypothesis

While the analysis of low molar mass waxes by GC is established, its application range is limited when it comes to higher molar masses and in the case that the waxes are oxidized. Therefore, the present research seeks to establish analysis conditions for the separation of oxidized and non-oxidized waxes using high temperature liquid chromatography, thereby answering the following fundamental questions:

1. Can oxidized waxes be separated according to their oligomer length?
2. If so, do they behave differently from non-oxidized waxes?
3. Can a preparative fractionation method enhance the microstructure elucidation of the waxes?
4. Can oxidized waxes be separated and detected using high-temperature liquid adsorption chromatography (HT-LAC)?
5. If so, what are the best chromatographic conditions and do waxes with different oxidation levels show any differences?
6. Can chemical composition separations in the first dimension be adapted for two-dimensional analyses?
7. Can these differences be quantified?

The separation range of HT-SGIC in comparison to crystallization-based techniques such as CRYSTAF is well established for most polyolefin materials. However, the relatively new HT-TGIC has several advantages regarding the use of multiple detectors. Here, the main aim is to compare the two chromatographic techniques for the separation of ethylene-propylene elastomers. The fundamental questions are:

1. What is the separation range of ethylene-propylene elastomers on porous graphitic carbon (PGC) using HT-TGIC?

2. Can the separation range of HT-TGIC be improved by lowering operating temperatures?

Bimodal HDPE is a challenging polyolefin material to characterize owing to its complex and multimodal molecular properties. The low comonomer content, broad MMDs and presence of large amounts of low molar mass and high molar mass PE make it a challenging task to characterize bulk samples. In the present work, the main concerns with regard to the characterization of bimodal HDPE are summarized as follows:

1. Is the multiple preparative fractionation concept for the characterization of multimodal ethylene-1-hexene copolymers with crystallization-based methods feasible?
2. If so, what microstructural information is obtained from the coupling of the crystallization-based preparative method to advanced analytical techniques?
3. What other fractionation techniques can be applied to enhance the extraction of microstructural information?

1.3 Objectives and methodology

The first objective of the research work is to utilise the available high temperature chromatographic systems to unravel the microstructure of low molar mass oxidized and non-oxidized waxes. Owing to the low molar mass nature of waxes, conditions have to be tailored in order to allow for the adsorption, separation and detection of the waxes.

In the first part, separation of oligomers in oxidized and non-oxidized waxes is investigated on porous graphitic carbon. Both solvent gradient and thermal gradient modes are used to investigate the different behaviours of the oxidized and non-oxidized waxes. In the second part, separation of waxes according to polarity is investigated using HT-SGIC. For this to be achieved, several solvent combinations are tried at different column conditions. Detector conditions are also tailored to allow for the detection of the low molar mass materials.

The second objective is to compare HT-SGIC and HT-TGIC for the analysis of high comonomer content elastomers/plastomers. The separation ranges of both techniques are compared using a similar sample set.

The third objective is to combine a preparative fractionation technique with advanced analytical techniques for the structural elucidation of bimodal HDPE. Preparative temperature rising elution

fractionation (p-TREF) is used to fractionate bimodal HDPE into several fractions for analysis by SEC-IR, HT-SGIC and comprehensive high-temperature two-dimensional liquid chromatography (HT-2D-LC). A combination of preparative fractionation coupled offline to advanced analytical techniques gives more information regarding the microstructure of bimodal HDPE.

1.4 Layout of dissertation

The dissertation is divided into the following chapters:

Chapter 1

An introduction of the work to be done is given. The knowledge gaps, research hypothesis as well as the main objectives and a brief outline of the dissertation are also given.

Chapter 2

A brief literature review is given in this chapter, focusing on the polymer materials to be analysed as part of the thesis work. A review of the fundamental characterization instruments is given with more emphasis on chromatographic techniques.

Chapter 3

Detailed experimental methods of all the techniques in the thesis work are given in this chapter.

Chapter 4

The results of the study are presented herein. The first section contains results on work on the separation of oligomers in oxidized and non-oxidized waxes. In the second section, findings obtained from the functionality type separations of oxidized waxes are presented. Ethylene-propylene copolymers are used as model samples for the comparison of HT-SGIC and HT-TGIC in the third section. In the last section, a comprehensive report is given on bulk analysis as well as the preparative fractionation and offline analysis of a set of bimodal HDPE samples.

Chapter 5

The research findings of the work reported in Chapter 4 are given in a concise summary and recommendations for future work are presented.

1.5 References

(1) Pasch, H. *Adv. Polym. Sci.* **1997**, *128*, 1–45.

(2) Pasch, H.; Malik, M. I.; Macko, T. *Adv. Polym. Sci.* **2013**, *251*, 77–140.

(3) Macko, T.; Brüll, R.; Zhu, Y.; Wang, Y. *J. Sep. Sci.* **2010**, *33*, 3446–3454.

(4) Pasch, H.; Malik, M. I. *Advanced separation techniques for polyolefins*; Springer: Switzerland, 2014.

(5) Alt, F. P.; Böhm, L. L.; Enderle, H. F.; Berthold, J. *Macromol. Symp.* **2001**, *163*, 135–144.

(6) Chung, T. *Prog. Polym. Sci.* **2002**, *27*, 39–85.

(7) Prabhu, K.; Macko, T.; Brüll, R.; Remerie, K.; Tacx, J.; Garg, P.; Ginzburg, A. *J. Chromatogr. A* **2016**, *1441*, 96–105.

(8) Yau, W.; Kirkland, J.; Bly, D. *Modern Size-Exclusion Liquid Chromatography, Practice of Gel Permeation and Gel Filtration Chromatography*; John Wiley & Sons: New York, 1979.

(9) Carbognani, L. *J. Chromatogr. A* **1997**, *788*, 63–73.

(10) Mori, S.; Barth, H. G. *Size exclusion chromatography*; Springer: New York, 1999.

(11) Yoo, S.-H.; Jane, J.-l. *Carbohydr. Polym.* **2002**, *49*, 307–314.

(12) Striegel, A.; Yau, W. W.; Kirkland, J. J.; Bly, D. D. *Modern size-exclusion liquid chromatography: Practice of gel permeation and gel filtration chromatography*; John Wiley & Sons: New Jersey, 2009.

(13) Podzimek, S. In *Light Scattering, Size Exclusion Chromatography and Asymmetric Flow Field Flow Fractionation: Powerful Tools for the Characterization of Polymers, Proteins and Nanoparticles*; John Wiley & Sons: New Jersey, 2011, pp 99–206.

(14) Plüschke, L.; Mundil, R.; Sokolohorskyj, A.; Merna, J.; Sommer, J. U.; Lederer, A. *Anal. Chem.* **2018**, *90*, 6178–6186.

(15) Hiller, W.; Hehn, M.; Hofe, T.; Oleschko, K. *Anal. Chem.* **2010**, *82*, 8244–8250.

(16) Pasch, H. *Polym. Chem.* **2013**, *4*, 2628–2650.

(17) United States, US 6169148 B1, 2001.

(18) United States, US6348547 B1, 2002.

(19) de Klerk, A. *Ind. Eng. Chem. Res.* **2003**, *42*, 6545–6548.

(20) Czech, F.; Fuchs, R.; Antczak, H. *Anal. Chem.* **1961**, *33*, 698–704.

(21) O'Connor, J. G.; Burow, F. H.; Norris, M. S. *Anal. Chem.* **1962**, *34*, 82–85.

(22) Hyötyläinen, T.; Riekkola, M.-L. *J. Chromatogr. A* **2003**, *1000*, 357–384.

(23) Lawrence, J.; Iyengar, J.; Page, B.; Conacher, H. *J. Chromatogr. A* **1982**, *236*, 401–403.

(24) Heath, D. J.; Lewis, C.; Rowland, S. J. *Org. Geochem.* **1997**, *26*, 769–785.

(25) Albrecht, A.; Brüll, R.; Macko, T.; Pasch, H. *Macromolecules* **2007**, *40*, 5545–5551.

(26) Albrecht, A.; Heinz, L. C.; Lilge, D.; Pasch, H. *Macromol. Symp.* **2007**, *257*, 46–55.

(27) Ginzburg, A.; Macko, T.; Malz, F.; Schroers, M.; Troetsch-Schaller, I.; Strittmatter, J.; Brull, R. *J. Chromatogr. A* **2013**, *1285*, 40–47.

(28) Malik, M. I.; Pasch, H. *Prog. Polym. Sci.* **2014**, *39*, 87–123.

(29) Albrecht, A.; Brüll, R.; Macko, T.; Sinha, P.; Pasch, H. *Macromol. Chem. Phys.* **2008**, *209*, 1909–1919.

(30) Yuan, X.; Matsuyama, Y.; Chung, T. M. *Macromolecules* **2010**, *43*, 4011–4015.

(31) Phiri, M. J.; Cheruthazhekatt, S.; Dimeska, A.; Pasch, H. *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *53*, 863–874.

(32) Phiri, M. J.; Dimeska, A.; Pasch, H. *Macromol. Chem. Phys.* **2015**, *216*, 1619–1628.

(33) Cong, R.; deGroot, A. W.; Parrott, A.; Yau, W.; Hazlitt, L.; Brown, R.; Cheatham, M.; Miller, M. D.; Zhou, Z. *Macromol. Symp.* **2012**, *312*, 108–114.

(34) Macko, T.; Brüll, R.; Alamo, R. G.; Stadler, F. J.; Losio, S. *Anal. Bioanal.Chem.* **2011**, *399*, 1547–1556.

(35) Chitta, R.; Macko, T.; Brüll, R.; van Doremaele, G.; Heinz, L. C. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 1840–1846.

(36) Albrecht, A.; Heinz, L.-C.; Lilge, D.; Pasch, H. *Macromol. Symp.* **2007**, *257*, 46–55.

(37) Cheruthazhekatt, S.; Pijpers, T. F. J.; Harding, G. W.; Mathot, V. B. F.; Pasch, H. *Macromolecules* **2012**, *45*, 2025–2034.

(38) Pasch, H.; Heinz, L. C.; Macko, T.; Hiller, W. *Pure Appl. Chem.* **2008**, *80*, 1747–1762.

(39) Ginzburg, A.; Macko, T.; Dolle, V.; Brüll, R. *J. Appl. Polym. Sci.* **2013**, *129*, 1897–1906.

(40) Sun, X.; Shen, H.; Xie, B.; Yang, W.; Yang, M. *Polymer* **2011**, *52*, 564–570.

(41) Fan, Y.; Xue, Y.; Nie, W.; Xiangling, J.; Bo, S. *Polym. J.* **2009**, *41*, 622–628.

(42) Tian, Z.; Chen, K.-R.; Liu, B.-P.; Luo, N.; Du, W.-L.; Qian, F. *Chem. Eng. Sci.* **2015**, *130*, 41–55.

Chapter 2

Theoretical background

A general overview of the different polyolefin materials studied in the present work is given. Analytical techniques reported in the literature up to now used for the study of microstructural characteristics of complex polyolefins are also presented. The theoretical background of the work is briefly discussed.

2.1 Introduction

Of the synthetic polymers available on the market, polyolefins are by volume the most produced and most used. The huge and ever-growing demand of polyolefins is due to their wide range of applications, excellent cost-to-performance ratio, non-toxicity, chemical resistance, excellent processability and high mechanical strength. This set of advantages has made polyolefin materials virtually part of everyday life.

Polyolefins are available in a large array of classes depending on end-use or monomers used for synthesis. Each class has a set of properties which enable the polyolefin material to perform specific functions. Specific to this work, oxidized waxes, ethylene-propylene copolymers (EPCs) and bimodal high density polyethylene (HDPE) are some of the classes of polyolefins with very different applications, but almost similar starting raw materials. Common to these classes of polyolefins is the ethylene monomer responsible for forming the backbone on which short chain branches, polar/1-alkene comonomers or oxidized functionalities can be introduced. The main polyolefin materials relevant to this work are discussed in the following sections.

2.2 Bimodal high density polyethylene

Polyolefin blends/alloys provide better properties compared to their components as several components with different functions are combined. Bimodal HDPE is an example and it benefits from its complex multimodal microstructure by having the strength and stiffness of HDPE and high-stress-crack resistance and processability of unimodal medium density polyethylene. Several technologies of producing bimodal HDPE are available. In addition, different catalyst technologies are in the market depending on the producers.[1-8]

Bimodal HDPE resins are typically produced in the following manner: the first reactor is fed with ethylene and hydrogen to produce low molar mass linear PE. After hydrogen is removed, the low molar mass PE is transferred to a second reactor, where a 1-alkene (1-butene or 1-hexene) is added as the comonomer. Here, a high molar mass short chain-branched copolymer component is produced depending on the reactor conditions. Usually, the second reactor is loaded with much less hydrogen to allow the formation of high molar mass polyethylene. A reversed mode wherein the high molar mass component is produced first, followed by a low-molar-mass component is also available.[1]

The final product is typically characterized by three components. The first is low molar mass PE which aids in processability. The second is high comonomer content copolymer which provides resistance to environmental stress cracking and rapid crack propagation. Lastly, the bulk of the resin is characterized by very low-comonomer high-molar mass PE which provides the backbone properties of the resins such as tensile strength and toughness. Such bimodal HDPE resins find numerous applications in pipes for gas and water distribution.[5,9] As a result, the final product has a complex microstructure with broad molar mass (MMD) and chemical composition distributions (CCD) as illustrated in Fig. 2.1.

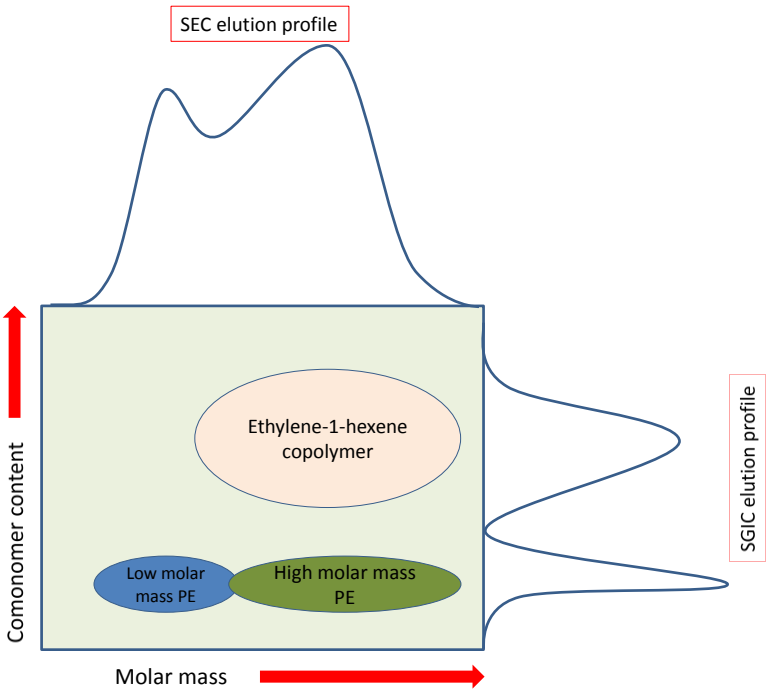


Figure 2.1 Schematic diagram showing the complex multimodal microstructural properties of bimodal HDPE resins.

2.3 Functionalized polyolefins

Polyolefins can be modified to introduce other functionalities. The introduction of polar functionalities on the polyolefin backbone has received much attention in the recent past. Polyolefins functionalized with polar groups have better adhesive properties, compatibility with additives and depending on their molar mass, they find a wide range of applications.[10-15] Polyolefins can be functionalized via a number of ways. Copolymerization, grafting and oxidation

are some of the ways of introducing functionalities onto the polyolefin backbone.[16-19] For low molar mass PE, oxidation is one the many methods of introducing polar functionalities.

Due to the low molar mass nature of waxes, they are easy to melt and oxidize via bubbling with air, oxygen or ozone.[18,20] Usually the residence time determines the level of oxidation. Once oxidized, a variety of oxygen containing functionalities are obtained. These functionalities range from ketones to aldehydes, carboxylic acids, alcohols and γ-lactones.[21-23] The established method of determining the oxidation level of the oxidised wax is via titration with a base to determine the acid level. The method has several shortcomings. Firstly, functional groups such as ketones and aldehydes may go unaccounted for. Secondly, the technique assumes that all the wax chains have similar types and numbers of functionalities. Oxidation is a statistical process and a distribution of functionalities is obtained for the wax chains present. This means that some polymer chains have more polar functionalities while others may go without oxidation. Such a distribution of functionalities can be defined only with appropriate separation and detection methods.

In certain applications such as the injection moulding of polyvinyl chloride (PVC), non-oxidized and oxidized waxes are used as the internal and external lubricants, respectively. The oxidation level of the wax is crucial to the migration or mobility of the oxidized wax chains towards the outer surfaces of the PVC moulding. The quality of lubricant determines the smoothness of the finished PVC product and hence its price. Oxidized waxes have several other applications which include use in inks, paints, polishes, paper and cloth coatings, wax paper, insulation, lubrication, wax figures and food coatings.[24]

Such a wide distribution in functionality can be advantageous depending on the application of the wax. The combination of wax chains with significantly different molar masses or chemical compositions provides products with versatile physical, mechanical and processing properties. However, these distributions must always be defined to enable prediction of product performance and distinguishing between batch-to-batch irregularities.

2.4 Elastomers and ethylene-propylene copolymers

The main types of polyolefin materials in the plastics market are polypropylene (PP) and polyethylene (PE). Smaller classes of polyolefins are produced through the copolymerization of ethylene or propylene with a variety of other comonomers. For example, when an ethylene-

propylene copolymer (EPC) is produced in a multistage reactor system, ethylene can be added in different quantities to produce different material grades for different impact polypropylene applications.[25-28]

Likewise, ethylene can be copolymerised with a variety of 1-olefins to produce linear low density polyethylene (LLDPE) via solution, slurry or gas phase reactor systems. Depending on the amount and type of 1-olefin comonomer, different classes of LLDPEs are produced. The LLDPE classes range from pipe grades (low comonomer content LLDPE) to elastomers (high comonomer content LLDPE). More sophisticated methods of LLDPE production include producing resins which are a blend of several components from different reactors. In such cases, it more likely to end up with a resin with very broad MMDs and CCDs, respectively. Such resins are often termed bimodal HDPE as discussed in Section 2.2.

In cases where the comonomer content is high such that rigid sections of the polymer chains are minimal, plastomers/elastomers are obtained. Polyolefin-based elastomers have received attention in comparison to other types of thermoplastic elastomers. This due to their better chemical resistance, lower density, excellent weatherability and lower cost for elasticity formation.[29,30] In addition, they are blended with other brittle polyolefin materials in order to increase impact strength.

The obvious challenge is the characterization of these materials since they cannot be separated or fractionated using classical crystallization-based techniques. For example, with differential scanning calorimetry (DSC), some of the materials do not show melting and crystallization events owing to their very low crystallinities. In crystallization analysis fractionation (CRYSTAF), the polymer chains remain soluble at ambient temperatures and, therefore, cannot be fractionated.[31,32] Likewise, analytical and preparative temperature rising elution fractionation (TREF) fail at fractionating these materials.

On the other hand, interaction chromatography at high temperature has been used previously to fractionate elastomers using solvent gradient based methods.[31-34] Porous graphitic carbon (PGC), which is used as the stationary phase under the trademark Hypercarb®, allows for the preferential adsorption and desorption of ethylene-based polyolefins from solution. Therefore, high comonomer content resins can be adsorbed and preferentially desorbed from the stationary phase

according to the comonomer content. The separation mechanisms of the ethylene-based materials using interaction chromatography are described in detail in the following sections.

2.5 Characterization of polyolefins

Polyolefin characterization follows similar trends to the discovery and improvement of new polymerization catalysts. For example, in the early 1960s after the Nobel Prize winning achievement by Ziegler and Natta, an array of characterization techniques were introduced into the field. Numerous techniques aimed at probing the microstructure of the new materials were put to test. With new polymerization methods, catalysts or polymeric materials comes the challenge of understanding their microstructure.

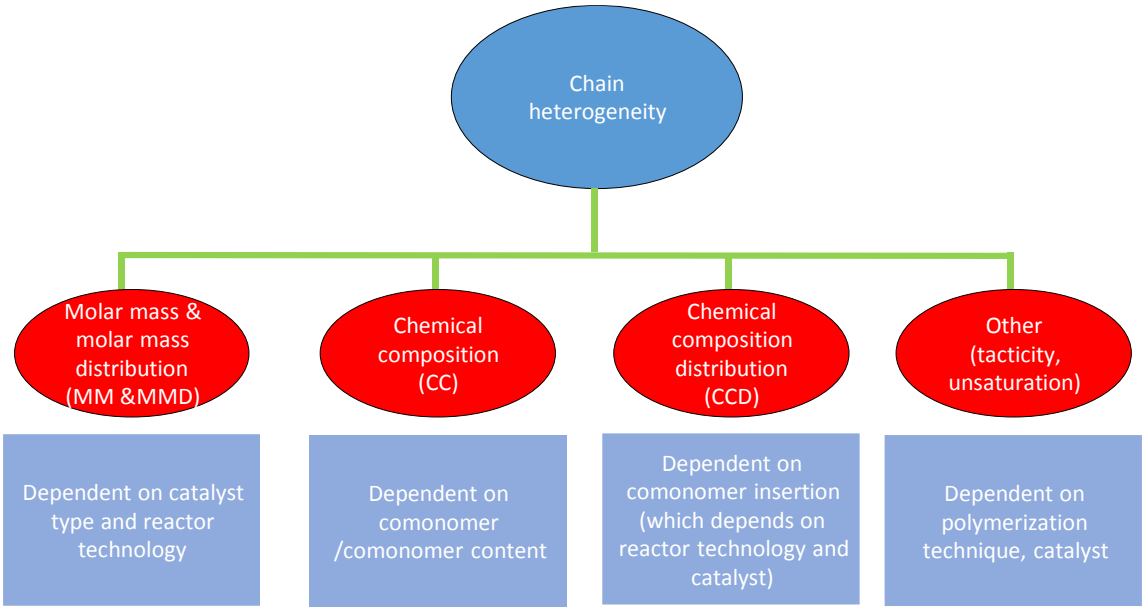


Figure 2.2 Summary of the molecular heterogeneity in polyolefins.

Polyolefin characterization methods to date can be classified according to the mode of action or instrumentation used i.e. crystallization-based, chromatographic or spectroscopic. Very often these methods are used in tandem to obtain more information as a single analysis technique cannot provide comprehensive information regarding the multivariate distributions of the complex polyolefins. The heterogeneity of polyolefins is summarized in Fig. 2.2. Several techniques are now available for the microstructural characterization of polyolefins as summarized in Fig. 2.3.

2.5.1 Crystallization-based techniques

Polyolefins can be classified as semi-crystalline materials. More so, polyolefins exhibit distributions in their crystallizability due to differences in chain microstructure. For copolymers and branched polyolefins, these differences can be directly related to their chemical composition although molar mass influences are present in some cases. Several solution-based techniques have been developed as alternatives to the melt-based differential scanning calorimetry. The obvious advantages are that concentration detectors are used with techniques such as CRYSTAF, CEF and analytical TREF. Therefore, amorphous or soluble components that would otherwise go undetected in DSC can be quantified.

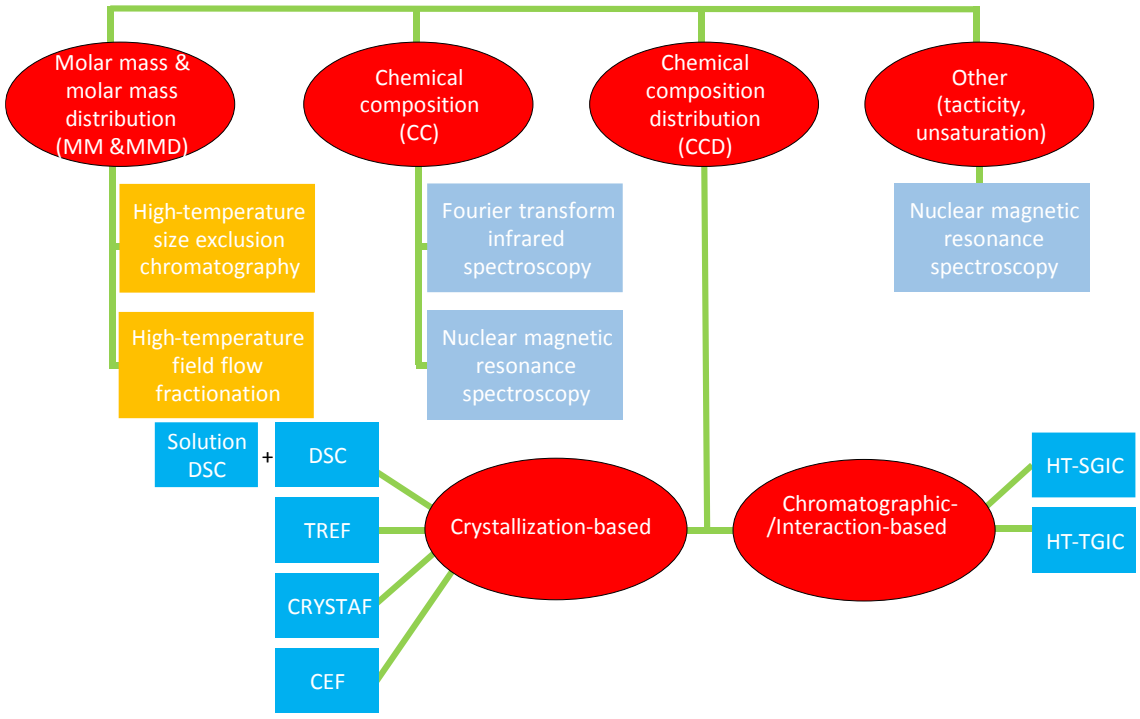


Figure 2.3 Summary of the different analytical techniques used for the characterization of polyolefins.

2.5.1.1 Temperature rising elution fractionation (TREF)

TREF is the oldest solution crystallization-based technique first reported by Desreux and Spiegels.[35] The technique was later used to fractionate several semi-crystalline polyolefins by Wild in a number of works.[36,37] Several other works reporting the use of TREF are available in literature.[38-47] Since the development of temperature rising elution fractionation (TREF) by Wild, the technique has become indispensable in the fractionation of semi-crystalline polyolefins. TREF has

two fundamental steps, namely the crystallization and elution steps. During the crystallization step, a polymer solution is cooled on a support from about 130 °C to ambient temperature. The polymer solution is usually a dilute solution of the polyolefin in solvents such as TCB or xylene. This step is typically done at slow cooling rates of 1 °C hr^{-1} to allow the polymer to crystallize onto the support. After that step the crystallized polyolefin is washed off the support using a pre-heated solvent in the elution step. The technique can be used with an on-flow detector to monitor concentration changes as function of temperature (analytical TREF) or fractions can be collected at predetermined elution steps (preparative TREF).

2.5.1.2 Crystallization analysis fractionation (CRYSTAF)

This technique was developed by Monrabal in the early 1990s as a fast alternative to TREF. This was achieved by eliminating the elution step which is present in TREF.[48-50] In CRYSTAF the polyolefin is dissolved in a thermodynamically good solvent. Typical solvents are 1,2-dichlorobenzene and 1,2,4-trichlorobenzene (ODCB and TCB, respectively). High dissolution temperatures of up to 160 °C are used. After stabilization of the temperature at 100 °C, aliquots of the polyolefin solution are filtered out and analyzed with a concentration sensitive detector. Commercial instruments are equipped with a concentration detector and five reactors and, therefore, can simultaneously analyze five samples. If a fraction of the polyolefin sample does not crystallize at room temperature, it is quantified as the soluble fraction.

CRYSTAF offers very little information with regard to the CCD of low molar mass polyolefins and elastomers since the majority of these materials remain in solution at ambient temperature. For oxidized waxes, this is also due to the enhanced solvation caused by the presence of polar functionalities. On the other hand, elastomers have very short crystallizable methylene sequences which are easily weakened in solution. Similar challenges are met when TREF is applied to these materials. Apart from co-crystallization effects in CRYSTAF, the operation range with regard to copolymers is limited. Wild and Kelusky analyzed ethylene-co-vinyl acetate copolymers (EVA) with 9 – 42 wt.% VA by TREF and found that copolymers with higher comonomer contents were soluble at ambient temperature.[36,37,51] In similar studies, the separation range of ethylene-co-1-octene using CRYSTAF was found to be 0 – 27 wt.% comonomer.[52,53]

2.5.1.3 Crystallization elution fractionation (CEF)

CEF offers dynamic crystallization and redissolution of the different components of a sample. Therefore, better resolution is obtained in comparison to TREF in which static crystallization is prevalent.[54] During the crystallization step, a very slow flow of solvent is maintained. Longer columns are, therefore, used in CEF to accommodate the dynamic crystallization step. The obvious advantage of CEF is the use of higher cooling rates that result in faster analysis by CEF as compared to TREF and CRYSTAF. Traditionally, TREF analysis required about 100 hrs for completion but developments in the field have reduced the experimental time to about 3 – 4 hrs. On the other hand, CEF analysis only takes about 30 min.[55] In addition, it has been shown that CEF is more robust and is less susceptible to co-crystallization as compared to CRYSTAF.[56]

2.5.1.4 Differential scanning calorimetry (DSC)

The introduction of DSC in the early 1960s by Watson and O'Neil was a fundamental step in understanding the thermal properties and complex processes in the formation, melting and crystallization of materials.[57,58] DSC was later applied to polyolefins and it has become one of the main analytical tools for the fast analysis of polymeric materials. Recent developments have seen the introduction of flash DSC and HyPer DSC which can work with minute amounts of sample and at very fast scanning rates.[59-63] However, these methods are more useful when applied in combination to other pre-fractionation and separation methods.

The technique is not applicable to amorphous polyolefins such as elastomers since very few meaningful thermal events such as the glass transition temperature (T_g) can be recorded. However, with regard to low molar mass waxes, several works have shown the importance of DSC as an analytical tool for characterizing wax blends and modified paraffin waxes.[64-67] In comparison to solution-based techniques, DSC offers more information regarding the microstructure of waxes since thermal events are observed. On the other hand, the low molar mass nature of waxes promotes solubility in TCB/ODCB even at room temperatures.

2.5.2 Chromatographic techniques

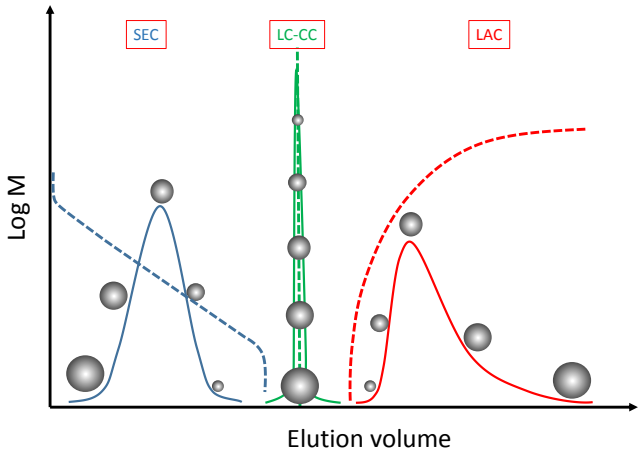


Figure 2.4 Three modes of operation of high performance liquid chromatography.

With regard to polyolefin characterization, high performance liquid chromatography (HPLC) has become a powerful, reliable and frequently used tool.[43,68-71] Three chromatographic modes are distinguished according to their mechanism of separation as illustrated in Fig. 2.4. The different retention volumes of the separated components are a result of the partitioning equilibrium between the stationary phase and the mobile phase. The equilibrium is expressed by the partitioning coefficient K_d as illustrated in Eq. 1.[72,73]

$$K_d = \frac{C_{SP}}{C_{Mp}} \quad (1)$$

C_{SP} and C_{MS} are the concentrations of the analyte on the stationary phase and in the mobile phase, respectively. K_d can be related to the Gibbs free energy (ΔG) of the analyte in the mobile phase and on the stationary phase using Eq. 2.[68,74]

$$\Delta G = \Delta H - T\Delta S = -RTlnK_d \quad (2)$$

where, R = gas constant, T= absolute temperature, ΔH and ΔS are the changes in the enthalpic and entropic contributions, respectively.

Eq. 2 summarises the differences between the enthalpic and the entropic contributions of the Gibbs free energy. The enthalpic and entropic contributions can be manipulated via the choice of the stationary and mobile phases as well as the column temperature. Using the enthalpic and entropic

contributions, the thermodynamics of the three chromatographic modes can be summarized as shown in Table 2.1.

Table 2.1 Summary of the thermodynamics in the three HPLC modes.

Chromatographic mode	**Thermodynamics**
SEC	$\Delta H = 0, K_d = \exp(\frac{\Delta S}{R})$
LC-CC	$\Delta H = T\Delta S, K_d = 1$
LAC	$\Delta S = 0, K_d = \exp(-\frac{\Delta H}{RT})$

The separation of polyolefins is carried out at high temperatures for all the three modes. Hence, the discussion will focus on literature related to the analysis of polyolefins at high temperatures.

2.5.2.1 Size exclusion chromatography (SEC)

Under ideal conditions, SEC separation is achieved with respect to hydrodynamic volume of macromolecules in dilute solution. No adsorptive interactions should exist between the macromolecules and the stationary phase. The separation of macromolecules is, ideally, entropy driven. Thermodynamically good solvents that are used include TCB, ODCB, and to some extent dibutoxymethane[75]. After injection of the hot polymer solution into a thermostated system, macromolecules are separated according to size/hydrodynamic volume as they enter pores accessible to them, which results in a loss of entropy. The loss in entropy results in the different retention volumes. Larger macromolecules experience a greater loss in entropy and elute first as compared to smaller ones. [76,77]

Usually, standards of known molar mass are used to create a calibration curve from which the molar masses of the analyte are estimated. For better molar mass estimation, the analyte and calibrant microstructure must closely resemble each other. However, it is challenging to find calibrants that suit the analyte and in such cases the molar mass values are expressed as relative values, e.g. polystyrene equivalent molar masses. One solution to the mentioned challenge is using a molar mass sensitive online detector such as the multiangle laser light scattering (MALLS) detector, which enables the determination of absolute molar masses.[78,79] The only challenge reported in literature with regard to MALLS detection is its application range, which requires molar masses of greater than 10 kg mol^{-1}. Recent publications have, however, argued against this assumption.[80]

Recent efforts targeted at getting more out of SEC analysis through the use of online multiple detector systems.[81] Each detector added to the series provides more information regarding the microstructure of the sample. Alternatively, the SEC eluent can evaporated leaving the analyte as solid spot using the LC-transform interface followed by offline scanning of the fractions using Fourier infrared spectroscopy (FTIR).[82,83] A much easier route is to use an online heated FTIR flow cell.[84,85]

2.5.2.2 High-temperature high performance liquid chromatography (HT-HPLC)

In HT-HPLC, liquid interaction chromatography (LC) is used to separate macromolecules according to chemical composition. As the name implies, the sample macromolecules must interact with the stationary phase after injection. Enthalpic interactions between the macromolecules and the stationary phase are the major driving force for separation. This is achieved in the presence of a suitable mobile phase and temperature. In most cases, finding the balance between temperature and the suitable solvent is easier said than done.

The main goal of using HT-HPLC is to separate macromolecules according to chemical composition (CC) in order to provide information regarding CCD of the given sample. This information is complementary to the molar mass information obtained by SEC. Still, the effects of molar mass in HT-HPLC separations present a major impediment. Regarding polyolefin analysis, the very first attempts were made by Pasch and Macko who showed the irreversible retention of linear PE and isotactic PP from dilute solution on zeolites as stationary phase.[86-88] In another article by Pasch and Heinz, a blend of HDPE and iPP was separated by using silica as stationary phase and a gradient of TCB→ethylene glycol monobutyl ether (EGMBE) via a precipitation/redissolution mechanism.[89]

Porous graphitic carbon (PGC, available as Hypercarb®) was later discovered as a stationary phase for liquid chromatography of polyolefins. Although the stationary phase had already been used in other studies at ambient temperature, work in high temperature applications was only done less than a decade ago. In cases where information regarding the CCD of functionalized polyolefin macromolecules is required, silica is used as the stationary phase. The stationary phase is available from a number of producers under various tradenames e.g. PerfectSil® or Nucleosil® [14,15,17].

In order to achieve separation, interaction chromatography can be conducted with or without the presence of a gradient. In some cases the analyte may adsorb onto the stationary phase irreversibly, elute in very broad peaks or require long elution volumes. In such cases a solvent or a temperature gradient can be used. These sub-techniques of interaction chromatography are referred to as solvent gradient interaction chromatography (SGIC) and thermal gradient interaction chromatography (TGIC), respectively. For the analyses of polyolefins, these techniques are applied at high temperatures and are referred to as high-temperature SGIC (HT-SGIC) and high-temperature TGIC (HT-TGIC).

The evaporative light scattering detector (ELSD) is the most used detector in HT-LC. However, the ELSD detector is not classified as a quantitative detector due to the non-linear dependence of the detector signal on sample concentration as well as solvent composition. In addition, detector settings have to be established for each solvent system and type of analyte to be separated.[90-93] Several other detectors are available, however, they are limited due to their cost (NMR detector)[94] or incompatibility with solvent gradients (IR, RI, MALLS etc.). In cases were HT-TGIC is used, several detector combinations are applicable due to the isocratic nature of the solvent.

Porous graphitic carbon (PGC): PGC has emerged as the most useful stationary phase in the HT-SGIC and HT-TGIC separation of polyolefin homopolymers and copolymers. PGC is available as Hypercarb® and its development is credited to Knox and co-workers.[95] PGC is made up of layers of graphite sheets which have hexagonally arranged carbon atoms, see Fig. 2.5. This structure of the stationary phase is widely agreed upon.

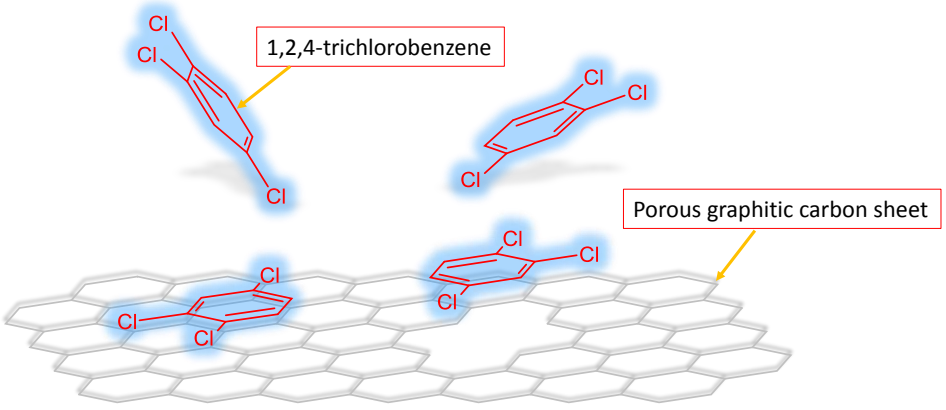


Figure 2.5 Schematic representation of the planar hexagonal structure of a PGC sheet and desorption promoting TCB molecules.

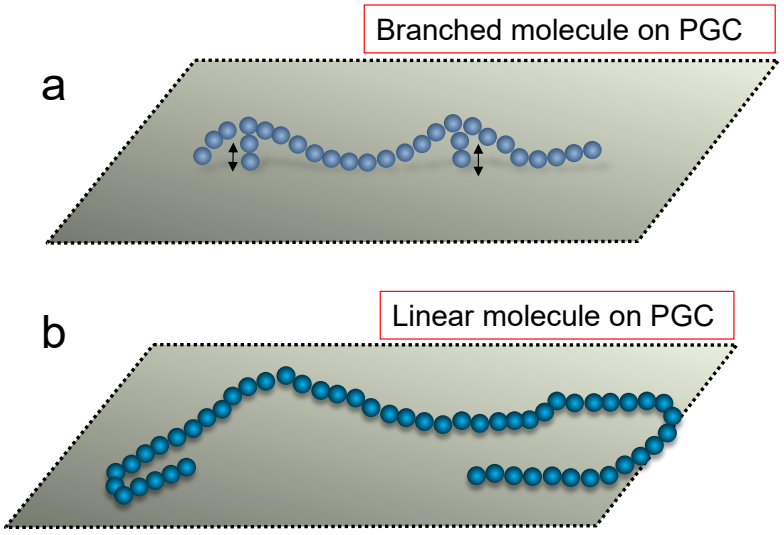


Figure 2.6 Proposed alignment of branched (a) and linear PE (b) molecules on the planar PGC surface as reported in Ref. [96].

The surface structure of the PGC is planar, hence, for interaction to occur the macromolecules must unravel and overcome internal steric forces to align onto the stationary phase surface, see Fig. 2.6a,b. The contact between the stationary phase and the macromolecule is influenced by the presence of side chains.

High-temperature solvent gradient chromatography (HT-SGIC): HT-SGIC is by far the most applied HT-HPLC technique for polyolefin characterization. Numerous separation methods and have been established in the fifteen year period since its inception. A solvent gradient is utilised to achieve separation of macromolecules at a constant temperature. The most common technique is one in which 1-decanol and TCB are used as the adsorption and desorption promoting solvents, respectively. Typical column temperatures used are above 150 °C.

The sample is dissolved and injected in the adsorption promoting solvent. Usually these solvents are poor at dissolving polyolefins and long dissolution times are required. The injected macromolecules then elute according to the strength of their interactions with the stationary phase. The interactions are influenced by the number of contacts the macromolecules have with the stationary phase, as previously indicated. In cases where the contact is influenced by branching or chemical composition, calibration curves can be established to relate elution volume to chemical composition. However, this is a challenging task.

For polyolefins, PGC has been established as a useful stationary phase although other similar stationary phases are available and have been tested.[97,98] Several polyolefin copolymers and homopolymers have been separated on PGC. Compared to crystallization-based techniques, HT-SGIC offers superior separation capabilities which in part increase the application range of copolymer separations and solves co-crystallization related issues. Silica-based stationary phases provide separations which are based on the polarity of macromolecules.[14,15,17]

High temperature thermal gradient chromatography (HT-TGIC): Although HT-SGIC is a very powerful technique, it has a few limitations. The first is related to the application of typical concentration sensitive detectors such as RI and IR and molar mass sensitive detectors such as viscometers and light scattering (LS) detectors.[99] Cong. et al. recently showed the conditions for the separation of polyolefins by HT-TGIC.[100] In HT-TGIC, the solvent gradient is replaced by a temperature gradient which normally starts at ambient temperature, depending on instrumentation capabilities. Several detailed works have also shown the separation capabilities of HT-TGIC on a number of different types of polyolefin resins.[42,52,53,101-104] Although the separation range of HT-TGIC is considerably better than that of crystallisation-based techniques which have a 0 – 9 mol% range, a controlled study to compare the separation ranges of HT-SGIC to HT-TGIC had not been done.

The separation principle with regard to polyethylene, polypropylene and ethylene-1-alkene copolymers is similar to that in HT-SGIC. Here, the weak van der Waals forces of interaction between the mentioned analytes and the PGC stationary phase are further weakened by the thermal gradient rather than by the solvent gradient. Similar stationary phases to PGC such as molybdenum sulphide, boron nitride and tungsten sulphide have been tested. The results were comparable to those obtained on PGC.[49]

Usually good solvents of polyolefins such as TCB and ODCB are used for HT-TGIC. In some instances, phenol and 1-chloronaphthalene have been used.[53,100-103] The obvious challenge is the lack of adsorption of high comonomer content analytes even at ambient temperatures when good solvents of polyolefins are used. Two solutions are available to remedy this problem. The first is to introduce cooling/cryogenic devices onto the HT-TGIC instrumentation to provide sub-ambient conditions. This allows for better adsorption/crystallization of the polyolefin copolymers onto the stationary phase. However, this brings additional costs to the instrumentation and eliminates the

use of solvents with high freezing points such as TCB. The second is to use poor and good solvent combinations. This technique was investigated by Mekap and co-workers[104,105] who also concluded that optimized binary solvent mixtures improved the resolution. This was confirmed by separating a model blend of two poly(ethylene-1-octene) samples with varying 1-octene contents.

2.5.2.3 Liquid chromatography at critical conditions (LC-CC)

Under LC-CC, macromolecules with similar repeating units elute independent of their molar mass. At LC-CC conditions, the entropic and enthalpic effects compensate each other. These conditions have to be established for a specific chromatographic system, i.e. for a given polymer, the stationary phase, mobile phase/composition and temperature conditions have to be established. Once these conditions are established, the molar masses of blocks in di- and tri-block copolymers can be determined. In addition, separation of polymers based on architecture, tacticity or type of functional groups can be achieved.[106-109] With regard to polyolefins, LC-CC conditions for polyethylene[105,110] and polypropylene[111] have only been established recently.

2.5.2.4 Cross-fractionation

With regard to polyolefins and synthetic polymers in general, the most important microstructural parameters are MMD and CCD. Cross-fractionation techniques provide a direct correlation between CCD and MMD, although these two microstructural parameters can also be obtained individually. The correlation of these two microstructural properties in one experiment is advantageous. While the MMD can be easily obtained via HT-SEC, CCD is obtained via crystallization- and/or chromatography-based techniques. TREF and CEF are common crystallization-based techniques that can be coupled to HT-SEC. The first report by Wild[74] showed the combination of TREF and HT-SEC offline. Nakano and Goto later automated the technique.[112]

HT-SGIC is the common chromatographic technique coupled to fast HT-SEC for high-temperature two-dimensional liquid chromatography (HT-2D-LC) of polyolefins. For comprehensive analysis of key microstructural features, chemical composition /functionality type separations are often combined offline[74,113-115] or online[25,61,116,117] to HT-SEC. It is predictable that the offline method is cumbersome since large numbers of fractions have to handled and re-injected into the second dimension. Several other problems including sample contamination and recrystallization of polyolefin fractions accompany this technique. The online version of HT-2D-LC is automated and has been applied in different groups that work with polyolefins.[17,25,116,118,119] Coupling of the two

dimensions is done using a switching valve (8 port and more recently 10 port valves). The first HT-2D-LC works with regard to polyolefin characterization were reported by Ginzburg and co-workers.[118,119]

HT-2D-LC is almost always done with the HT-HPLC separations in the first dimension and HT-SEC separations in the second dimension. The obvious advantage of this set up is the easy manipulation of the HT-SEC dimension with regard to speed in order to accommodate fraction collection from the first dimension. Speeding up separations in the second dimension with HT-HPLC is challenging due to flow rate effects on separation resolution, high backpressures and the need to apply solvent gradients. Detailed advantages and shortcomings of the SEC × HPLC or HPLC ×SEC set ups are given in literature.[120,121]

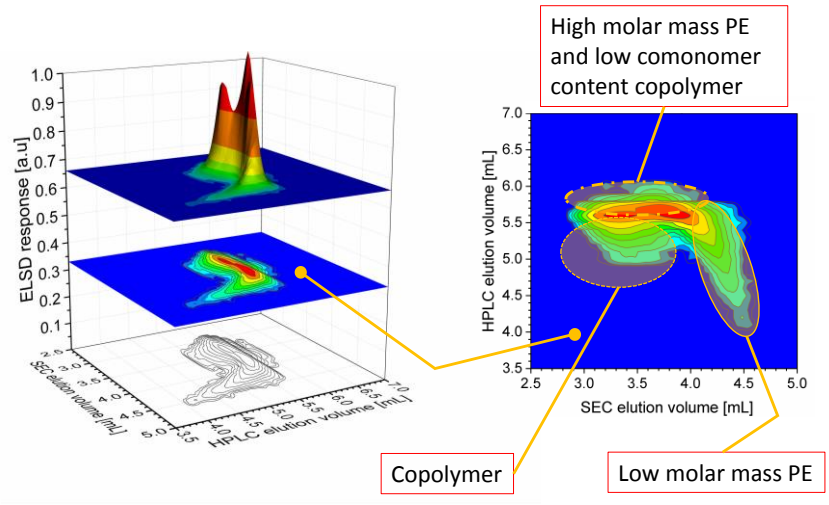


Figure 2.7 Correlation of the chemical composition distribution and molar mass distribution of a bimodal HDPE resin as obtained from HT-2D-LC separations.

2.5.3 Spectroscopic techniques

Spectroscopic techniques are important tools in the elucidation of polyolefin microstructure. Nuclear magnetic resonance spectroscopy (NMR) and Fourier transform infrared spectroscopy (FTIR) are two of the most used spectroscopic techniques and are often coupled to fractionation techniques. The principles of operation of these two techniques are widely presented in literature.

Specific to this work, carbon-thirteen magnetic resonance spectroscopy (^{13}C-NMR) is used for the determination of the average chemical composition and comonomer insertion of elastomers and bimodal HDPE resins. Although NMR is a powerful tool, its application is limited to the

determination of average values of chemical composition.[21-23,122] For polyolefin analysis long runs at elevated temperature are required for quantitative purposes. When combined online with separation techniques such as SEC and HPLC, NMR spectroscopy is the ultimate detector due to its ability to quantify and distinguish eluting species.[94,108,123-125] Offline coupling has been reported although it is cumbersome. The major drawback is the expensive nature of instrumentation and operation as well as the difficulty of adaptation for high temperature purposes.

FTIR is often used due to its ease of use, rapidness and inexpensive nature. FTIR is not an ideal method for quantification purposes due to the non-linear correlation of chemical composition/functional group concentration and signal intensity. However, when coupled to fractionation techniques, valuable information regarding the eluting fractions can be obtained. Online coupling can be done using a flow cell, and in the case of polyolefin characterization, heating is required. Online coupling is limited due to the nature of solvents used or the need to apply solvent gradients. Offline coupling is more frequently applied as compared to the online method. Here, the LC-transform interface is used to collect dried fractions on an IR transparent target such as a germanium disc and then followed by scanning on the FTIR instrument. The disc rotation angle is a function of the elution volume.[60-62,85,126-128]

2.5.4 Preparative fractionation

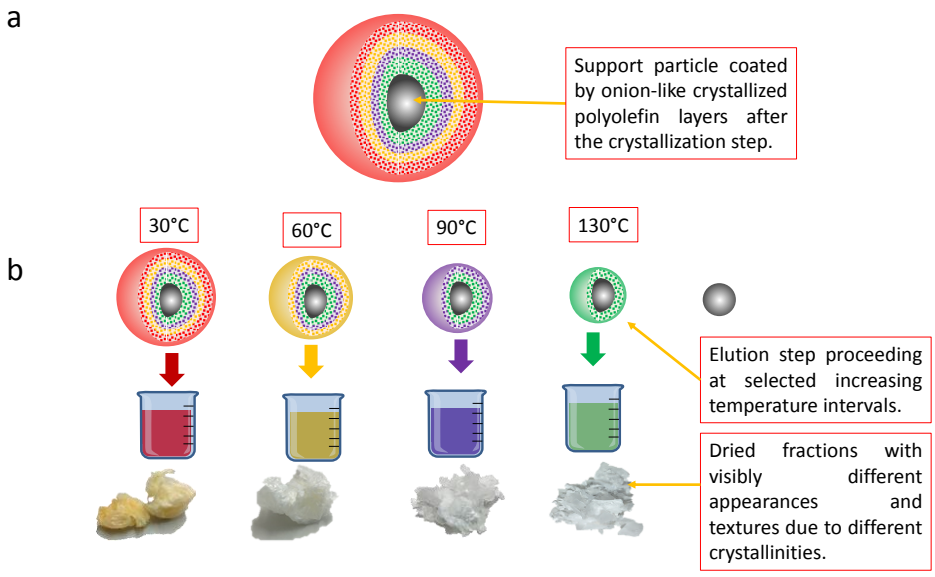


Figure 2.8 Schematic representation of crystallized polyolefin layers after the TREF crystallization step (a); unwinding of the crystallized polyolefin layers with increasing temperature during the elution step (b).

Preparative fractionation has become a fundamental step in the analysis of polyolefins. Analysis on the bulk sample level has shortcomings in the sense that some minor, but important polyolefin fractions can go undetected. Therefore, preparative fractionation can serve as a pre-concentration step. In addition, bulk samples can be too complex such that analysis requires the simplification of at least one of the dimensions of a sample's microstructure e.g. chemical composition or molar mass. For preparative fractionation according to chemical composition, preparative temperature rising elution fractionation (p-TREF) is usually applied.[59-62,129,130] In some cases it is better to simplify the bulk sample microstructure by fractionating according to molar mass.[2,131] The preparative fractionation techniques relevant to this work are discussed.

The operation principle of TREF has been discussed in Section 2.5.1.1. If polymer fractions are collected by p-TREF, further processing involves removing the solvent to obtain dry fractions that are then subjected to offline analysis with a variety of techniques, see Fig. 2.8. This method undoubtedly yields more information regarding the microstructure of the polymers as compared to the analytical TREF technique. Preparative TREF has been used to fractionate a wide array of polyolefin materials including polyethylene and polypropylene copolymers. The application of TREF falls short when the polyolefin material does not crystallize in solution.

Preparative fractionation in the absence of support can be done in small laboratory setups. Although this method is not widely used, it is easier to manipulate for fractionation purposes which would be otherwise difficult with conventional TREF. Cheruthazhekatt and Pasch[132] employed the technique for the fractionation of complex ethylene-propylene copolymers. Another variation of the technique was reported by Prabhu et al.[13] to obtain fractions for the separation of maleic anhydride grafted polypropylene.

Recently, there has been a resurgence of molar mass based fractionation techniques. Bungu and Pasch[131] recently used the technique to fractionate low density polyethylene (LDPE) homopolymers. In this technique, solvent and non-solvent mixtures are used to sequentially precipitate polyolefin macromolecules out of solution according to molar mass. Typical solvents such as xylene, TCB or trimethylbenzene are used.[2,133] A variety of non-solvents such as 2-butoxyethanol and 2-ethoxyethanol are used to force the polymer macromolecules out of solution.

Alternatively, preparative SEC can be used as a method of fractionation according to molar mass. However, smaller amounts of fractions are recovered due to sample loading limitations. The

fractions may, therefore, be insufficient for subsequent analysis with multiple advanced analytical techniques. Coupling of HPer DSC[134] or FTIR using offline techniques via the LC-transform interface are possible solutions.

2.6 References

(1) Alt, F. P.; Böhm, L. L.; Enderle, H. F.; Berthold, J. *Macromol. Symp.* **2001**, *163*, 135–144.

(2) Fan, Y.; Xue, Y.; Nie, W.; Xiangling, J.; Bo, S. *Polym. J.* **2009**, *41*, 622–628.

(3) Ginzburg, A.; Macko, T.; Dolle, V.; Brüll, R. *J. Appl. Polym. Sci.* **2013**, *129*, 1897–1906.

(4) Kim, J. D.; Soares, J. B. P.; Rempel, G. L. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 331–339.

(5) Prabhu, K.; Brüll, R.; Macko, T.; Remerie, K.; Tacx, J.; Garg, P.; Ginzburg, A. *J. Chromatogr. A* **2015**, *1419*, 67–80.

(6) Sun, X.; Shen, H.; Xie, B.; Yang, W.; Yang, M. *Polymer* **2011**, *52*, 564–570.

(7) Tian, Z.; Chen, K.-R.; Liu, B.-P.; Luo, N.; Du, W.-L.; Qian, F. *Chem. Eng. Sci.* **2015**, *130*, 41–55.

(8) Krishnaswamy, R. K.; Lamborn, M. J.; Sukhadia, A. M.; Register, D. F.; Maeger, P. L.; Leevers, P. S. *Polym. Eng. Sci.* **2006**, *46*, 1358–1362.

(9) Albrecht, A.; Jayaratne, K.; Jeremic, L.; Sumerin, V.; Pakkanen, A. *J. Appl. Polym. Sci.* **2016**, *133*.

(10) Gupta, S.; Yuan, X.; Chung, T. M.; Kumar, S.; Cakmak, M.; Weiss, R. *Macromolecules* **2013**, *46*, 5455–5463.

(11) Wang, C.; Pilania, G.; Ramprasad, R.; Agarwal, M.; Misra, M.; Kumar, S.; Yuan, X.; Mike Chung, T. *Appl. Phys. Lett.* **2013**, *102*, 152901.

(12) Yuan, X.; Matsuyama, Y.; Chung, T. M. *Macromolecules* **2010**, *43*, 4011–4015.

(13) Prabhu, K.; Macko, T.; Brüll, R.; Remerie, K.; Tacx, J.; Garg, P.; Ginzburg, A. *J. Chromatogr. A* **2016**, *1441*, 96–105.

(14) Albrecht, A.; Brüll, R.; Macko, T.; Pasch, H. *Macromolecules* **2007**, *40*, 5545–5551.

(15) Albrecht, A.; Brüll, R.; Macko, T.; Sinha, P.; Pasch, H. *Macromol. Chem. Phys.* **2008**, *209*, 1909–1919.

(16) Chung, T. *Prog. Polym. Sci.* **2002**, *27*, 39–85.

(17) Ginzburg, A.; Macko, T.; Malz, F.; Schroers, M.; Troetsch-Schaller, I.; Strittmatter, J.; Brull, R. *J. Chromatogr. A* **2013**, *1285*, 40–47.

(18) de Klerk, A. *Ind. Eng. Chem. Res.* **2003**, *42*, 6545–6548.

(19) United States, US 5420303 A, 1996.

(20) United States, US 6169148 B1, 2001.

(21) Reynhardt, E. *J. Phys. D: Appl. Phys.* **1985**, *18*, 2519.

(22) Reynhardt, E. *J. Phys. D: Appl. Phys.* **1985**, *18*, 1185–1197.

(23) Lourens, J.; Reynhardt, E. *J. Phys. D: Appl. Phys.* **1979**, *12*, 1963.

(24) United States, US6348547 B1, 2002.

(25) Cheruthazhekatt, S.; Pasch, H. *Macromol. Symp.* **2014**, *337*, 51–57.

(26) Jung, W. Y.; Weon, J. I. *J. Mater. Sci.* **2013**, *48*, 1275–1282.

(27) Botha, L.; van Reenen, A. J. *Eur. Polym. J.* **2013**, *49*, 2202–2213.

(28) Xue, Y.; Fan, Y.; Bo, S.; Ji, X. *Eur. Polym. J.* **2011**, *47*, 1646–1653.

(29) Liu, W.; Zhang, X.; Bu, Z.; Wang, W.-J.; Fan, H.; Li, B.-G.; Zhu, S. *Polymer* **2015**, *72*, 118–124.

(30) Svoboda, P.; Theravalappil, R.; Svobodova, D.; Mokrejs, P.; Kolomaznik, K.; Mori, K.; Ougizawa, T.; Inoue, T. *Polym. Test.* **2010**, *29*, 742–748.

(31) Chitta, R.; Macko, T.; Brüll, R.; van Doremaele, G.; Heinz, L. C. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 1840–1846.

(32) Chitta, R.; Ginzburg, A.; Macko, T.; Brüll, R.; van Doremaele, G. *LC-GC Eur.* **2012**, *25*, 352–358.

(33) Phiri, M. J.; Dimeska, A.; Pasch, H. *Macromol. Chem. Phys.* **2015**, *216*, 1619–1628.

(34) Phiri, M. J.; Cheruthazhekatt, S.; Dimeska, A.; Pasch, H. *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *53*, 863–874.

(35) Desreux, V.; Spiegels, M. *Bull. Soc. Chim. Belg* **1950**, *59*, 476.

(36) Wild, L.; Glöckner, G. In *Separation Techniques Thermodynamics Liquid Crystal Polymers*; Springer, Heidelberg-New York, 1991, pp 1–47.

(37) Wild, L.; Ryle, T.; Knobeloch, D.; Peat, I. *J. Polym. Sci., Part B: Polym. Phys.* **1982**, *20*, 441–455.

(38) Anantawaraskul, S.; Soares, J. B. P.; Wood-Adams, P. M. *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 1762–1778.

(39) Anantawaraskul, S.; Soares, J. B. P.; Wood-Adams, P. M. In *Polymer Analysis Polymer Theory*; Springer, 2005, pp 1–54.

(40) Anantawaraskul, S.; Sottesakul, S.; Siriwongsarn, E.; Soares, J. B. P. *Macromol. Symp.* **2013**, *330*, 123–131.

(41) Karbashewski, E.; Kale, L.; Rudin, A.; Tchir, W. J.; Cook, D. G.; Pronovost, J. O. *J. Appl. Polym. Sci.* **1992**, *44*, 425–434.

(42) Monrabal, B.; Romero, L. *Macromol. Chem. Phys.* **2014**, *215*, 1818–1828.

(43) Pasch, H.; Malik, M. I.; Macko, T. *Adv. Polym. Sci.* **2013**, *251*, 77–140.

(44) Starck, P. *Polym. Int.* **1996**, *40*, 111–122.

(45) Xu, J.; Feng, L. *Eur. Polym. J.* **2000**, *36*, 867–878.

(46) Xu, J.; Feng, L.; Yang, S.; Yang, Y.; Kong, X. *Eur. Polym. J.* **1998**, *34*, 431–434.

(47) Zhang, M.; Lynch, D. T.; Wanke, S. E. *J. Appl. Polym. Sci.* **2000**, *75*, 960–967.

(48) Monrabal, B. *J. Appl. Polym. Sci.* **1994**, *52*, 491–499.

(49) Monrabal, B. *Adv. Polym. Sci.* **2013**, *257*, 203–252.

(50) Pasch, H.; Brüll, R.; Wahner, U.; Monrabal, B. *Macromol. Mater. Eng.* **2000**, *279*, 46–51.

(51) Kelusky, E. C.; Elston, C. T.; Murray, R. E. *Polym. Eng. Sci.* **1987**, *27*, 1562–1571.

(52) Monrabal, B.; López, E.; Romero, L. In *Macromol. Symp.*; Wiley, 2013, pp 9–21.

(53) Monrabal, B.; Mayo, N.; Cong, R. *Macromol. Symp.* **2012**, *312*, 115–129.

(54) Monrabal, B.; Sancho-Tello, J.; Mayo, N.; Romero, L. *Macromol. Symp.* **2007**, *257*, 71–79.

(55) Pasch, H. *Polym. Adv. Technol.* **2015**, *26*, 771–784.

(56) Suriya, K.; Anantawaraskul, S.; Soares, J. B. P. *J. Polym. Sci., Part B: Polym. Phys.* **2011**, *49*, 678–684.

(57) Watson, E. S.; O'Neill, M. J.; Justin, J.; Brenner, N. *Anal. Chem.* **1964**, *36*, 1233–1238.

(58) United states, US3263484A, 1966.

(59) Cheruthazhekatt, S.; Pijpers, T. F. J.; Mathot, V. B. F.; Pasch, H. *Macromol. Symp.* **2013**, *330*, 22–29.

(60) Cheruthazhekatt, S.; Pijpers, T. F. J.; Mathot, V. B. F.; Pasch, H. *Anal. Bioanal.Chem.* **2013**, *405*, 8995–9007.

(61) Cheruthazhekatt, S.; Pijpers, T. F. J.; Harding, G. W.; Mathot, V. B. F.; Pasch, H. *Macromolecules* **2012**, *45*, 2025–2034.

(62) Cheruthazhekatt, S.; Pijpers, T. F. J.; Harding, G. W.; Mathot, V. B. F.; Pasch, H. *Macromolecules* **2012**, *45*, 5866–5880.

(63) Vanden Poel, G.; Mathot, V. B. F. *Thermochim. Acta* **2007**, *461*, 107–121.

(64) Hlangothi, S.; Krupa, I.; Djoković, V.; Luyt, A. *Polym. Degrad. Stab.* **2003**, *79*, 53–59.

(65) Krump, H.; Alexy, P.; Luyt, A. *Polym. Test.* **2005**, *24*, 129–135.

(66) Krupa, I.; Luyt, A. *Thermochim. Acta* **2001**, *372*, 137–141.

(67) Luyt, A.; Krupa, I.; Assumption, H.; Ahmad, E.; Mofokeng, J. *Polym. Test.* **2010**, *29*, 100–106.

(68) Pasch, H.; Trathnigg, B. *HPLC of Polymers*; Springer: Heidelberg-New York, 1999.

(69) Mori, S.; Barth, H. G. *Size exclusion chromatography*; Springer: New York, 1999.

(70) Malik, M. I.; Pasch, H. *Prog. Polym. Sci.* **2014**, *39*, 87–123.

(71) Pasch, H.; Albrecht, A.; Brüll, R.; Macko, T.; Hiller, W. *Macromol. Symp.* **2009**, *282*, 71–80.

(72) Pasch, H. In *Polymer Analysis Polymer Physics*; Springer, 1997, pp 1–45.

(73) Snyder, L. R.; Kirkland, J. J.; Dolan, J. W. *Introduction to modern liquid chromatography*; John Wiley & Sons, 2011.

(74) Glöckner, G. In *Gradient HPLC of Copolymers and Chromatographic Cross-Fractionation*; Springer, 1991, pp 148–174.

(75) Boborodea, A.; Collignon, F.; Brookes, A. *Int. J. Polym. Anal. Charact.* **2015**, *20*, 316–322.

(76) Striegel, A.; Yau, W. W.; Kirkland, J. J.; Bly, D. D. *Modern size-exclusion liquid chromatography: Practice of gel permeation and gel filtration chromatography*; John Wiley & Sons: New Jersey, 2009.

(77) Yau, W.; Kirkland, J.; Bly, D. *Modern Size-Exclusion Liquid Chromatography, Practice of Gel Permeation and Gel Filtration Chromatography*; John Wiley & Sons: New York, 1979.

(78) Wyatt, P. J. *Anal. Chim. Acta* **1993**, *272*, 1–40.

(79) Wyatt, P. J. *Instrum Sci. Technol.* **1997**, *25*, 1–18.

(80) Podzimek, S. *J. Appl. Polym. Sci.* **2014**, *131*.

(81) Plüschke, L.; Mundil, R.; Sokolohorskyj, A.; Merna, J.; Sommer, J.-U.; Lederer, A. *Anal. Chem.* **2018**, *90*, 6178–6186.

(82) Pasch, H. *Polym. Chem.* **2013**, *4*, 2628–2650.

(83) Pasch, H.; De Goede, E.; Mallon, P. *Macromol. Symp.* **2012**, *312*, 174–190.

(84) Hyötyläinen, T.; Riekkola, M.-L. *J. Chromatogr. A* **2003**, *1000*, 357–384.

(85) Piel, C.; Albrecht, A.; Neubauer, C.; Klampfl, C. W.; Reussner, J. *Anal. Bioanal.Chem.* **2011**, *400*, 2607–2613.

(86) Macko, T.; Denayer, J. F.; Pasch, H.; Baron, G. V. *J. Sep. Sci.* **2003**, *26*, 1569-1574.

(87) Macko, T.; Pasch, H.; Denayer, J. F. *J. Chromatogr. A* **2003**, *1002*, 55–62.

(88) Macko, T.; Pasch, H.; Denayer, J. F. *J. Sep. Sci.* **2005**, *28*, 59–64.

(89) Heinz, L.-C.; Pasch, H. *Polymer* **2005**, *46*, 12040–12045.

(90) Schultz, R.; Engelhardt, H. *Chromatographia* **1990**, *29*, 517–522.

(91) Arndt, J.; Macko, T.; Brüll, R. *J. Chromatogr. A* **2013**, *1310*, 1–14.

(92) Dreux, M.; Lafosse, M.; Morin-Allory, L. *LC-GC* **1996**, *9*, 148–156.

(93) Megoulas, N. C.; Koupparis, M. A. *Crit. Rev. Anal. Chem.* **2005**, *35*, 301–316.

(94) Hiller, W.; Sinha, P.; Hehn, M.; Pasch, H. *Prog. Polym. Sci.* **2014**, *39*, 979–1016.

(95) Knox, J. H.; Kaur, B.; Millward, G. R. *J. Chromatogr. A* **1986**, *352*, 3–25.

(96) Monrabal, B. *Macromol. Symp.* **2015**, *356*, 147–166.

(97) Chitta, R. *Development of high temperature liquid chromatography for chemical composition Separation of polyolefins*. PhD Thesis, Technical University of Darmstadt, Darmstadt, 2014.

(98) Chitta, R.; Macko, T.; Brüll, R.; Kalies, G. *J. Chromatogr. A* **2010**, *1217*, 7717–7722.

(99) Pasch, H.; Malik, M. I. *Advanced separation techniques for polyolefins*; Springer: Switzerland, 2014.

(100) Cong, R.; Degroot, W.; Parrott, A.; Yau, W.; Hazlitt, L.; Brown, R.; Miller, M.; Zhou, Z. *Macromolecules* **2011**, *44*, 3062–3072.

(101) Cong, R.; deGroot, A. W.; Parrott, A.; Yau, W.; Hazlitt, L.; Brown, R.; Cheatham, M.; Miller, M. D.; Zhou, Z. *Macromol. Symp.* **2012**, *312*, 108–114.

(102) Alghyamah, A.; Soares, J. B. P. *Ind. Eng. Chem. Res.* **2014**, *53*, 9228–9235.

(103) Al-Khazaal, A. Z.; Soares, J. B. P. *Macromol. Chem. Phys.* **2014**, *215*, 465–475.

(104) Mekap, D.; Macko, T.; Brüll, R.; Cong, R.; deGroot, A. W.; Parrott, A. R. *Ind. Eng. Chem. Res.* **2014**, *53*, 15183–15191.

(105) Mekap, D. *Development of novel methodologies and fundamental studies on the compositional separation of polyethylene by high temperature liquid adsorption chromatography*. PhD Thesis, Technical University of Darmstadt, Darmstadt, 2014.

(106) Malik, M. I.; Sinha, P.; Bayley, G. M.; Mallon, P. E.; Pasch, H. *Macromol. Chem. Phys.* **2011**, *212*, 1221-1228.

(107) Hehn, M.; Wagner, T.; Hiller, W. *Anal. Chem.* **2013**, *86*, 490–497.

(108) Hiller, W.; Pasch, H.; Sinha, P.; Wagner, T.; Thiel, J. r.; Wagner, M.; Müllen, K. *Macromolecules* **2010**, *43*, 4853–4863.

(109) Heinz, L. C.; Macko, T.; Pasch, H.; Weiser, M. S.; Mülhaupt, R. *Int. J. Polym. Anal. Charact.* **2006**, *11*, 47–55.

(110) Mekap, D.; Macko, T.; Brull, R.; Cong, R.; deGroot, A. W.; Parrott, A.; Cools, P. J. C. H.; Yau, W. *Polymer* **2013**, *54*, 5518–5524.

(111) Bhati, S. S.; Macko, T.; Brüll, R.; Mekap, D. *Macromol. Chem. Phys.* **2015**, *216*, 2179–2189.

(112) Nakano, S.; Goto, Y. *J. Appl. Polym. Sci.* **1981**, *26*, 4217–4231.

(113) Gerber, J.; Radke, W. *Polymer* **2005**, *46*, 9224–9229.

(114) Malik, M. I.; Trathnigg, B.; Bartl, K.; Saf, R. *Anal. Chim. Acta* **2010**, *658*, 217–224.

(115) Lindemann, T.; Hintelmann, H. *Anal. Chem.* **2002**, *74*, 4602–4610.

(116) Cheruthazhekatt, S.; Harding, G. W.; Pasch, H. *J. Chromatogr. A* **2013**, *1286*, 69–82.

(117) Raust, J. A.; Brüll, A.; Sinha, P.; Hiller, W.; Pasch, H. *J. Sep. Sci.* **2010**, *33*, 1375–1381.

(118) Ginzburg, A.; Macko, T.; Dolle, V.; Brüll, R. *J. Chromatogr. A* **2010**, *1217*, 6867–6874.

(119) Ginzburg, A.; Macko, T.; Dolle, V.; Brüll, R. *Eur. Polym. J.* **2011**, *47*, 319–329.

(120) Schoenmakers, P. J.; Vivó-Truyols, G.; Decrop, W. M. *J. Chromatogr. A* **2006**, *1120*, 282–290.

(121) van der Horst, A.; Schoenmakers, P. J. *J. Chromatogr. A* **2003**, *1000*, 693–709.

(122) Randall, J. C. *J. Polym. Sci., Part B: Polym. Phys.* **1973**, *11*, 275–287.

(123) Hiller, W.; Hehn, M.; Sinha, P.; Raust, J.-A.; Pasch, H. *Macromolecules* **2012**, *45*, 7740–7748.

(124) Hiller, W.; van Aswegen, W.; Hehn, M.; Pasch, H. *Macromolecules* **2013**, *46*, 2544–2552.

(125) Hiller, W.; Pasch, H.; Macko, T.; Hofmann, M.; Ganz, J.; Spraul, M.; Braumann, U.; Streck, R.; Mason, J.; van Damme, F. *J. Magn. Reson.* **2006**, *183*, 290–302.

(126) Graef, S. M.; Brüll, R.; Pasch, H.; Wahner, U. M. *e-Polymers* **2003**, *3*, 51–59.

(127) Marengo, E.; Longo, V.; Robotti, E.; Bobba, M.; Gosetti, F.; Zerbinati, O.; Di Martino, S. *J. Appl. Polym. Sci.* **2008**, *109*, 3975–3982.

(128) Luyt, A.; Brüll, R. *Polym. Bull.* **2004**, *52*, 177–183.

(129) Ndiripo, A.; Pasch, H. *Anal. Bioanal.Chem.* **2015**, *407*, 6493–6503.

(130) De Goede, E.; Mallon, P.; Pasch, H. *Macromol. Mater. Eng.* **2010**, *295*, 366–373.

(131) Eselem Bungu, P.; Pasch, H. *Polym. Chem.* **2017**, *31*, 4565–4575.

(132) Cheruthazhekatt, S.; Pasch, H. *Anal. Bioanal.Chem.* **2014**, *406*, 2999–3007.

(133) Jørgensen, J. K.; Larsen, A.; Helland, I. *e-Polymers* **2010**, *10*, 1596–1612.

(134) Krumme, A.; Basiura, M.; Pijpers, T.; Vanden Poel, G.; Heinz, L. C.; Brüll, R.; BF Mathot, V. *Mater Sci.* **2011**, *17*, 260–265.

Chapter 3

Experimental details

Detailed experimental information i.e. methods, reagents and equipment setups are given in this chapter. Brief explanations are given as to why certain conditions were chosen.

3.1 Reagents and solvents

Xylene (Sigma-Aldrich, South-Africa, > 99 %) was used as received for all p-TREF elution steps. 1,1,2,2-tetrachloroethane (Merck, South Africa > 99.5 %) was used as an internal reference as well as a solvent for all solution ^{13}C-NMR preparations. 1,2,4-trichlorobenzene (TCB) Chromasolv® (Sigma-Aldrich, South Africa ≥ 99 %) was used as the mobile phase in HT-HPLC while TCB and 1,2-dichlorobenzene, both Reagent plus® (Sigma-Aldrich, South Africa ≥ 99 %) were used as the mobile phase in high temperature-size exclusion chromatography (HT-SEC). 1-decanol (Sigma-Aldrich, South Africa > 99 %) was used as the primary mobile phase in HT-HPLC. Decane, cyclohexanone and decalin of HPLC grade were purchased from Sigma-Aldrich, South Africa.

3.2 Chromatographic techniques

3.2.1 High-temperature size exclusion chromatography (HT-SEC) with refractive index detection

This method was used for the molar mass determinations of wax samples at Stellenbosch University. The instrumentation for this technique is shown in Fig. 3.1.

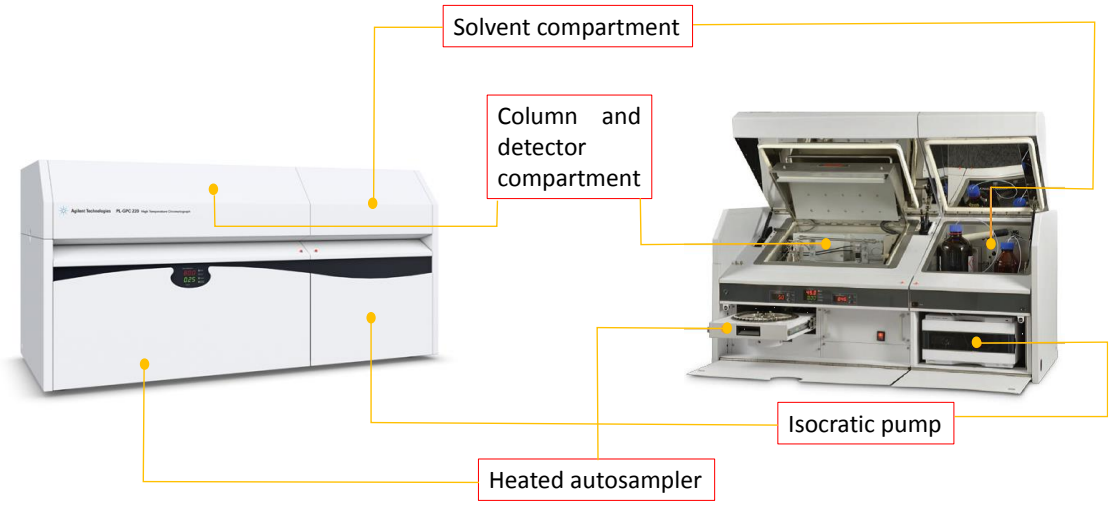


Figure 3.1 HT-SEC instrumentation used for molar mass determinations.

Molar mass and molar mass dispersity were determined on a PL-GPC 220 High-temperature chromatograph (Polymer Laboratories, Church Stretton, U.K., now Agilent) equipped with a differential refractive index (RI) detector. The samples (4.0 mg) were dissolved in 2 mL of TCB for 0.5 – 3 hrs (depending on sample type) together with 0.025 % BHT which acted as a stabiliser

to prevent sample decomposition/degradation. TCB with 0.0125 % BHT was used as the mobile phase at a flow rate of 1 mL min^{-1}. Three 300 × 7.5 mm^2 PLgel Olexis columns (Agilent Technologies, Cheadle, U.K.) were used together with a 50 × 7.5 mm^2 PLgel Olexis guard column and 200 µL of each sample was injected. All experiments in HT-SEC were carried out at 150 °C. The instrument was calibrated using narrowly distributed polystyrene standards (Agilent Technologies, Cheadle, U.K.) and polyethylene standards (Polymer Standards Services, Mainz, Germany).

3.2.2 High-temperature size exclusion chromatography (HT-SEC) with infrared detection

This method was used for the molar mass determinations of ethylene-propylene copolymers and bimodal HDPE samples and their respective fractions at Borealis (Linz, Austria).

A high temperature chromatograph GPC-IR (PolymerChAR, Valencia, Spain) equipped with a five band infrared detector (IR5) was used for the determination of the molar mass distribution and the ethylene content along the molar mass.[1] The chromatographic separation was carried out by using three PLgel Olexis columns and 1 × PLgel Olexis guard column (Agilent Technologies, Church Stretton, UK). As sample solvent and mobile phase 1,2,4-trichlorobenzene (TCB) stabilized with 250 mg L^{-1} 2,6-di-tert-butyl-4-methyl-phenol (BHT) was used. The chromatographic system was operated at 160 °C and at a constant flow rate of 1 mL min^{-1}. 200 µL of sample solution was injected per analysis. The column set was calibrated using universal calibration with narrow molar mass polystyrene (PS) standards in the range of 0.5 kg mol^{-1} to 11 500 kg mol^{-1}. Mark-Houwink constants for PS (K= 0.00019 and α=0.655) and PE (K= 0.00039 and α=0.725) are used for converting the PS equivalent molar masses into PE equivalent molar masses. The IR5 detector was calibrated with narrow distributed ethylene-hexene, ethylene-butene and ethylene-octene copolymer standards having SCB contents between 0 and 85 SCB/1000TC. The SCB/1000TC content of the GPC-IR standards were determined by ^{13}C-NMR as described in the NMR Analysis Section. Data collection was performed by using the PolymerChAR GPC-IR control software.

3.2.3 High-temperature liquid adsorption chromatography (HT-LAC)

High temperature liquid adsorption chromatography experiments were performed on a solvent gradient interaction chromatograph (SGIC) instrument constructed by PolymerChAR (Valencia, Spain). For solvent gradient elution in HPLC, a high-pressure binary gradient pump (Agilent,

Waldbronn, Germany) was utilized. The evaporative light scattering detector [ELSD, model PL ELS 1000, Polymer Laboratories, Church Stretton, U.K. (now Agilent)] was used. The instrumentation set up is illustrated in Fig. 3.2.

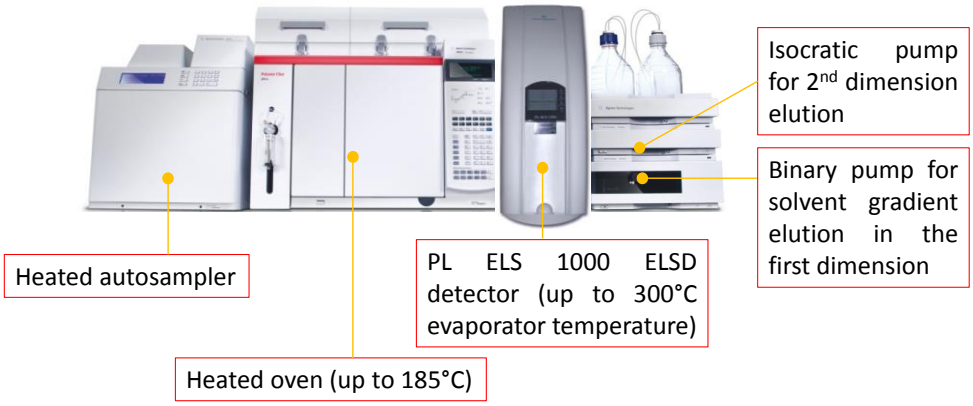


Figure 3.2 Instrumentation used for HT-LAC experiments in the first and second dimension.

3.2.4 High-temperature solvent gradient interaction chromatography (HT-SGIC)

Separations on porous graphitic carbon: For solvent gradient elution, a high-pressure binary gradient pump (Agilent, Waldbronn, Germany) was utilized. The evaporative light scattering detector [ELSD, model PL-ELS 1000, Polymer Laboratories, Church Stretton, U.K. (Now Agilent)] was used for all detection purposes. A Hypercarb column (Hypercarb®, Thermo Scientific,Dreieich, Germany) with 100 × 4.6 mm^2 internal diameter packed with porous graphite particles which have a particle diameter of 5 µm (making a surface area of 120 m^2 g^{-1}) and pore size of 250 Å was used for separations according to ethylene sequence length. The column was placed in an oven at the desired temperature.

For wax analyses, the mobile phase comprised of a solvent combination of decane and ODCB with a constant flow rate of 0.5 mL min^{-1}. A sample concentration of 2 mg mL^{-1} was used and 50 µL of each sample were injected for all the experiments. The evaporative light scattering detector (ELSD) settings used were as follows: a gas flow rate of 0.5 SLM, 140 °C nebulizer temperature and an evaporative temperature of 200 °C.

For ethylene-propylene copolymer and bimodal HDPE, a 10 min gradient of 1-decanol to TCB was used. A sample concentration of 1 mg mL^{-1} was used and 50 µL of each sample were injected for

all the experiments. The evaporative light scattering detector (ELSD) settings used were as follows: a gas flow rate of 1.5 SLM, 160 °C nebulizer temperature and an evaporative temperature of 270 °C.

Separations on silica: A silica column (Nucleosil®, Macherey-Nagel, Düren, Germany) with 250 × 4.6 mm^2 length and internal diameter packed with silica particles of 5 μm and pore size of 300 Å was used. The mobile phase flow rate used was 0.5 mL min^{-1}. The ELSD settings used were as follows: a gas flow rate of 0.5 SLM, 140 °C nebulizer temperature, and an evaporative temperature of 200 °C. Sample concentrations of 2 mg mL^{-1} were used, and 50 μL of each sample were injected. All samples were prepared for injection in decane.

3.2.5 High-temperature thermal gradient interaction chromatography (HT-TGIC)

For separation of waxes using HT-TGIC, the method described below was used at Stellenbosch University.

A silica column described above was used for all the experiments. All valve switches in the first dimension, sample injection, and temperature programing were done manually. Sample injection was done with a flow of 0.05 mL min^{-1} at 140 °C. The sample was allowed to move to the column from the injection loop at a flow rate of 0.05 mL min^{-1} for 3 min. The oven containing the column was then cooled at a rate of 5 °C min^{-1} to 30 °C and kept isothermally for 15 min at 0.05 mL min^{-1} flow. The flow rate was increased to 0.5 mL min^{-1} after 40 min of sample injection and a temperature gradient of 0.5 °C min^{-1} was applied after 45 min. The injection loop was housed in a separate oven which was kept at 140 °C. A volume of 50 μL of a 2 mg mL^{-1} sample dissolved in decane were injected.

The method and instrumentation described below was used for the HT-TGIC experiments at Polymer Char laboratories in Valencia for the separation of elastomers.

HT-TGIC experiments were performed using a crystallization elution fractionation (CEF) instrument from PolymerChAR (Valencia, Spain). The instrument was equipped with a Hypercarb® column, from Thermo Scientific, to be used as a HT-TGIC instrument. Column specifications are given in the HT-SGIC section. An autosampler was used to dissolve and inject all samples in a fully automated mode. The samples were dissolved for 60 min at 160 °C with

ortho-dichlorobenzene (ODCB), containing 300 ppm of BHT, in 10 mL vials purged with nitrogen. The sample concentration was 1 mg mL^{-1}, and 100 µL were injected into the Hypercarb® column at 160 °C, followed by a cooling ramp of 20 °C min^{-1} down to 40 °C to adsorb/precipitate all the components. Some experiments were performed with cooling ramps down to minus 20 °C to promote adsorption of the most amorphous resins. Elution begins, isothermally, at the lowest temperature during five minutes at a flow rate of 0.5 mL min^{-1} of ODCB, followed by a heating ramp at 2 °C min^{-1} to desorb/dissolve the various components.

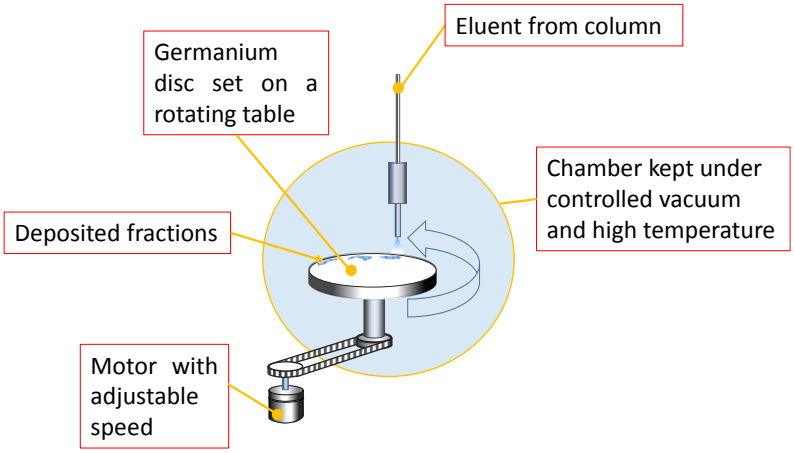


Figure 3.3 Schematic diagram showing the operating principle of the LC-transform interface.

Collection of fractions using the LC-transform interface and FTIR analysis: A LC-transform series model 303 (Lab Connections, Florida, USA) was coupled to the PolymerChAR SGIC instrument, in order to collect the HPLC and TGIC eluates. For each sample, 200 µL was injected from 2 mg mL^{-1} solutions. The outlet of the chromatographic column was connected to the LC-transform interface through a heated transfer line set at 140 °C. The fractions were deposited by rotating a germanium disc (sample target in the LC-transform) at a speed of rotation of 10° min^{-1}, see Fig. 3.3. The disc stage and nozzle temperatures of the LC-transform were set to 140 °C. The disc with the dry fractions was scanned on a Thermo Nicolet iS10 spectrometer (Thermo Scientific, Waltham, MA), equipped with the LC-transform FTIR interface which was connected to a standard transmission baseplate. Spectra were recorded at a resolution of 4 cm^{-1} with 16 scans being recorded for each spectrum. The speed of disc rotation during scanning was set at 3° min^{-1}.

3.2.6 High-temperature two-dimensional liquid chromatography (HT-2D-LC)

HT-HPLC was coupled to fast HTSEC with the aid of an electronically controlled eight-port valve system (VICI Valco Instruments, Houston, Texas, USA) equipped with two 100 µL sample loops. Injection into the first dimension (HT-HPLC) was carried out using a 200 µL sample loop and the flow rate was 0.05 mL min^{-1}. A similar gradient as in the one-dimensional HT-HPLC analyses was used in the first dimension and three times the concentration of the sample was used (i.e., 6 mg mL^{-1}). A flow rate of 3.25 mL min^{-1} was used in the second dimension (HT-SEC), and ODCB was used as the mobile phase. In the second dimension, a PL Rapide M (Agilent, U.K.) 100 × 10 mm^2 internal diameter column with a 10 µm particle diameter was used at 140 °C. The evaporative light scattering detector was used with the following parameters: gas flow rate of 1.5 SLM, 140 °C nebulizer temperature, and an evaporative temperature of 230 °C.

3.2.7 Cross-fractionation chromatography (CFC)

All samples were analysed using a fully automated Cross-Fractionation Chromatography (CFC, PolymerChAR, Valencia, Spain) device to determine the chemical heterogeneity and to be able to determine the molar mass distributions and the corresponded molar mass averages (M_n, M_w and M_v) at certain elution temperatures. A CFC instrument was used to perform the cross-fractionation (TREF × SEC).[2] An IR5 infrared detector (PolymerChAR, Valencia, Spain) was used to monitor the concentration. Around 50 mg of the polymer sample was dissolved in 40 mL TCB in a stainless steel vessel for 180 min at 160 °C. Once the sample was completely dissolved an aliquot was loaded into the TREF column and stabilised for a while at 110 °C. The following analytical parameters were chosen for analysing the samples, see Table 3.1.

Table 3.1 Experimental parameters for the CFC analysis.

Dissolution temperature [°C]	Dissolution time [min]	Cooling rate [°C min^{-1}]	Elution steps
160	180	0.07	24 steps from 30 to 140 °

A discontinuous elution process was performed using the temperature profile given in Fig 3.4.

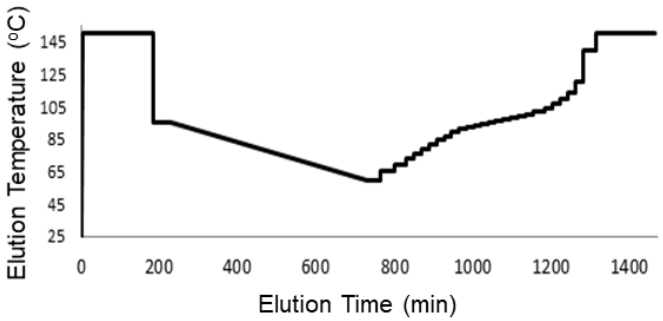


Figure 3.4 Temperature profile of CFC analysis.

In the 2nd dimension (SEC), three PL Olexis columns and an Olexis guard column from Agilent (Church Stretton, UK) were used as the stationary phase. As eluent 1,2,4-trichlorobenzene (TCB, stabilized with 250 mg L^{-1} 2,6-di-tert-butyl-4-methyl-phenol) at 150 °C and a constant flow rate of 1 mL min^{-1} were applied. The column set was calibrated using universal calibration (according to ISO 16014-2:2003) with at least 15 narrow molar mass PS standards in the range of 0.5 kg mol^{-1} to 11 500 kg mol^{-1}.

3.3 Spectroscopic techniques

3.3.1 Fourier Transform infrared spectroscopy (FTIR)

Attenuated total reflectance (ATR) measurements were recorded on a Thermo Nicolet iS10 spectrometer (Waltham, USA). Solid samples were used in all the analyses with no prior modifications. Spectra recorded from 4 000 to 650 cm^{-1} were obtained from a collection of 64 scans at a resolution of 4 cm^{-1} with automatic background subtraction. Thermo Scientific OMNIC software (version 8.1) was used for data collection and processing.

3.3.2 Carbon-thirteen nuclear magnetic resonance analysis (^{13}C-NMR)

Quantitative $^{13}C[^{1}H]$ NMR spectra were recorded in melt-state using a Bruker Avance III 500 NMR spectrometer operating at 500.13 and 125.76 MHz for ^{1}H and ^{13}C, respectively. All Spectra were recorded using a ^{13}C optimized 7 mm magic-angle spinning (MAS) probe head at 150 °C using nitrogen gas for all pneumatics. Approximately 200 mg of polymer sample was packed into a 7 mm outer diameter zirconia MAS rotor and spun at 4 kHz. A total of 1024 (1k) transients were acquired per spectrum. The quantification of the comonomer fraction and the corresponding triad distribution was performed as described by Parkinson et al.[3,4]

3.4 Thermal analysis techniques

3.4.1 Differential scanning calorimetry (DSC)

A TA Instruments Q100 calorimeter calibrated with indium metal standard was used for all melting and crystallisation determinations. Calibration was carried out according to standard procedures. All measurements were carried out under the same conditions of heating and cooling at a rate of 10° C min^{-1} for a temperature range of 10 to 200 °C .The samples were subjected to three cycles with the first cycle (first heating) used to erase the thermal history of the sample. After each cycle, the temperature was kept constant for 2 min. The second and third cycle (first cooling and second heating, respectively) were used for quantitative and qualitative purposes. Measurements were conducted in a nitrogen atmosphere at a purge gas flow rate of 50 mL min^{-1}. 4 – 5 mg of each sample were used for analysis and aluminium pans and flat lids were used as sample containers. An empty aluminium pan and lid were used as a reference.

3.4.2 Crystallisation analysis fractionation (CRYSTAF)

A model 200 PolymerChAR (Valencia, Spain) CRYSTAF instrument was used for all crystallization analysis fractionation experiments. Approximately 20 mg of each sample were dissolved in 35 mL of TCB/ODCB in five stainless steel reactors simultaneously at 160 °C. Dissolution was carried out for 90 to 150 min depending on sample type with constant stirring. The temperature was then brought down to 100 °C and stabilised for 1 hr before the solution was slowly cooled to 30 °C at the rate of 0.1 °C min^{-1} to minimise the effects of co-crystallisation[5] During the crystallisation stage, the solution concentration was measured as a function of temperature and the results recorded.

3.5 Preparative fractionation techniques

3.5.1 Preparative temperature rising elution fractionation (p-TREF)

Preparative fractionations of the samples were performed using a semi-automated fractionation instrument PREP-MC^2 (PolymerChAR, Valencia, Spain). Around 1 g of the polymer samples was dissolved in 180 mL TCB, stabilized with 250 mg L^{-1} 2,6-di-tert-butyl-4-methyl-phenol at 160 °C for 90 min under discontinuous gentle stirring (discontinuously at 200 rpm, 30 sec on, 5 sec off).

The solution was cooled down to 95 °C (20 °C min^{-1} cooling rate) for stabilization for 45 min and afterwards the solution was cooled down to 30 °C with a cooling rate of 0.1 °C min^{-1}. The elution temperature was obtained by increasing the temperature with a heating rate of 20 °C min^{-1} and after 30 min of stabilization the polymer solution was taken out by pressing it through a filter placed inside the vessel using nitrogen overpressure. This step was repeated for each individual p-TREF fraction.

After adding 200 mL of acetone to each of the obtained fraction solutions, they was allowed to precipitate overnight at 7 °C and filtrated thereafter through 5 µm PTFE filters by vacuum filtration. After drying under vacuum at 55 °C, the fractions were weighed on a precision scale.

3.5.2 Preparative solution crystallization fractionation (p-SCF)

Preparative solution crystallization fractionation was carried out using a simple experimental set up as shown in Fig. 3.4. Approximately 3.0 g of wax was dissolved in 300 mL of 1,2-dichlorobenzene (ODCB) at 110 °C for 2 hr in a glass reactor. After the complete dissolution of the wax, the temperature of the solution was reduced at the rate of 2 °C min^{-1} to 45 °C. After that, the temperature was maintained for 2 hr with constant stirring. A further 2 hr was required to allow the crystallized wax to settle after the stirring was stopped. Using a glass syringe, the layer of crystallized wax was extracted and treated with acetone to remove any residual ODCB. The residual ODCB solution was cooled to 25 °C and 0 °C and the extraction repeated at these temperatures. In order to bring the solution to 0 °C, the glass reactor was transferred to an ice bath and stirred for 2 hr. (Melting ice is in equilibrium with liquid water at 0 °C). The last fraction was obtained by collecting the acetone filtrate discarded from all the other fractions and combining it with the remaining ODCB solution. The excess acetone and ODCB were removed using a rotor vapor before precipitating the last fraction in ethanol. All the fractions were dried to a constant weight before recording their respective masses.

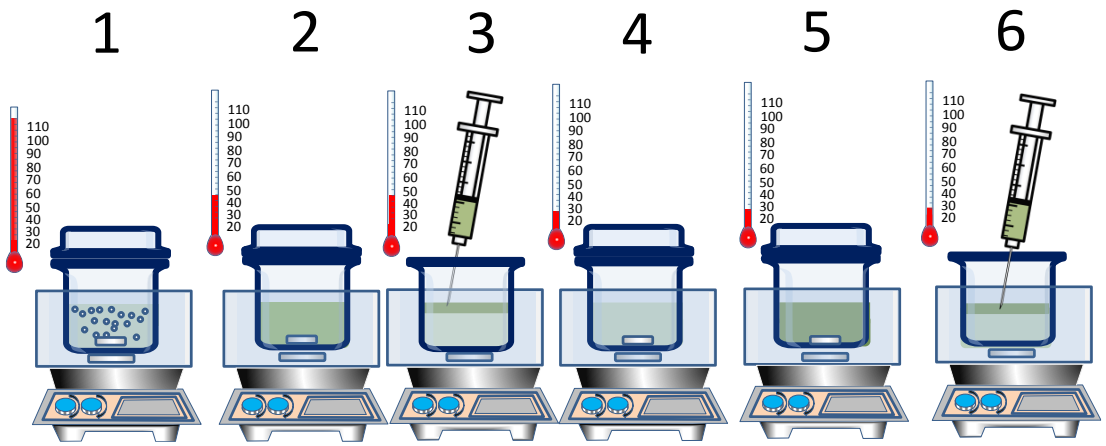


Figure 3.5 Illustration of the preparative solution crystallisation fractionation process.

3.6 References

(1) Ortin, A.; Monrabal, B.; Montesinos, J.; Del Hierro, P. *Macromol. Symp.* **2009**, *282*, 65–70.

(2) Ortin, A.; Monrabal, B.; Sancho-Tello, J. *Macromol. Symp.* **2007**, *257*, 13–28.

(3) Klimke, K.; Parkinson, M.; Piel, C.; Kaminsky, W.; Spiess, H. W.; Wilhelm, M. *Macromol. Chem. Phys.* **2006**, *207*, 382–395.

(4) Parkinson, M.; Klimke, K.; Spiess, H. W.; Wilhelm, M. *Macromol. Chem. Phys.* **2007**, *208*, 2128–2133.

(5) Pasch, H.; Brüll, R.; Wahner, U.; Monrabal, B. *Macromol. Mater. Eng.* **2000**, *279*, 46–51.

Chapter 4

Results and discussion

The chapter presents the detailed results obtained from the studies conducted on the different polyolefin materials using various high-temperature multidimensional approaches. Brief summaries are given for each subsection (Sections 4.1-4.3) and detailed information is given in the attached publications. The last subsection (Section 4.4) presents the study on bimodal HDPE.

4.1 Separation and identification of oligomers in oxidized and non-oxidized wax by HT-SGIC and HT-2D-LC

When waxes are oxidized, the majority of their properties improve as compared to the alkanes they are derived from. The introduction of oxygen containing functionalities also changes the evaporation behaviour of the waxes and this makes the use of gas chromatography (GC) difficult. Liquid interaction chromatography offers a different pathway for the separation and analysis of oligomers. More so, it is interesting to compare the retention and detection behaviour of oxidized and non-oxidized waxes.

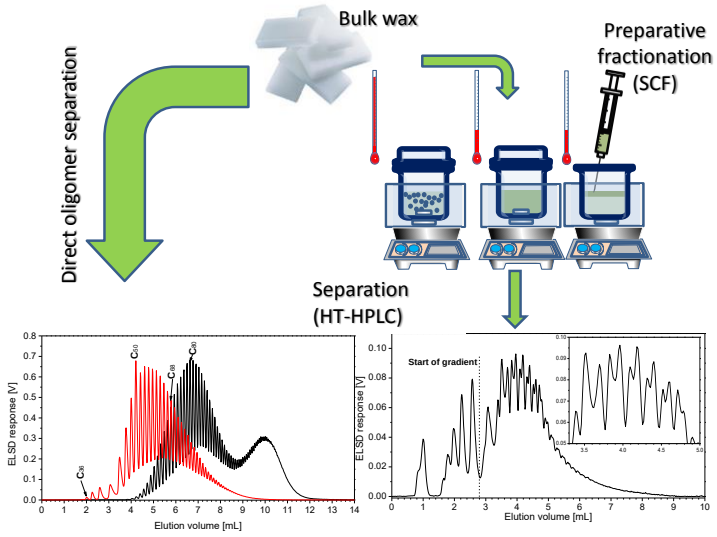


Figure 4.1 Illustration of the multiple fractionation concept for the separation and identification of oligomers in wax.

In this work it is shown that oligomers in oxidized and non-oxidized waxes can be separated and identified using the mentioned techniques. In addition, the use of a preparative technique followed by coupling to HT-HPLC gives more information on the oligomer composition. The influence of oxidation levels on the ELSD detector response is also shown. HT-HPLC is coupled to HT-SEC to obtain HT-2D-LC plots for oxidized and non-oxidized waxes. Here, the effects of oxidation on the low molar mass oligomer fractions are exposed. Lastly, solution crystallization is used as a preparative fractionation technique. As illustrated in Fig. 4.1, better identification of shorter and possibly odd-numbered oligomers is achieved.

Analytica Chimica Acta 1027 (2018) 137–148

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

A multidimensional fractionation protocol for the oligomer analysis of oxidized waxes

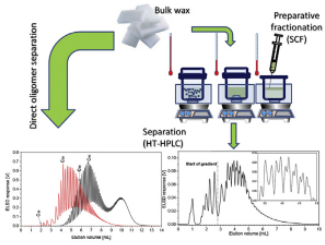
Anthony Ndiripo, Harald Pasch*

Department of Chemistry and Polymer Science, University of Stellenbosch, 7602, Matieland, South Africa

HIGHLIGHTS

- High-temperature HPLC separation of oxidized and non-oxidized waxes on PGC is investigated for the first time.
- Separation of oxidized and non-oxidized polyethylene waxes is optimized and adapted for use in comprehensive HT-2D-LC.
- The solution crystallization process is used to obtain narrow wax fractions for analysis using advanced analytical methods.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 December 2017
Received in revised form
28 February 2018
Accepted 2 March 2018
Available online 19 March 2018

Keywords:
Ethylene oligomer
High temperature HPLC
Oxidized wax
Porous graphitic carbon
Evaporative light scattering
Fractionation

ABSTRACT

Oxidized waxes possess far superior properties as compared to the alkanes they are derived from. The separation of alkane oligomers via gas chromatography (GC) becomes a challenge when polar oxygen-containing functional groups are introduced or when higher molar masses are targeted. In the present study, the separation and analysis of oligomers in oxidized and non-oxidized waxes using different liquid chromatographic techniques are investigated. Oligomers in two oxidized waxes and a non-oxidized wax from which they are derived, are separated using high-temperature solvent gradient interaction chromatography (HT-SGIC) and high-temperature two-dimensional liquid chromatography (HT-2D-LC). Evaporative light scattering detector conditions are tailored to provide the best detection with the solvent system at use. It is shown that oligomers in oxidized and non-oxidized waxes can be separated and identified using the mentioned techniques. It has been found that the ELSD detector response systematically decreases as the oxidation levels of the waxes increase. Coupling of HT-HPLC and high-temperature size exclusion chromatography (HT-SEC) in a comprehensive 2D-LC setup shows a broadening of the molar mass distributions of the lower oligomer fractions as a consequence of the modification indicating changes in the oligomer chain microstructures. A preparative fractionation technique is utilized to collect specific oligomer fractions from the bulk waxes followed by hyphenation to HT-HPLC and other techniques. HPLC is shown to provide more detailed information on the oligomer composition of waxes when coupled to a pre-fractionation technique.

1. Introduction

When alkanes/ethylene oligomers are oxidized or modified to introduce oxygen functionalities, the majority of their physical and mechanical properties are significantly improved. This expands

* Corresponding author.
E-mail address: hpasch@sun.ac.za (H. Pasch).

https://doi.org/10.1016/j.aca.2018.03.007
0003-2670/

their areas of application including solubility in polar media, compatibility with polar organic/inorganic materials and better adhesion [1–3]. The latter is crucial when waxes are used as coatings in food and packaging as migration into food is reduced. Industrially fabricated waxes are usually a mixture of a wide range of oligomers and in some cases, small amounts of high density polyethylene (HDPE). The oxidation of waxes is typically done by bubbling oxygen or oxygen containing gases through molten wax [4]. Reaction conditions can vary depending on the degree of oxidation required for the end product. Deckers et al. [2] oxidized wax at 160 °C whereby a steel autoclave with pressure maintenance device was used. Molten wax is stirred continuously while air bubbled at the desired flow rate. Gas chromatography (GC) has been the main workhorse in the separation and identification of olefin oligomers [5–9] due to its outstanding peak resolution and selectivity. However, GC has distinct limitations when separating alkanes of 30 or more carbons. The incorporation of oxygen functionalities increases the wax vaporisation temperatures and hence it requires higher GC operational temperatures. Furthermore, even when higher operation temperatures are employed, peak resolution of higher oligomers (90–100 carbons) is lost.

Liquid chromatography (LC) offers an alternative route for the separation and identification of wax oligomers. Of the several modes of operation available in liquid chromatography, size exclusion chromatography (SEC) has been largely employed to separate wax/oligomer macromolecules [10–12]. The technique has been preferred due to its rapid nature and possibility of functional group determination when coupled to infrared spectroscopy online or offline. However, the technique does not provide sufficient resolution to separate individual oligomers in a single experiment. There have been several attempts to separate oligomers using stationary phases with small pores. Oligomers with 5–150 carbon atoms have been separated with silica gel and porous glass [11,13–17] being used as stationary phases for SEC separations.

Separations based on adsorptive interactions have been investigated using weak eluents and at ambient temperatures to promote adsorption onto silica gel, alumina, or zeolites which were employed as stationary phases [18–23]. The development of high temperature liquid chromatography by Macko and Pasch [24–27] brought new possibilities in the separation and identification of complex components in polyolefins with high molar masses. Porous graphitic carbon (PGC, e.g. Hypercarb®) has been repeatedly shown to separate ethylene-based polyolefins according to the number of linear methylene sequences in a given polymer chain [28–31]. Möckel et al. [32] demonstrated the ability of porous graphitic carbon to have stronger retention of oligomers with 6–15 carbon atoms as compared to silica gel C18 with methanol as the eluent. Recently, Mekap et al. [33] separated oligomers present in low molar mass linear high density polyethylene (HDPE) standards with almost baseline resolution on Hypercarb®. This has been an important starting point, demonstrating the ability of HT-HPLC to separate a wide range of oligomers with high precision. The presence of the functional groups has not been shown to influence the separations on the Hypercarb®. On the other hand, the detector response has been shown to change when functional groups have been introduced in polyolefin polymer chains [34–36].

Fractionation of bulk materials (e.g. polyolefins) into homogeneous fractions by chemical composition/branching or molar mass has been shown to greatly aid the complete unravelling of polyolefin microstructures [37–43]. Preparative temperature rising elution fractionation (p-TREF) [30,40,43–47], solution crystallisation fractionation (SCF) [48], and preparative molar mass fractionation (p-MMF) [47,49] have been presented as important and indispensable tools for the fractionation of semicrystalline polyolefins by chemical composition or molar mass. Hyphenation of these techniques to other new chromatographic techniques provides a wealth of information especially when coupled to information-rich detectors. Applying these techniques to low molar mass waxes presents a challenge especially when oxidized functionalities are introduced. This is due to the changes in solubility of the waxes in the solvents used for fractionation at ambient temperatures.

In the present study, we investigate the oligomer separation, selectivity and retention behaviour of non-oxidized and oxidized waxes on PGC using solvent gradients and isocratic solvent techniques. A suitable preparative technique is employed in the fractionation of the bulk waxes. A combination of separations in the first dimension (on PGC) to separations according to size (HT-SEC) in tailored comprehensive high-temperature two-dimensional liquid chromatography (HT-2D-LC) experiments is presented and discussed.

2. Experimental

2.1. Samples and solvents

Three waxes (designated as No. 1, No. 2 and No. 3) were used for the present study. Wax No. 1 is the starting material obtained from Sigma Aldrich, South Africa, from which oxidized waxes No. 2 and No. 3 were derived by passing oxygen through a melt of wax No. 1 for different times. Ethylene oligomers C_{18} - C_{50} were purchased from Sigma-Aldrich, South Africa, and the C_{40} as well as the C_{50} standards were used for SEC calibration. High density polyethylene standards (1, 2, 33 and 55 kg mol^{-1}) were obtained from Polymer Standards Service, Mainz, Germany. Narrowly distributed polystyrene standards used for SEC calibration were obtained from Agilent Technologies, UK.

1,2,4-trichlorobenzene (TCB) was used for size exclusion chromatography. *n*-Decane and 1,2-dichlorobenzene (ODCB) of HPLC grade were used for solvent gradient experiments. *n*-Heptane was used for isocratic experiments. The solvents were obtained from Sigma-Aldrich, South Africa and were used as received.

2.2. Size exclusion chromatography (SEC)

Molar mass and molar mass dispersity values were determined on a PL-GPC 220 High Temperature Chromatograph [Polymer Laboratories, Church Stretton, UK (now Agilent)] equipped with a differential refractive index (RI) detector. The samples (4 mg) were dissolved in 2 mL of TCB for 0.5 h together with 0.025% BHT which acted as a stabiliser to prevent sample decomposition/degradation. TCB with 0.0125% BHT was the mobile phase at a flow rate of 1 mL min^{-1}. Three 300 × 7.5 mm^2 PLgel Olexis columns (Agilent Technologies, UK) were used together with a 50 × 7.5 mm^2 PLgel Olexis guard column and 200 μL of each sample was injected. All experiments were carried out at 150 °C. The instrument was calibrated using narrowly distributed polystyrene standards as well as narrowly distributed polyethylene standards (Table 1s). The Cirrus GPC Version 3.3 (Polymer Laboratories) was used for data acquisition and evaluation.

2.3. Fourier transform infrared spectroscopy (FTIR)

Attenuated total reflectance (ATR) measurements were recorded on a Thermo Nicolet iS10 spectrometer. Solid samples were used in all the analyses with no prior modifications (except drying in the case of fractions). Spectra recorded from 4000 to 650 cm^{-1} were obtained from a collection of 64 scans at a resolution of 4 cm^{-1} with automatic background subtraction. Thermo Scientific

OMNIC software (version 8.1) was used for data collection and processing.

2.4. Differential scanning calorimetry (DSC)

The wax samples were analysed using the Q100 DSC system at heating and cooling rates of 10 °C min^{-1} across a temperature range of 0–200 °C. An aluminium pan and lid folded and pressed were used as a reference and approximately 5 mg of each wax sample were used.

2.5. Crystallisation analyses fractionation (CRYSTAF)

A commercial CRYSTAF apparatus Model 200 was used for the measurement of crystallisation properties in solution. Approximately 20 mg of each sample were dissolved in 35 mL of ODCB. Crystallisation was carried out under constant stirring in stainless steel reactors which are equipped with automatic agitation and filtration devices. The samples were dissolved for 90 min at 160 °C before the solution was stabilized at 100 °C. After stabilisation, the temperature was decreased from 100 °C to approximately 30 °C at a rate of 0.2 °C min^{-1}. The concentration of the solution was monitored automatically by an infrared detector operating at a fixed wavelength of 3.5 μm.

2.6. Preparative solution crystallisation fractionation (p-SCF)

Preparative solution crystallisation fractionation was carried out using a simple experimental set up as shown in Fig. 1s (Supporting Information). Approximately 3.0 g of wax was dissolved in 300 mL of 1,2-dichlorobenzene (ODCB) at 110 °C for 2 h in a glass reactor. After the complete dissolution of the wax, the temperature of the solution was reduced at the rate of 2 °C min^{-1} to 45 °C. After that, the temperature was maintained for 2 h with constant stirring. A further 2 h was required to allow the crystallized wax to settle after the stirring was stopped. Using a glass syringe, the layer of crystallized wax was extracted and treated with acetone to remove any residual ODCB. The residual ODCB solution was cooled to 25 °C and 0 °C and the extraction repeated at these temperatures. In order to bring the solution to 0 °C, the glass reactor was transferred to an ice bath and stirred for 2 h (Melting ice is in equilibrium with liquid water at 0 °C). The last fraction was obtained by collecting the acetone filtrate discarded from all the other fractions and combining it with the remaining ODCB solution. The excess acetone and ODCB were removed using a rotor vapour before precipitating the last fraction in ethanol. All the fractions were dried to a constant weight before recording their respective masses.

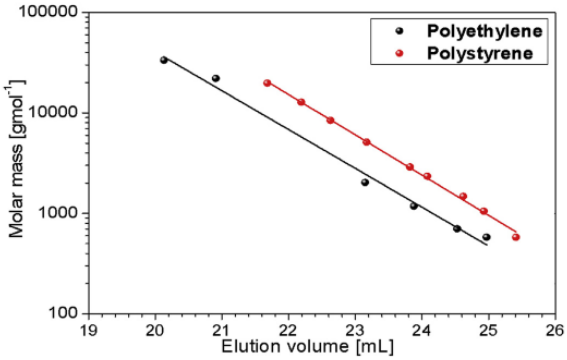


Fig. 1. Plots of molar mass against elution volume obtained by SEC for polyethylene (black spheres) and polystyrene (red spheres) standards; temperature 150 °C; detector RI. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

2.7. High-temperature high performance liquid chromatography (HPLC)

All chromatographic experiments were performed on a solvent gradient interaction chromatograph (SGIC) instrument constructed by Polymer*ChAR* (Valencia, Spain). For solvent gradient elution in HPLC, a high-pressure binary gradient pump (Agilent, Waldbronn, Germany) was utilized. The evaporative light scattering detector [ELSD, model PL-ELS 1000, Polymer Laboratories, Church Stretton, U.K. (Now Agilent)] was used for all detection purposes. A Hypercarb column (Hypercarb®, Thermo Scientific, Dreieich, Germany) with 100 × 4.6 mm^2 internal diameter packed with porous graphite particles which have a particle diameter of 5 μm (making a surface area of 120 m^2 g^{-1}) and pore size of 250 Å was used for separations according to ethylene sequence length. The column was placed in an oven at the desired temperature. The mobile phase comprised of a solvent combination of decane and ODCB with a constant flow rate of 0.5 mL min^{-1}. A sample concentration of 2 mg mL^{-1} was used and 50 μL of each sample were injected for all the experiments. The evaporative light scattering detector (ELSD) settings used were as follows: a gas flow rate of 0.5 SLM, 140 °C nebuliser temperature and an evaporative temperature of 200 °C.

2.8. High-temperature two-dimensional liquid chromatography (HT-2D LC)

HT-HPLC and HT-SEC were coupled with the aid of an electronically controlled eight-port valve system (VICI Valco instruments, Houston, Texas) equipped with two 100 μL sample loops. Injection into the first dimension (HT-HPLC) was carried out using a 200 μL sample loop and the flow rate was 0.05 mL min^{-1}. The gradient conditions used were similar to those used for one-dimensional analyses. A flow rate of 3.25 mL min^{-1} was used in all second dimension experiments (HT-SEC) and ODCB was used as the mobile phase. In the second dimension, a PL Rapide M (Agilent Technologies, U.K.) 100 × 10 mm^2 internal diameter column with a 6 μm particle diameter was used at 140 °C. The column was kept in an oven at this temperature during the analyses. The ELSD was used with the following settings: a gas flow rate of 1.5 SLM, 140 °C nebuliser temperature and an evaporative temperature of 230 °C.

3. Results and discussion

In order to explore the use of solvent gradient interaction chromatography on porous graphitic carbon for the separation oxidized/functionalized waxes bulk analysis has been conducted on selected samples. Three waxes (designated No. 1, 2 and 3) are serving as model compounds in this work. Table 1 summarizes the molar mass properties and carbonyl contents of the waxes.

For SEC, PS standards are calibration materials of choice due to their easy preparation, availability as well ease of use. However, the use of PS standards for the calibration of the present SEC separations of waxes gives rise to molar mass estimation errors. Low molar mass PE standards are more suited for the calibration of the present SEC system providing more accurate molar masses since the chain microstructures of the waxes and the PE standards are closely related. Fig. 1 shows the differences in the SEC calibration curves for polystyrene (PS) and polyethylene (PE) under similar analysis conditions. As such, the molar masses of the waxes are quoted for both PS and PE calibrations to illustrate the overestimation by PS calibration. Therefore, the use of PE standards for

Table 1
Summary of molar masses and carbonyl contents of waxes No. 1, No. 2 and No. 3.

Wax sample	M_p[a] (kg mol^{-1})	M_n[a] (kg mol^{-1})	M_w[a] (kg mol^{-1})	M_p[b] (kg mol^{-1})	M_n[b] (kg mol^{-1})	M_w[b] (kg mol^{-1})	Đ[b]	Carbonyl cont.[c]
No. 1	1.54	1.07	7.61	0.80	0.59	3.84	6.5*	0
No. 2	1.24	0.75	2.00	0.66	0.43	0.94	2.2	0.98
No. 3	1.10	0.78	1.67	0.59	0.45	0.82	1.8	1.40

[a] Polystyrene equivalent molar mass.
[b] Polyethylene equivalent molar mass.
[c] Area ratio of carbonyl to methylene group absorbances (CO/CH_2).
* High dispersity is due to the presence of small quantities of HDPE.

the molar mass determination of waxes is encouraged.

3.1. Chemical composition separation of oxidized waxes

3.1.1. Separations on porous graphitic carbon (high temperature solvent gradient)

Waxes are low molar mass materials and are comprised of various ethylene oligomers. The separation of ethylene oligomers on porous graphitic carbon was recently shown by Mekap et al. [33]. In their work, a linear gradient from the adsorption promoting decane to the desorption promoting 1,2-dichlorobenzene (ODCB) was applied to achieve almost baseline separation of constituent oligomers in low molar mass PE standards. The aim of the present work is to establish conditions for the separation and detection of ethylene oligomers in non-oxidized and oxidized waxes. Bearing in mind that industrially manufactured waxes may not resemble well defined polyethylene oligomer standards, the first aim was to establish suitable column temperature conditions for efficient oligomer separation.

It is known that temperature is an active variable in the enhancement of separation efficiency [50]. Fig. 2a–d shows elugrams obtained for column temperatures of 140, 120 and 100 °C. Fig. 2a and b shows the changes in the peak resolution as the column temperature is lowered. Overlays of oxidized and non-oxidized waxes are shown in Fig. 2c and d. The oven housing the injection loop was kept at 140 °C in all experiments. As can be seen, the waxes elute before the gradient reaches 100% of the desorption promoting solvent (ODCB) i.e. within the solvent gradient range. Reducing the column temperature was also shown to increase the retention of the waxes on PGC, hence the peak elution onset volumes of the wax oligomers increased, see Fig. 2c and d where elugrams of wax No. 1 and No. 3 respectively, are overlaid. This effect is observed for both oxidized and non-oxidized waxes. However, the oxidation of the wax chains appears to have no effect on the retention even at lower column temperatures when the chromatograms are compared to those of the non-oxidized waxes. The retention volumes and the peak widths (full width at maximum height) of the first sixteen peaks in the three chromatograms of wax No. 1 are presented in Table 2s (Supporting Information). The retention volumes of the oligomer peaks shift towards higher volumes as the column temperature is decreased. The differences between the peaks (resolution) slightly improves as shown by the determined differences in the peak maxima when the temperature is decreased, see Table 2s. Interactions of ethylene based linear oligomer/polymer chains on PGC are well understood to be dominated by van der Waals forces, which increase as the linear chain length increases [31,44,51,52]. The decrease in the column temperature, therefore, significantly improves the separation of the oligomers in the waxes and this is observable for both oxidized and non-oxidized waxes.

Column temperatures can be adjusted to suit the particular sample depending on the molar mass and chemical composition. The reduction of column temperature below 100 °C was impractical for the waxes under study due to their poor desorption from the PGC stationary phase. Similarly, a PE standard with a molar mass of 2 kg mol^{-1} was not fully desorbed under these conditions. Industrially manufactured waxes may well require lower column temperatures depending on their molar masses.

Decreasing the slope of the linear solvent gradient also improves the separation of individual oligomers [33]. Fig. 3 shows the elugrams obtained after wax No. 1 was subjected to three different gradients under the same system conditions. 10 min additions to the original gradient time were made. A 30 min gradient was found to be efficient in the separation of the oligomers without significant loss of detector response as well as having reasonable experiment times. It must be understood that first dimension method development is often the first step to comprehensive two-dimensional chromatography (LC × LC) methods where both resolution and experimental time are of importance. A longer first dimension method may improve resolution but will consequently result in a more time-consuming two-dimensional method.

While separation on any stationary phase under appropriate conditions is important, it cannot be disputed that detector conditions are crucial in ensuring that all the eluted material is completely detected. Previous studies have addressed issues related to the dependence of the ELS detector response on the solvent composition, injection mass and sample molar mass [34,43,53] as well as the evaporator temperature. The mobile phase flow rate, temperature, sample loop volume, the concentration of the analyte and nebuliser nozzle diameter also contribute to the detector response. It is also known that under conditions used for the analyses of high molar mass polyolefins, low molar mass material goes undetected. At lower temperatures and in cases where isocratic alkane mobile phases are used (hexane, heptane, decane etc.), lower carbon alkanes can be detected. Low molar mass alkanes below C_{50} are known to evaporate along with the solvent at evaporator temperatures of above 250 °C [33]. The evaporator temperature setting depends on the solvents used in a gradient. Recently, it was shown that evaporator temperatures as low as 190 °C can be used for a decane → ODCB gradient [33]. Fig. 2s (Supporting Information) illustrates the effect of lowering the evaporator temperature from 230 °C to 200 °C. It can be seen that lowering the evaporator temperature improves the visibility of lower alkanes by at least two more carbons.

The high temperatures used in the ELSD for the evaporation and detection of polyolefins are often accompanied by high nebuliser gas flow rates of above 1 SLM. The gas aids in the nebulisation of the eluent into an aerosol with a distribution of droplets from which the solvent can easily evaporate, leaving the polymer as particles that are detected by light scattering [36,54]. The nature of the particle plume produced in this process is highly dependent on the solvent nature/composition [26,34], flow rate [53,55,56] as well as the nebuliser gas flow [55,57]. The relationship between the gas flow and the detector response was investigated using the decane → ODCB gradient system.

The relationship between the elugram area and the gas flow

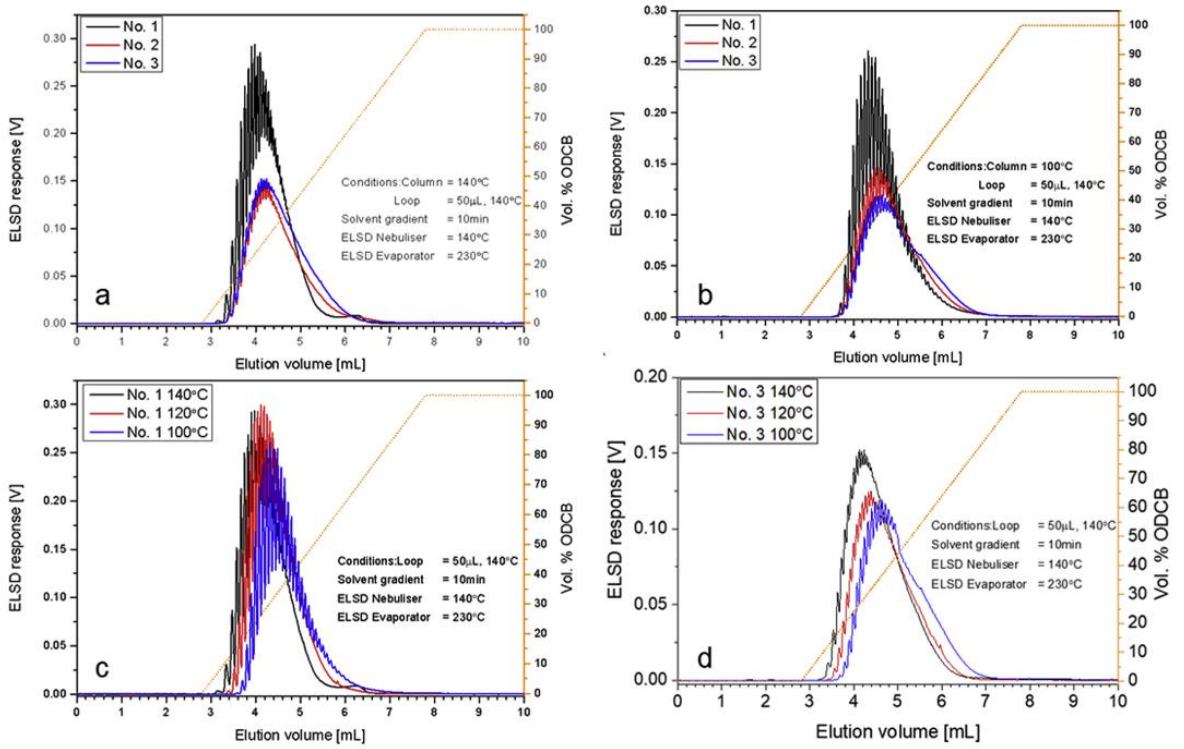


Fig. 2. HT-HPLC chromatograms for waxes No. 1, No. 2 and No. 3 obtained after separations on PGC at column temperatures of 140 °C (a) and 100 °C (b). A 10 min decane → ODCB gradient was used with the injection loop being kept at 140 °C, overlay of chromatograms of wax No. 1 (c) and wax No. 3 (d) at different column temperatures.

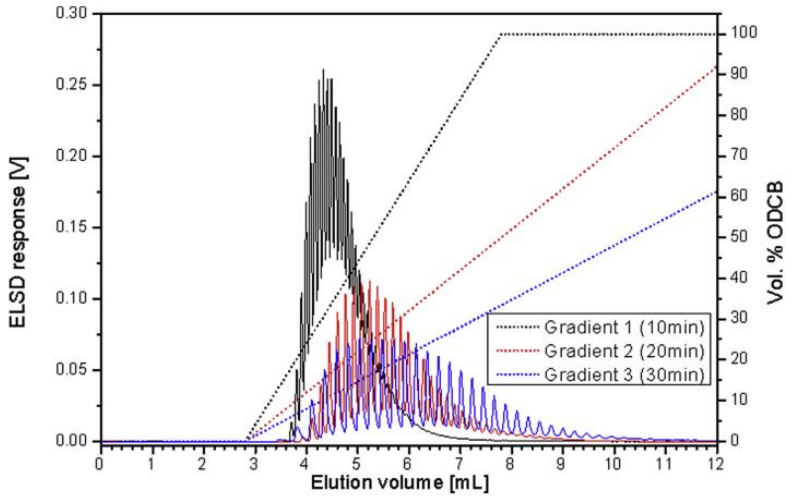


Fig. 3. Overlay of HT-HPLC elugrams showing the separation of oligomers in wax No. 1 under different gradient conditions, column temperature 100 °C.

used to nebulize the eluent is shown in Fig. 3s (Supporting Information). At gas flow rates below 0.5 SLM, the nebulisation is poor which results in only a fraction of the particle plume reaching the light scattering compartment. Above 0.5 SLM, it can be observed that the elugram area decreases. As the nebulisation gas becomes stronger, evaporation may occur too rapidly such that the wax polymer chains do not reach the light scattering compartment, but instead stick to the walls of the evaporator. Better detector response allows for smaller peaks to become more visible without the need to inject more sample, thereby preventing column

overloading and enhancing resolution. Under the given chromatographic conditions, a blend of low molar mass polyethylene standards can be used to establish the dependence of molar mass on elution volume. Fig. 4 shows the chromatograms obtained when different blend ratios of HDPE 2030 g mol^{-1}, 1180 g mol^{-1} and C_{50} standards are used. The blends can be adjusted to enable the better visibility of the lower carbon oligomers. Changing the ratio of the standards e.g. from a weight ratio of 1/1 of HDPEs 2030 g mol^{-1} and 1080 g mol^{-1} to 8/1 HDPE 2030 g mol^{-1}/1080 g mol^{-1} does not significantly alter the elution volumes of the oligomers.

Alternatively, doping the sample with a minute quantity of a known standard can help to identify the rest of the oligomers in the wax sample [33]. Standards fall short in the sense that they do not necessarily represent industrial waxes in the best way possible. Standards have a narrow oligomer distribution while industrial waxes can be broad. The lowest useful available standard on the market with a sufficient range of oligomers is the 1180 g mol^{-1} standard. Fig. 5 illustrates the differences in the elution behaviour of a 1/1 blend of HDPEs 2030 g mol^{-1} and 1080 g mol^{-1} in comparison to wax No. 1. To obtain the best calibration, a known hydrocarbon standard (e.g. C_{50} or C_{60}) must be added to a sample for the best prediction of the separated oligomer fractions.

As mentioned before, the accurate determination of molar mass is important for the tailoring of conditions of analyses especially for the HPLC system. As can be seen in Fig. 5, the elution profile of the standard blend (1180 + 2030 g mol^{-1}) is significantly different from that of wax No. 1 with a determined peak molar mass of 1610 g mol^{-1} (PS calibration). This is strong evidence that polyethylene calibration or PS calibration conversion to PE values may provide better information with less error in the molar mass determination. Apart from that, HPLC can provide sufficient information regarding molar mass as well as the chemical composition in a single experiment. As an example, each peak can be integrated and quantified and mean quantities determined for the statistical distributions of the oligomers to come up with number average molar mass (M_n) average molar mass (M_w) and the dispersity ($Đ$).

When the three waxes are fractionated using HT-HPLC, differences in the microstructure of the waxes with regard to the

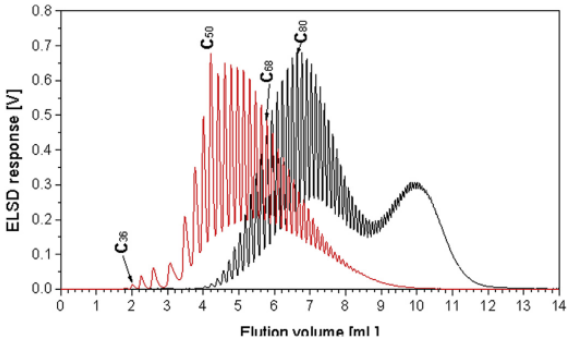


Fig. 5. Chromatogram of a 1/1 blend of PE 1180 g mol^{-1} and 2030 g mol^{-1} (black) and wax No. 1 doped with C_{50} (ratio: 400/2) (red). A gradient of decane →ODCB$_{30min}$ was used. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

oligomers present are seen. Firstly, the detector response decreases for the oxidized waxes, see Fig. 6a. The decrease in the detector response is related to the level of oxidation. This can be attributed to some of the material in the oxidized waxes going undetected under the conditions of analyses used. This is by no means a reason to discredit the influence of changed chemical structure (i.e. introduction of oxidized functionalities on the backbone and end groups) on the light scattering properties of the wax materials. It is known that the nature of the analyte does indeed affect the ELS detector response [34,35,58,59]. Functionalized polymers with oxygen functionalities have been shown to exhibit low ELSD responses [34,43]. In addition, we found the recovery of oxidized and no-oxidized waxes to be similar which only indicates to the effect of oxidation of detector response.

In addition to the observed decrease in detector response, the oligomers eluting between 3.0 and 5.0 mL show differences in their peak elution volumes, see Fig. 6b. However, from 5.0 mL onwards, the peak elution volumes of the oligomers are in sync, see Fig. 6c for

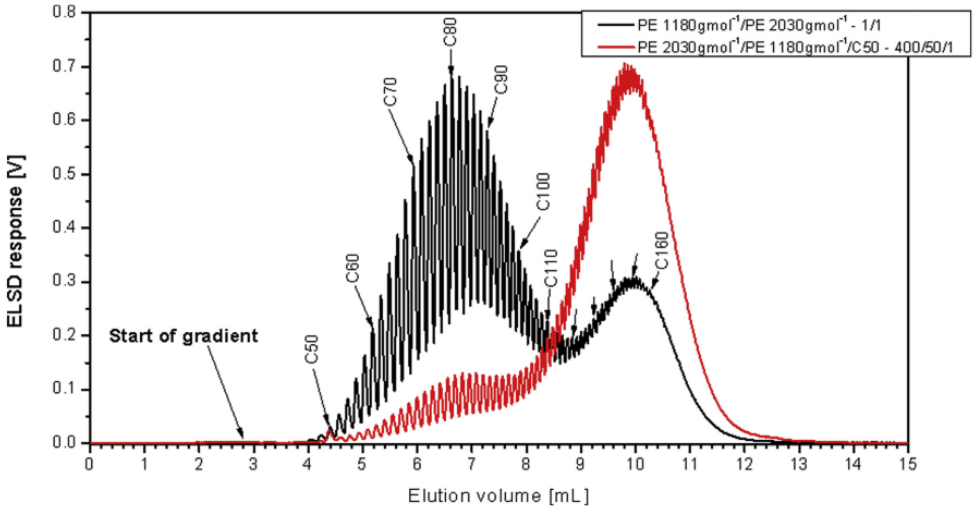


Fig. 4. Chromatograms of blends consisting of different ratios of HDPE 2030 g mol^{-1}, 1180 g mol^{-1} and C_{50} standards. 1/1 HDPEs 2030 g mol^{-1} and 1080 g mol^{-1} (black). 400/50/1 HDPE (2030/1180/C_{50}) (red). System temperature: 130 °C. Eluent: n-decane → ODCB. Gradient time: 30 min. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

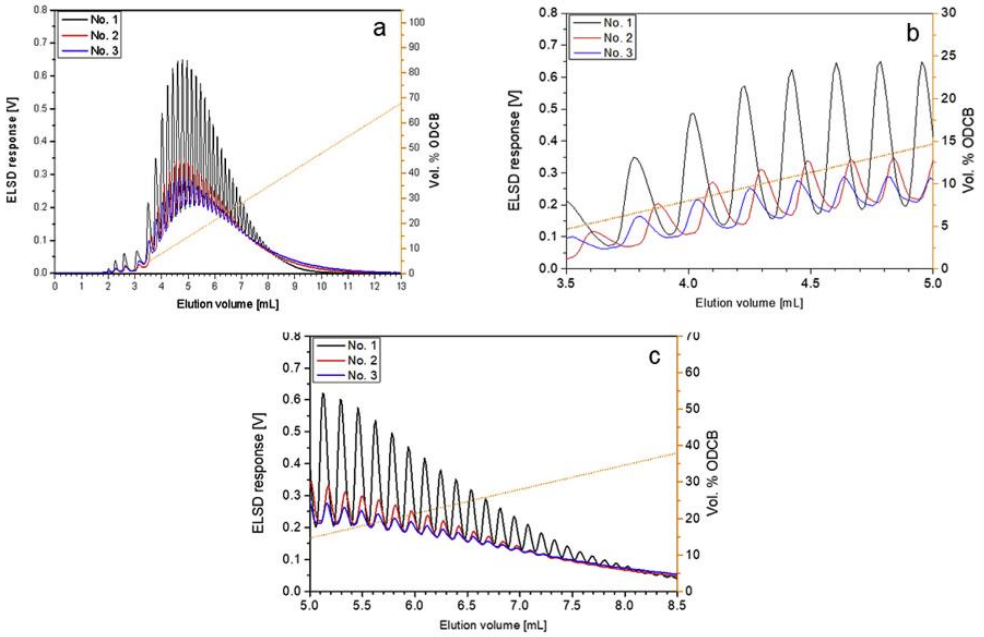


Fig. 6. Chromatograms obtained from the analyses of waxes No. 1, 2 and 3, column temperature 130 °C (a). Zoomed presentations of first part (b) and second part (c) of chromatograms.

the zoomed in plot. This may be an indication as to the oligomers most affected by the oxidation processes. The shift in the peak elution volumes can be attributed to products of chain scission reactions which produce odd-numbered oligomers.

Having noted that some of the material elutes in the isocratic mode with slight retention on the PGC, it became necessary to investigate the effect of lowering the column temperature to improve separation. Fig. 4s (Supporting Information) shows the elugrams of wax No. 1 obtained at 100 °C before and after doping with 400/2 and 400/3 w/w ratio of C50. It is clear that separation of the constituent oligomers in the wax can be done at this temperature in reasonable run times. More importantly, when waxes No. 1, 2 and 3 are compared in Fig. 7a–c, it can be seen that lowering the column temperature to 100 °C allows the gradient to be used to influence the retention. For better visibility of the separated oligomer peaks, Fig. 7b and c shows the zoomed in areas between 3.5 and 5.0 and the 5.0–8.5 mL.

As pointed out before, temperature is an important variable to influence separation efficiency [32]. Fig. 8a shows the relationship between elution volume and oligomer carbon number. The elution volumes obtained for the 1180 + 2030 g mol^{-1} standard blend are in agreement with those obtained for wax No. 1 with the exception of oligomers that elute in isocratic mode. The elution behaviour of oligomers in wax No. 1 at 130 and 100 °C is shown in Fig. 8b. Lowering the column temperature to 100 °C increases the retention volumes of the oligomers. However, the identification of oligomers with carbon numbers above a hundred decreases in comparison to experiments at 130 °C where at least 20 more carbons can be identified. This information is important prior to analyzing unknown samples and can be determined for each instrument and its settings. The same effect was observed on the oxidized waxes. It must be noted that under these conditions, higher oligomers of the 2030 g mol^{-1} PE standard cannot be separated due to strong adsorption of the oligomers on the stationary phase. It is, therefore, recommended that waxes with molar masses of 2000 g mol^{-1} or greater be analysed at temperatures higher than 100 °C.

3.1.2. High-temperature two-dimensional chromatography (HT-2D-LC)

The coupling of oligomer separations by HPLC to a size-based separation by SEC can provide more information on the changes which occur when waxes are chemically modified via oxidation. The coupling of HT-HPLC and SEC was achieved via an 8-port electronically controlled valve installed on a PolymerChAR SGIC instrument. In SEC, the separations are size-based and the governing factor is hydrodynamic volume of the polymer chains. In the present case, the introduction of oxidized functionalities may change the hydrodynamic volumes of the oligomers but does not affect the separations in the first dimension.

A change in the second dimension mobile phase from the predominantly used TCB was necessary due to the poor detection of low molar mass oligomers in this solvent. With ODCB, lower evaporator temperatures (230 °C in the present case) allow for a better detection of low molar mass oligomers. This solvent is seen more as a compromise between good detection and good solvation of the analyte molecules.

On PGC, separations of ethylene-based oligomers/polymers are based on the ethylene sequence length and no studies as of yet claim the interactions of other types of functionalities (oxygen containing) to influence the sorption/desorption properties of functionalized polyethylene. Probably this has been mainly due to the choice of stationary phases and the types of separations, which are targeted when functionalized polymers are analysed.

Fig. 9a–c shows the contour plots of waxes No. 1, 2 and 3, respectively, as analysed by 2D-LC. The solvent peaks from the first dimension (decane) were included although in most two-dimensional applications they are not included for obvious reasons. In the present case these peaks are a result of decane being

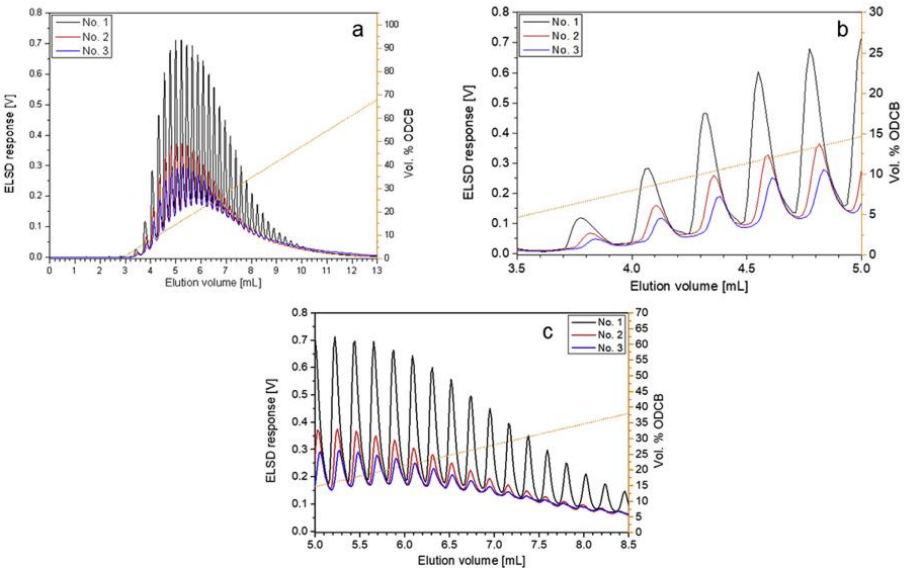


Fig. 7. Elution profiles of waxes No. 1, 2 and 3 (a) obtained after the gradient elution at a column temperature of 100 °C (a). Zoomed presentations of first part (b) and second part (c) of chromatograms.

transferred from the first dimension and eluting in ODCB in the second dimension. These can serve as good reference peaks especially during method development. The contour plots in Fig. 9 are adjusted to the same minimum and maximum logarithmic color scales for comparison. As can be seen, the detector response of wax No. 1 in ODCB is higher in comparison to waxes No. 2 and 3. It is observed that the trends in the detector response seen in the first dimension are also prevalent in the second dimension. In addition, broadening of the chromatograms in the molar mass dimension is observed as the waxes become more oxidized.

3.2. Solution crystallisation fractionation (SCF) and analysis of fractions

It has been repeatedly shown [37–43] that for the comprehensive characterisation of complex polyolefins with functionality type distributions (FTD), chemical composition distributions (CCD) and molar mass distributions (MMD), proper fractionation techniques are required to pre-concentrate polymer/oligomer species according to similar microstructural properties i.e. crystallinity/CCD or molar mass. Here, the use of solution crystallisation fractionation (SCF) was explored specifically for low molar mass oxidized waxes.

Fig. 10a shows the recovered and unrecovered fractions of the three waxes at selected temperatures. Quantitatively, wax No. 1 has a larger fraction which crystallises above 45 °C (more than half the material). In addition, the fraction quantities of the second third and fourth fractions (25, 0 and below 0 °C) decrease as the crystallisation temperatures decrease. A small quantity of the wax cannot be accounted for and this can be attributed to losses (material sticking to the glass containers, or being washed away with the waste solvents) during the fractionation process. The first fraction (collected at 45 °C) is much less for waxes No. 2 and No. 3. The fourth recovered fractions (below 0 °C) increase in quantity as the average oxidation levels of the bulk wax increase. The introduction of oxidized functionalities increases their solubility in ODCB, and some polymer chains fail to crystallize from the solution at higher temperatures.

Preparative fractionation techniques can be hyphenated to a number of techniques to provide a wealth of information. The fourth fraction of wax No. 1 is used to illustrate the importance of fractionating wax materials. Fig. 10b–e shows the results that were obtained after analysing the fraction with CRYSTAF, DSC, SEC and HT-HPLC, respectively. CRYSTAF analyses in ODCB, Fig. 10b, do not yield much useful information regarding the fraction crystallinity distribution. The entire sample is quantified as being soluble at temperatures below 30 °C. The observation was made with similar fractions as illustrated in Fig. 5s (Supporting Information). Both DSC second heating and first crystallisation curves (see Fig. 10c) show bimodality in the melting and crystallisation properties of fraction 4. However, this is not a true representation of the oligomer chains present. Co-crystallisation can account for the lack of individual oligomer peaks. This was observed with all the fractions as shown in Fig. 6s (Supporting Information). The molar mass distribution curve of the fraction illustrated in Fig. 10d is monomodal and does not provide much information on the oligomers present. However, the average molar masses obtained from SEC are important as they are the starting point for choosing analysis conditions for HT-HPLC.

The superiority of HPLC over the other mentioned techniques is illustrated in Fig. 10e where fraction 4 is fractionated according to the oligomer ethylene sequence length. A component of fraction 4 elutes in SEC mode at 130 °C, which means that some ethylene oligomers are not retained on the Hypercarb PGC at the column temperature. The rest of the eluting components are either just before the gradient with minimum interactions or after the start of the gradient with interactions proportional to their ethylene sequence length. In addition, the peaks eluting after 3.5 mL are split, which indicates possibly the separation of oligomers with differences of only one carbon.

As seen in Fig. 11a–c, the chromatogram peaks shift towards lower retention volumes as the fraction crystallinity decreases.

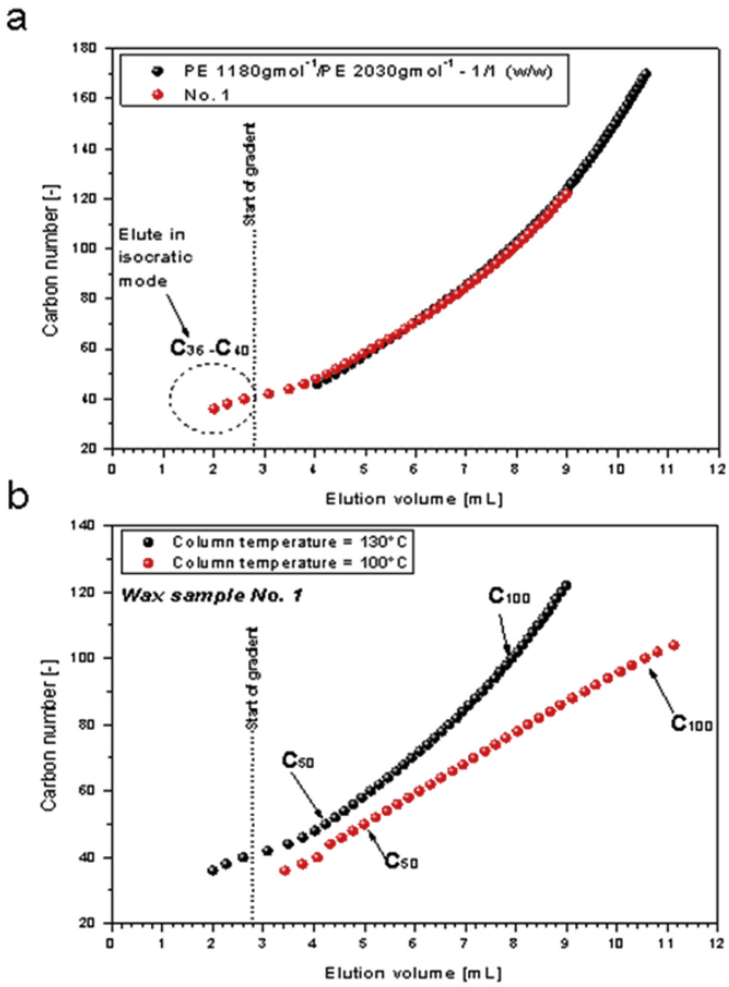


Fig. 8. Overlays showing the elution volumes of the oligomers in wax No. 1 and the PE (1180 + 2030 g mol^{-1}) blend as a function of the oligomer carbon number (a); comparison of the elution behaviour of the oligomers in wax No. 1 at 130 °C (black) and at 100 °C (red) (b). A gradient of decane →$ODCB_{30min}$ was used. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

With reference to Fig. 11a, it can be seen that a significant amount of material in fraction 4 elutes in isocratic mode at 130 °C. Some material also elutes in SEC mode, which means that under the experimental conditions, it is not retained due to the high temperatures in use. The material eluting after the start of the gradient shows peak splitting, an indication of oligomers eluting with differences of only one carbon. However, this can be fully confirmed by coupling HPLC to MALDI-TOF or mass spectrometry. Perhaps, the most important observation is the behaviour of the fraction in comparison to the bulk material. The presence of a significant quantity of material not seen in the bulk wax as well as the peak splitting shows the importance of a pre-fractionation technique. It must be noted that the recovery in all chromatographic experiments was above 90%.

As pointed out before, separations on the PGC have not been shown to be influenced by the presence of oxidized functionalities. Therefore, it is expected that fractions elute according to their respective ethylene sequence lengths. A comparison of the third and fourth fractions is made in Fig. 11d and e, respectively. Detailed information on the molar masses and carbonyl contents of the fractions are given in Table 2. An important observation is the loss of oligomer resolution as the fraction carbonyl content increases. Chain scission products which include odd-numbered chains elute between the even numbered oligomers. In addition, the fraction composition changes as longer oxidized chains "co-elute" with shorter oligomers at lower temperatures in SCF. This "co-elution" in SCF explains the change in the elution behaviour of fractions as shown in Fig. 11d and e. Molar mass distributions obtained from SEC show the subtle changes which are in agreement with the "co-elution" of larger oligomer chains, see Figs. 7s and 8s (Supporting Information).

4. Conclusions

Oligomer separation of oxidized and non-oxidized waxes into oligomers can be achieved on porous graphitic carbon using high

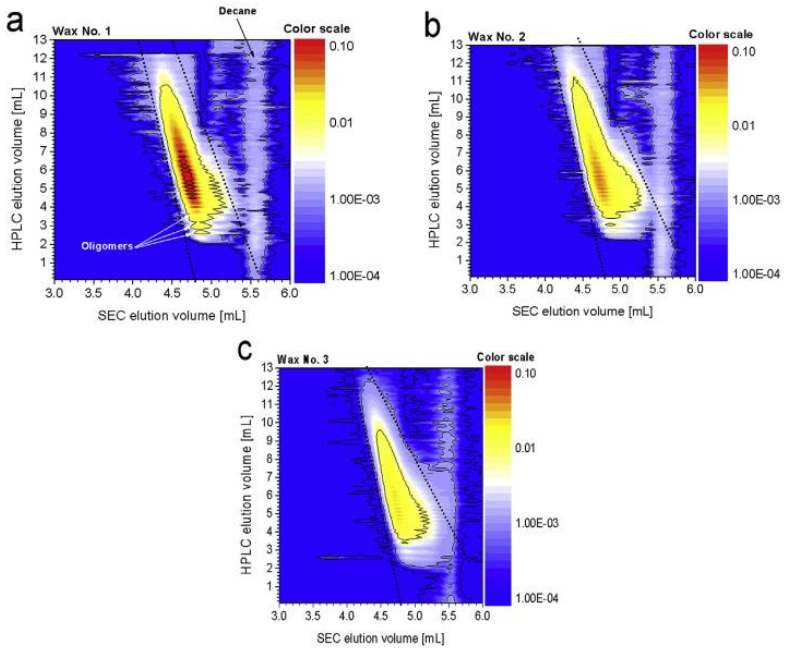


Fig. 9. 2D contour diagrams of waxes No. 1, 2 and 3 in (a–c) respectively obtained with PGC in the first dimension. A Rapide M column was used in the 2nd dimension. The analyses conditions were as follows: 1st dimension flow = 0.05 mL min^{-1}; column temperature = 130 °C; 2nd dimension valve switching time = 120 s; 2nd dimension column temperature = 140 °C; 2nd dimension solvent = 1,2-dichlorobenzene (ODCB); solvent flow rate = 3.25 mL min^{-1}. ELSD conditions used were as follows: evaporator temperature = 230 °C; gas flow = 1.5 SLM.

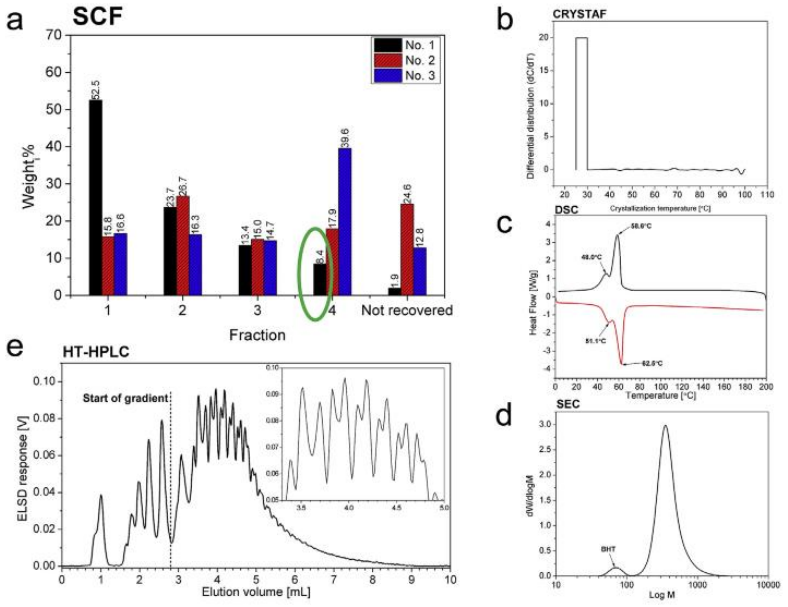


Fig. 10. Fractions recovered from the solution crystallisation fractionation process for waxes No. 1, 2 and 3 (a); CRYSTAF, DSC, SEC and HT-HPLC (gradient = decane → $ODCB_{30min}$) analyses of wax No. 1 fraction 4 in (b–e) respectively. A PE calibration was used in (d).

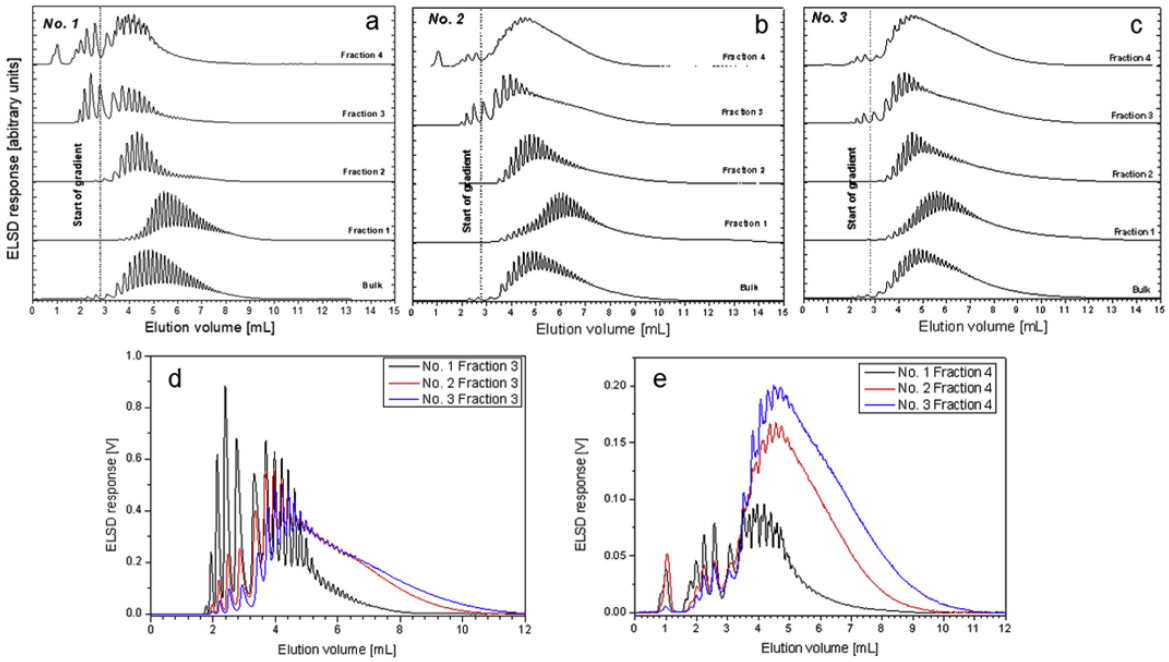


Fig. 11. Stack plots of HPLC chromatograms comparing the bulk waxes to their solution crystallisation fractions in (a)–(c). An overlay of the third and forth fractions from waxes No. 1–3 are shown in (d) and (e), respectively. The analyses conditions were as follows: column temperature = 130 °C; mobile phase flow rate = 0.5 mL min^{-1}; gradient = decane →ODCB$_{30min}$; ELSD evaporator temperature = 200 °C. The sample concentration was 2 mg mL^{-1} and 50 μL were injected.

Table 2
Summary of molar mass properties and carbonyl contents of the solution crystallisation fractions of waxes No. 1, No. 2 and No. 3.

Wax sample	M_n[a] (kg mol^{-1})	M_w[a] (kg mol^{-1})	Đ	Carbonyl cont.[b]
No. 1 F1	1.05	6.34	6.1[c]	0.00
No. 1 F2	0.76	3.61	4.8[c]	0.00
No. 1 F3	0.53	0.62	1.1	0.00
No. 1 F4	0.36	0.41	1.2	0.00
No. 2 F1	1.00	2.03	2.0	0.58
No. 2 F2	0.81	1.20	1.5	0.58
No. 2 F3	0.57	0.75	1.3	0.66
No. 2 F4	0.33	0.44	1.3	1.56
No. 3 F1	0.83	1.40	1.7	0.82
No. 3 F2	0.76	1.20	1.6	0.86
No. 3 F3	0.60	0.93	1.6	0.98
No. 3 F4	0.38	0.57	1.5	1.35

[a] Polyethylene equivalent molar mass.
[b] Ratio of FTIR absorbances of carbonyl functionalities to those of methylene groups (CO/CH_2).
[c] High dispersities are due to the presence of small amounts of high molar mass PE.

temperature solvent gradient chromatography (HT-SGIC). This was shown using two oxidized waxes and a non-oxidized wax from which they are derived. The waxes were separated into their oligomers using a high-temperature solvent gradient interaction chromatography technique and high-temperature two-dimensional liquid chromatography. The first dimension separated oligomers from oxidized and non-oxidized waxes irrespective of their oxidation levels although a decrease in the detector response was observed as the wax oxidation levels increased. Two-dimensional liquid chromatography showed a broadening of the molar mass distributions of shorter oligomers and this was attributed to oligomer chain modification. Two-dimensional analyses were therefore useful in showing the oligomers that are most affected by oxidation with regard to chain microstructure.

As part of the system optimization, it was shown that better detection of low molar mass waxes can be achieved with the evaporative light scattering detector when not only the evaporator temperature is lowered but when the nebulizing gas flow rate is optimized. Such determinations have to be done for each system and its detector for better results.

As was seen with high molar mass polyolefins in previous studies, it was also possible to show that a pre-fractionation technique is required to pre-concentrate oligomers from the bulk waxes in order to obtain fractions for further analysis. Hyphenation to HT-HPLC was shown to provide more information on the oligomer composition of waxes in comparison to DSC, SEC, and CRYSTAF. The waxes were shown to contain even shorter oligomers and possibly odd numbered oligomers.

Acknowledgements

The authors would like to thank The National Research Foundation of South Africa (NRF) for financial support.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.aca.2018.03.007.

References

[1] T. Chung, Synthesis of functional polyolefin copolymers with graft and block structures, Prog. Polym. Sci. 27 (2002) 39–85.

[2] A. Deckers, A.J. Kingma, U. Moll, W. Weber, Oxidized Metallocene-polyolefin Waxes, United States, US6348547 B1, 2002.
[3] A. Deckers, W. Weber, D. Ebisch, Preparation of Oxidized Polyolefin Waxes, United States, US 6169148 B1, 2001.
[4] E.L. Breet, A.S. Luyt, S. Oranje, Oxidation kinetics of a Fischer-Tropsch wax. Part 1. A simple method for measuring oxygen consumption, S. Afr. J. Chem. 43 (1990) 83.
[5] D.J. Heath, C. Lewis, S.J. Rowland, The use of high temperature gas chromatography to study the biodegradation of high molecular weight hydrocarbons, Org. Geochem. 26 (1997) 769–785.
[6] M. Regert, J. Langlois, S. Colinart, Characterisation of wax works of art by gas chromatographic procedures, J. Chromatogr. A 1091 (2005) 124–136.
[7] J.G. O'Connor, F.H. Burow, M.S. Norris, Determination of normal paraffins in C_{20} to C_{32} paraffin waxes by molecular sieve adsorption. Molecular weight distribution by gas-liquid chromatography, Anal. Chem. 34 (1962) 82–85.
[8] F. Czech, R. Fuchs, H. Antczak, Identification of components in paraffin wax by high temperature gas chromatography and mass spectrometry, Anal. Chem. 33 (1961) 698–704.
[9] J. Lawrence, J. Iyengar, B. Page, H. Conacher, Characterization of commercial waxes by high-temperature gas chromatography, J. Chromatogr. A 236 (1982) 401–403.
[10] T. Macko, H. Pasch, Y. Wang, Liquid chromatographic separation of olefin oligomers and its relation to separation of polyolefins - an overview, Macromol. Symp. 282 (2009) 93–100.
[11] L. Carbognani, Fast monitoring of C_{20}-C_{160} crude oil alkanes by size-exclusion chromatography-evaporative light scattering detection performed with silica columns, J. Chromatogr. A 788 (1997) 63–73.
[12] G. Hilken, Zukunft der Kunststofferzeugung in Deutschland, Europa und in der Welt, Kunststoffe 10 (2005) 34–40.
[13] M. Minárik, R. Komers, J. Coupek, Liquid chromatography of hydrocarbons on porous poly (ethylene glycol) methacrylate (spheron P-300), J. Chromatogr. A 148 (1978) 175–181.
[14] E. Ozaki, K. Saitoh, N. Suzuki, Gel chomatography of n-alkanes on a polystyrene gel with various organic solvents, J. Chromatogr. A 177 (1979) 122–126.
[15] K. Saitoh, E. Ozaki, N. Suzuki, Solvent dependence of gel chromatographic retention of low-molecular-weight compounds on polystyrene-divinylbenzene gel, J. Chromatogr. A 239 (1982) 661–670.
[16] Y.V. Kazakevich, H. McNair, Low-energy interactions in high-performance liquid chromatography, J. Chromatogr. A 872 (2000) 49–59.
[17] D.H. Freeman, I.C. Poinescu, Particle porosimetry by inverse gel permeation chromatography, Anal. Chem. 49 (1977) 1183–1188.
[18] J.F. Denayer, A. Bouyermaouen, G.V. Baron, Adsorption of alkanes and other organic molecules in liquid phase and in the dense vapor phase: influence of polarity, zeolite topology, and external fluid density and pressure, Ind. Eng. Chem. Res. 37 (1998) 3691–3698.
[19] L. Snyder, Perfluorocyclic ethers as very weak solvents for the separation of saturated and olefinic hydrocarbons by liquid-solid chromatography, J. Chromatogr. A 36 (1968) 476–488.
[20] J. Suatoni, R. Swab, HPLC preparative group-type separation of olefins from synfuels, J. Chromatogr. Sci. 18 (1980) 375–378.
[21] B. Bogdoll, W. Böhme, H. Engelhardt, I. Halasz, Perfluoralkane als eluenten in der flüssigkeits-cromatographie, Fresenius' J. Anal. Chem. 298 (1979) 349–357.
[22] G.E. Berendsen, P.J. Schoenmakers, L.d. Galan, G. Vigh, Z. Varga-puchony, J. Inczédy, On the determination of the hold-up time in reversed phase liquid chromatography, J. Liq. Chromatogr. 3 (1980) 1669–1686.
[23] H. Möckel, T. Freyholdt, Column dead-time for a bonded C 18 phase with pure alcohols as eluents, Chromatographia 17 (1983) 215–220.
[24] T. Macko, H. Pasch, R. Brüll, Selective removal of polyethylene or polypropylene from their blends based on difference in their adsorption behaviour, J. Chromatogr. A 1115 (2006) 81–87.
[25] T. Macko, H. Pasch, J.F. Denayer, Adsorption of polyethylene standards from decalin on liquid chromatography column packings, J. Chromatogr. A 1002 (2003) 55–62.
[26] T. Macko, H. Pasch, J.F. Denayer, Adsorption of polypropylene from dilute solutions on a zeolite column packing, J. Separ. Sci. 28 (2005) 59–64.
[27] T. Macko, H. Pasch, Y.V. Kazakevich, A.Y. Fadeev, Elution behavior of polyethylene in polar mobile phases on a non-polar sorbent, J. Chromatogr. A 988 (2003) 69–76.
[28] T. Macko, R. Brüll, Y. Zhu, Y. Wang, A review on the development of liquid chromatography systems for polyolefins, J. Separ. Sci. 33 (2010) 3446–3454.
[29] S. Cheruthazhekatt, G.W. Harding, H. Pasch, Comprehensive high temperature two-dimensional liquid chromatography combined with high temperature gradient chromatography-infrared spectroscopy for the analysis of impact polypropylene copolymers, J. Chromatogr. A 1286 (2013) 69–82.
[30] S. Cheruthazhekatt, T.F.J. Pijpers, V.B.F. Mathot, H. Pasch, Combination of TREF, high-temperature HPLC, FTIR and HPer DSC for the comprehensive analysis of complex polypropylene copolymers, Anal. Bioanal. Chem. 405 (2013) 8995–9007.
[31] M.I. Malik, H. Pasch, Novel developments in the multidimensional characterization of segmented copolymers, Prog. Polym. Sci. 39 (2014) 87–123.
[32] H. Möckel, A. Braedikow, H. Melzer, G. Aced, A comparison of the retention of homologous series and other test solutes on an ODS column and a Hypercarb carbon column, J. Liq. Chromatogr. 14 (1991) 2477–2498.
[33] D. Mekap, T. Macko, R. Brüll, R. Cong, A. deGroot, A. Parrott, W. Yau, One-step method for separation and identification of n-alkanes/oligomers in hdpe using high-temperature high-performance liquid chromatography, Macromolecules 46 (2013) 6257–6262.
[34] A. Albrecht, R. Brüll, T. Macko, H. Pasch, Separation of ethylene-vinyl acetate copolymers by high-temperature gradient liquid chromatography, Macromolecules 40 (2007) 5545–5551.
[35] T. Kawai, S. Teramachi, S. Tanaka, S. Maeda, Comparison of chemical composition distributions of poly (methyl methacrylate)-graft-polydimethylsiloxane by high-performance liquid chromatography and demixing-solvent fractionation, Int. J. Polym. Anal. Char. 5 (2000) 381–399.
[36] J. Arndt, T. Macko, R. Brüll, Application of the evaporative light scattering detector to analytical problems in polymer science, J. Chromatogr. A 1310 (2013) 1–14.
[37] S. Cheruthazhekatt, H. Pasch, Preparative solution crystallization fractionation: a simple and rapid fractionation method for the chemical composition separation of complex ethylene-propylene copolymers, Anal. Bioanal. Chem. 406 (2014) 2999–3007.
[38] S. Cheruthazhekatt, H. Pasch, Fractionation and characterization of impact poly(propylene) copolymers by high temperature two-dimensional liquid chromatography, Macromol. Symp. 337 (2014) 51–57.
[39] E. De Goede, P. Mallon, H. Pasch, Fractionation and analysis of an impact poly(propylene) copolymer by TREF and SEC-FTIR, Macromol. Mater. Eng. 295 (2010) 366–373.
[40] A. Ndiripo, H. Pasch, On the multimodality of preparative TREF fractionation as detected by advanced analytical methods, Anal. Bioanal. Chem. 407 (2015) 6493–6503.
[41] H. Pasch, Hyphenated separation techniques for complex polymers, Polym. Chem. 4 (2013) 2628–2650.
[42] H. Pasch, M.I. Malik, T. Macko, Recent Advances in High-temperature Fractionation of Polyolefins, Polymer Composites–polyolefin Fractionation–polymeric Peptidomimetics–collagens, Springer, 2013, pp. 77–140.
[43] A. Albrecht, R. Brüll, T. Macko, P. Sinha, H. Pasch, Analysing the chemical composition distribution of ethylene-acrylate copolymers: comparison of HT-HPLC, CRYSTAF and TREF, Macromol. Chem. Phys. 209 (2008) 1909–1919.
[44] S. Cheruthazhekatt, T.F.J. Pijpers, G.W. Harding, V.B.F. Mathot, H. Pasch, Compositional analysis of an impact polypropylene copolymer by fast scanning DSC and FTIR of TREF-SEC cross-fractions, Macromolecules 45 (2012) 5866–5880.
[45] S. Cheruthazhekatt, T.F.J. Pijpers, V.B.F. Mathot, H. Pasch, Preparative TREF - HT-HPLC - HPer DSC: linking molecular characteristics and thermal properties of an impact poly(propylene) copolymer, Macromol. Symp. 330 (2013) 22–29.
[46] A. Ndiripo, D. Joubert, H. Pasch, Ethylene/1-heptene copolymers as interesting alternatives to 1-octene-based LLDPE: molecular structure and physical properties, J. Polym. Sci., Part A: Polym. Chem. 54 (2016) 962–975.
[47] J.K. Jørgensen, A. Larsen, I. Helland, Study on LLDPE molecular structure characterization by preparative and analytical cross-fractionation, E-Polymers 10 (2010) 1596–1612.
[48] S. Cheruthazhekatt, D.D. Robertson, M. Brand, A. van Reenen, H. Pasch, Solution crystallization and dissolution of polyolefins as monitored by a unique analytical tool: solution crystallization analysis by laser light scattering, Anal. Chem. 85 (2013) 7019–7023.
[49] S. Hosoda, Structural distribution of linear low-density polyethylenes, Polym. J. 20 (1988) 383–397.
[50] T. Teutenberg, Potential of high temperature liquid chromatography for the improvement of separation efficiency—a review, Anal. Chim. Acta 643 (2009) 1–12.
[51] S. Cheruthazhekatt, N. Mayo, B. Monrabal, H. Pasch, Chemical composition separation of EP copolymers by CEF and HT-SGIC: crystallization versus adsorption, Macromol. Chem. Phys. 214 (2013) 2165–2171.
[52] R. Chitta, A. Ginzburg, T. Macko, R. Briill, G. van Doremaele, Interactive liquid chromatography of olefin-based elastomers, LC-GC Eur. 25 (2012) 352–358.
[53] N.C. Megoulas, M.A. Koupparis, Twenty years of evaporative light scattering detection, Crit. Rev. Anal. Chem. 35 (2005) 301–316.
[54] L.-E. Magnusson, D.S. Risley, J.A. Koropchak, Aerosol-based detectors for liquid chromatography, J. Chromatogr. A 1421 (2015) 68–81.
[55] M. Righezza, G. Guiochon, Effects of the nature of the solvent and solutes on the response of a light-scattering detector, J. Liq. Chromatogr. 11 (1988) 1967–2004.
[56] K. Rissler, High-performance liquid chromatography and detection of polyethers and their mono (carboxy) alkyl and-arylalkyl substituted derivatives, J. Chromatogr. A 742 (1996) 1–54.
[57] R. Schultz, H. Engelhardt, The application of an evaporative light scattering detector in polymer analysis, Chromatographia 29 (1990) 517–522.
[58] X. Jiang, V. Lima, P.J. Schoenmakers, Robust isocratic liquid chromatographic separation of functional poly (methyl methacrylate), J. Chromatogr. A 1018 (2003) 19–27.
[59] V. Mass, V. Bellas, H. Pasch, Two-dimensional chromatography of complex polymers, 7—detailed study of polystyrene-block-polyisoprene diblock copolymers prepared by sequential anionic polymerization and coupling chemistry, Macromol. Chem. Phys. 209 (2008) 2026–2039.

4.2 Separation of oxidized waxes according to polarity using high temperature solvent and thermal gradient interaction chromatography and HT-2D-LC.

The oxidation of waxes is a non-homogenous process. Several techniques are used to determine the number of oxidized functionalities. These include acid and saponification number determination, FTIR and ^{13}C-NMR. However, these techniques give average values of oxidation or functionalization. It is shown here for the first time that separation of oxidized wax from non-oxidized wax through tailored high-temperature interaction chromatography can be conducted in solvent gradient (HT-SGIC) and thermal gradient (HT-TGIC) modes. Three model wax samples with different degrees of oxidation are used for the chromatographic separations on a polar silica-based stationary phase.

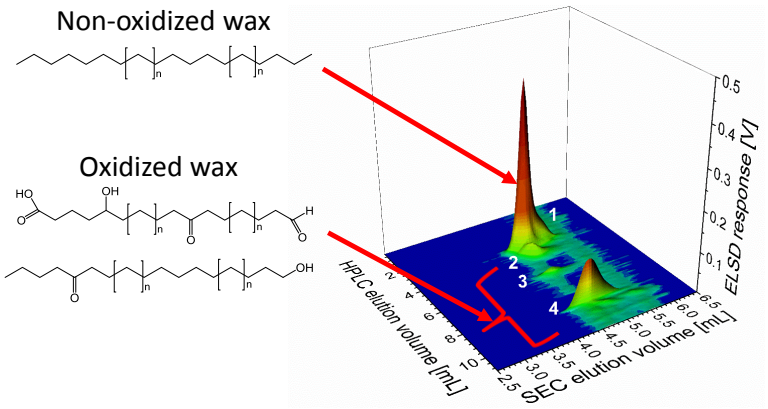


Figure 4.2 3D contour plot generated from HT-2D-LC analysis of an oxidized wax showing the separation of wax chains in the first dimension according to polarity and in the second dimension according to molar mass. Peak 1 is not retained while peaks 2-4 are retained due to oxidized functionality content.

By manipulating column temperature and gradient conditions, chromatographic separation with good resolution is achieved. Furthermore it is shown that HT-TGIC separations can be obtained in which a solvent mixture of 90% decane and 10% cyclohexanone is used as the mobile phase in isocratic mode. HT-SGIC and HT-TGIC provide different types of separation although in both scenarios differences in functionality play a major role.

analytical chemistry

Article

Cite This: *Anal. Chem.* 2018, 90, 7626−7634

pubs.acs.org/ac

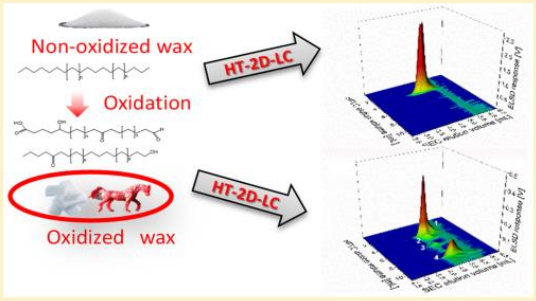
Comprehensive Analysis of Oxidized Waxes by Solvent and Thermal Gradient Interaction Chromatography and Two-Dimensional Liquid Chromatography

Anthony Ndiripo and Harald Pasch*

Department of Chemistry and Polymer Science, University of Stellenbosch, 7602 Matieland, South Africa

Supporting Information

ABSTRACT: This report addresses the comprehensive analysis of oxidized/functionalized polyethylene waxes according to chemical composition and molar mass by selective chromatographic methods. For the first time, tailored high-temperature interaction chromatography in solvent gradient (HT-SGIC) and thermal gradient (HT-TGIC) modes are used for the chemical composition separation of these materials. Separation protocols are developed using three model wax samples with different degrees of oxidation. For the chromatographic separations polar silica gel is used as the stationary phase. Solvent gradients of decane and cyclohexanone are used in HT-SGIC at 110 °C to separate the bulk waxes into several heterogeneous fractions according to polarity and the type of functionality. Column temperature and gradient manipulation are shown to influence chromatographic resolution and retention. The HT-SGIC investigations are complemented by HT-TGIC separations where a solvent mixture of decane and cyclohexanone is used as the mobile phase in isocratic mode. It is shown that HT-SGIC and HT-TGIC provide different types of separation, however, both are predominantly based on differences in functionality. To provide comprehensive information on chemical composition (functionality) and molar mass, HT-SGIC and HT-TGIC are coupled to HT-SEC, using ortho-dichlorobenzene as the second dimension mobile phase. Clear differences between oxidized and nonoxidized waxes are detected in HT-2D-LC providing comprehensive information on the molecular heterogeneity of these materials.



Oxidized/functionalized waxes possess superior properties as compared to the linear nonfunctionalized alkanes from which they are derived. The introduction of oxygen or other polar functionalities gives rise to better adhesion,[1] solubility in polar media, solvent retention capacity, compatibility with inorganic materials (e.g., colorants),[2] and even the ability to mimic the properties of natural waxes. These added properties are due to oxygen functionalities interacting via hydrogen bonds, permanent polar interactions, as well coordinative bonds. One of many ways of introducing polar groups is through controlled oxidation achieved by bubbling air/oxygen through molten wax.[3,4] Low molar mass waxes can also be obtained by copolymerizing ethylene or grafting polyethylene with maleic anhydride (MA).[5−7]

The oxidation of polyolefins is a statistical process and, therefore, the products exhibit molar mass and functionality type distributions, and in some cases branching and branch type distributions. These distributions are often dependent on each other and make it virtually impossible to fully characterize such materials using one single technique.

Gas chromatography (GC) has been largely employed to separate and characterize waxes with very low molar masses (paraffin waxes).[8−13] Limitations to its use arise when the waxes have increased molar masses (polyethylene waxes) and when oxygen functionalities are introduced. Even higher operating temperatures for the GC may be inadequate for comprehensive separation and analysis.

Liquid chromatography (LC) is an important alternative method since virtually any soluble material can be analyzed with the added advantages of shorter experimental times, lower operating temperatures and multiple operation modes. Size exclusion chromatography (SEC) has been explored for the separation/characterization of low molar mass waxes,[14,15] but it is clear that this mode of LC does not provide any information regarding differences in functionality distribution unless coupled to information-rich detectors such as Fourier transform-infrared spectroscopy (FT-IR). Still, the distributions obtained from SEC tend to give average values of oxidation as oxidized and nonoxidized waxes coelute in the event of similar hydrodynamic volumes.

Liquid interaction chromatography (IC) or liquid adsorption chromatography (LAC) have been used by Macko and Pasch[16−18] to separate high molar mass polyolefins. Polyolefins and polyolefin waxes are insoluble in most solvents at ambient

Received: April 2, 2018
Accepted: May 29, 2018
Published: May 29, 2018

DOI: 10.1021/acs.analchem.8b01480
Anal. Chem. 2018, 90, 7626−7634

temperatures and require elevated temperatures (up to 160 °C). As a detector system, the evaporative light scattering detector (ELSD) has been largely employed in work related to polyolefin separations due to its ability to work under solvent gradient interaction chromatography (SGIC) conditions.[18−25] However, for low molar mass waxes, lower ELSD temperatures are required for better detection. Separation of polar polyolefins using the ELSD has been reported in several studies[26−29] and detailed information regarding the solvent influence on detection is given.[26]

Recently, as an alternative to SGIC, high temperature-thermal gradient interaction chromatography (HT-TGIC) has been developed for high molar mass polyolefins.[30−33] The technique enables the use of solvent sensitive detectors such as the infrared detector (IR)[32] since isocratic solvents/solvent mixtures are used. A multidetector approach can be used to obtain more structural information on the given sample.

Other methods that are established as standard techniques for polyolefin analysis include differential scanning calorimetry (DSC)[5,34] and crystallization analysis fractionation (CRYSTAF).[35] These techniques offer a wealth of information when used to analyze high molar mass polyolefins although CRYSTAF and DSC fall short when it comes to amorphous/soluble random copolymers. In addition to the low molar mass nature of waxes, the introduction of polar functionalities makes it virtually impossible to separate heterogeneous fractions via crystallization-based methods such as CRYSTAF, crystallization elution fractionation (CEF) and temperature rising elution fractionation (TREF). This is primarily because the solubility of the waxes in TCB/ODCB is very good despite having considerably long crystallizable ethylene sequences in their molecular structures. SGIC and TGIC do not have these limitations and, therefore, this paper is dedicated to the use of these methods for the separation of oxidized waxes according to functionality followed by coupling to HT-SEC for comprehensive HT-2D-LC to provide functionality vs molar mass information.

■ EXPERIMENTAL SECTION

Materials. Three waxes (designated as No. 1, No. 2, and No. 3) were used for the present study. Wax No. 1 is the starting material obtained from Sigma-Aldrich, South Africa, from which oxidized waxes No. 2 and No. 3 were derived by passing oxygen through a melt of wax No. 1 for different times. Narrowly distributed polystyrene standards were obtained from Agilent (U.K.). Narrow dispersity polyethylene standards (D = 1.00−1.31) were sourced from Polymer Standards Service GmbH (PSS, Mainz, Germany) for SEC calibration.

Solvents. 1,2-Dichlorobenzene (ODCB, 99.0% HPLC grade), cyclohexanone (99.8%), decane (99.0% anhydrous grade), and 1,2,4-trichlorobenzene (TCB, 99% ReagentPlus grade) were purchased from Sigma-Aldrich (now Merck). With the exception of TCB, which was distilled before use, all other solvents were used as received.

Size Exclusion Chromatography. Molar masses and molar mass dispersities of the wax samples were determined on a PL-GPC 220 High Temperature Chromatograph. Further details are given in the Supporting Information.

Fourier Transform-Infrared Spectroscopy. Attenuated total reflectance (ATR) measurements of the waxes and their fractions were recorded on a Thermo Nicolet iS10 spectrometer. Further details are given in the Supporting Information.

Differential Scanning Calorimetry. The wax samples were analyzed using the Q100 DSC system. Further details are given in the Supporting Information.

Crystallization Analysis Fractionation. A commercial CRYSTAF apparatus model 200 (PolymerChAR, Valencia, Spain) was used for crystallization analysis fractionation experiments. Further details are given in the Supporting Information.

High-Temperature High-Performance Liquid Chromatography. All chromatographic experiments were performed on a solvent gradient interaction chromatograph (SGIC) instrument constructed by PolymerChAR (Valencia, Spain). For solvent gradient elution in HPLC, a high-pressure binary gradient pump (Agilent, Waldbronn, Germany) was utilized. The evaporative light scattering detector [ELSD, model PL-ELS 1000, Polymer Laboratories, Church Stretton, U.K. (now Agilent)] was used.

Solvent Gradient Interaction Chromatography. A silica column (Nucleosil, Macherey-Nagel, Düren, Germany) with 250 × 4.6 mm^2 length and internal diameter packed with silica particles of 5 μm and pore size of 300 Å was used. The mobile phase flow rate used was 0.5 mL min^{-1}. The ELSD settings used were as follows: a gas flow rate of 0.5 SLM, 140 °C nebulizer temperature, and an evaporative temperature of 200 °C. Sample concentrations of 2 mg mL^{-1} were used, and 50 μL of each sample were injected. All samples were prepared for injection in decane.

High-Temperature Thermal Gradient Interaction Chromatography. The PolymerChAR SGIC instrument was also used for HT-TGIC experiments. The silica column described above was used for all the experiments. All valve switches in the first dimension, sample injection, and temperature programing were done manually. Sample injection was done with a flow of 0.05 mL min^{-1} at 140 °C. The sample was allowed to move to the column from the injection loop at a flow rate of 0.05 min mL min^{-1} for 3 min. The oven containing the column was then cooled at a rate of 5 °C min^{-1} to 30 °C and kept isothermally for 15 min at 0.05 mL min^{-1} flow. The flow rate was increased to 0.5 mL min^{-1} after 40 min of sample injection and a temperature gradient of 0.5 °C min^{-1} was applied after 45 min. A schematic description is also given in Figure S1 (Supporting Information). The injection loop was housed in a separate oven which was kept at 140 °C. A volume of 50 μL of a 2 mg mL^{-1} sample dissolved in decane were injected.

Collection of Fractions Using the LC-Transform Interface and FT-IR Analysis. A LC-transform series model 303 (Lab Connections) was coupled to the PolymerChAR SGIC instrument, in order to collect the HPLC and TGIC eluates. For each sample, 200 μL was injected from 2 mg mL^{-1} solutions. The outlet of the chromatographic column was connected to the LC-transform interface through a heated transfer line set at 140 °C. The fractions were deposited by rotating a germanium disc (sample target in the LC-transform) at a speed of rotation of 10° min^{-1}. The disc stage and nozzle temperatures of the LC-transform were set to 140 °C. The disc with the dry fractions was scanned on a Thermo Nicolet iS10 spectrometer (Thermo Scientific, Waltham, MA), equipped with the LC-transform FT-IR interface which was connected to a standard transmission baseplate. Spectra were recorded at a resolution of 4 cm^{-1} with 16 scans being recorded for each spectrum. The speed of disc rotation during scanning was set at 3° min^{-1}.

DOI: 10.1021/acs.analchem.8b01480
Anal. Chem. 2018, 90, 7626−7634

Table 1. Molar Mass Data and Carbonyl Contents of Waxes No. 1, No. 2, and No. 3

wax	M_p[a] (kg mol^{-1})	M_n[a] (kg mol^{-1})	M_w[a] (kg mol^{-1})	M_p[b] (kg mol^{-1})	M_n[b] (kg mol^{-1})	M_w[b] (kg mol^{-1})	D[b]	carbonyl cont.[c]
No. 1	1.54	1.07	1.93	0.80	0.59	1.06	1.8	0
No. 2	1.24	0.75	2.00	0.66	0.43	0.94	2.2	low
No. 3	1.10	0.78	1.67	0.59	0.45	0.82	1.8	high

[a]Polystyrene equivalent molar mass. [b]Polyethylene equivalent molar mass. [c]Based on ratio of absorbance of carbonyl functionalities to those of methylene groups (CO/CH_2) obtained from FT-IR.

High-Temperature Two-Dimensional Liquid Chromatography (HT-2D-LC). HT-HPLC was coupled to fast HT-SEC with the aid of an electronically controlled eight-port valve system (VICI Valco Instruments, Houston, TX) equipped with two 100 μL sample loops. Injection into the first dimension (HT-HPLC) was carried out using a 200 μL sample loop and the flow rate was 0.05 mL min^{-1}. A similar gradient as in the one-dimensional HT-HPLC analyses was used in the first dimension and three times the concentration of the sample was used (i.e., 6 mg mL^{-1}). A flow rate of 3.25 mL min^{-1} was used in the second dimension (HT-SEC), and ODCB was used as the mobile phase. In the second dimension, a PL Rapide M (Agilent, U.K.) 100 × 10 mm^2 internal diameter column with a 10 μm particle diameter was used at 140 °C. The evaporative light scattering detector was used with the following parameters: gas flow rate of 1.5 SLM, 140 °C nebulizer temperature, and an evaporative temperature of 230 °C.

■ RESULTS AND DISCUSSION

This study explores the capabilities of solvent gradient interaction chromatography (SGIC) and high-temperature-thermal gradient interaction chromatography (HT-TGIC) for the separation and analysis of oxidized/functionalized waxes according to functionality. To the best of our knowledge, up until now such method development has not been carried out and separations of functionalized waxes according to functionality have been limited to high-temperature-gas chromatography (HT-GC). A nonoxidized wax (No. 1) from which the two other waxes having increasing oxidation levels were obtained (No. 2 and No. 3, respectively) are subject to investigation in this work.

Bulk Analyses. Established techniques of polyolefin analysis may provide limited information regarding molecular heterogeneity of the wax samples. Figure S2 (Supporting Information) presents the results obtained by analyzing waxes Nos. 1, 2, and 3 with CRYSTAF, DSC, and SEC, respectively. The detailed experimental details of these techniques are given in the Supporting Information.

CRYSTAF provides information regarding the presence of crystallizable fractions in the samples. This information can be correlated to the chemical composition distribution (branching or functionality type distributions). The combination of the low molar mass nature of waxes and the use of good solvents (TCB or ODCB) renders this technique impractical especially for oxidized waxes. As clearly illustrated in Figure S2, the majority of the sample components do not crystallize at the given conditions. In addition, the solubility of the waxes increases with increasing oxidation levels, see Table 1. Useful information can only be obtained for the crystallizable parts of the samples which is low for all samples. Thermal properties in solid/melt state were determined using DSC (see Figure S2). While the thermograms show some differences in the melting and crystallization behaviors, very little information can be deducted on the influence of oxidation, apart from the change in crystallinity. However, the differences in crystallinity for waxes No. 2 and No. 3 are rather negligible and do not reflect the increasing degree of oxidation.

The molar mass distribution curves as detected by refractive index detector (RI) are presented in Figure S2. Research on the use of SEC for the separation of polyolefin oligomers has largely been limited to low molar mass oligomers which are soluble at ambient temperatures to about 80 °C.[14,15,36] The oligomers studied in these works are derived from a variety of sources and consist of linear and branched *n*-alkanes with 5−50 carbons in most cases. Under conventional conditions used for high molar mass polyolefins, a fundamental challenge is met. The use of columns with large pore sizes does little to separate oligomers efficiently. The lower oligomers elute in volumes close to the total permeation volumes and may coelute with additives, which makes the calculation of molar masses challenging. We shall not, however, go into the details of these challenges in this paper.

In addition to these system shortcomings, the use of polystyrene (PS) standards for standard SEC calibration overestimates the molar masses of the waxes to a significant degree. To illustrate this, the molar mass properties of the waxes are presented for both PS and polyethylene (PE) calibrations, see Table 1. For example, the peak molar masses (M_p) of the waxes determined using a PE calibration are approximately half of those determined when a PS calibration is used.

A simple and fast tool to follow the changes in the chemical composition of waxes is FT-IR. The spectra of the waxes are shown in Figure S3 (Supporting Information). Of interest are the changes in the carbonyl region (1850−1650 cm^{-1}) which indicate the formation of oxidized functionalities (ketones, aldehydes, esters, lactones etc.). The change in the oligomer chain chemistry occurs randomly and throughout the chains resulting in a complex array of absorbances being observed in the 1400−650 cm^{-1} region. Primary and secondary alcohols are also likely to be formed, but in small quantities and are, therefore, less detectable in bulk waxes.

From Figure S3 (Supporting Information), it can be clearly seen that wax No. 1 does not have carbonyl functionalities while waxes No. 2 and No. 3 have increasing amounts of carbonyl absorbances, see also insert in Figure S3. It is known that the absorbances of carbonyl functionalities do not linearly correlate to their concentration increase and this makes FT-IR quantification rather less ideal for such purposes.[37−40] However, for the purpose of this study, we found FT-IR to be beneficial in differentiating the three waxes.

Chromatographic Separation According to Carbonyl Functionalities. *High-Temperature Solvent Gradient Interaction Chromatography.* Solvent gradient interaction chromatography (SGIC) is known to be a suitable tool for the separation of complex polymers according to chemical composition. This also includes the separation with regard to functional groups. In the present study, high-temperature SGIC

DOI: 10.1021/acs.analchem.8b01480
Anal. Chem. 2018, 90, 7626−7634

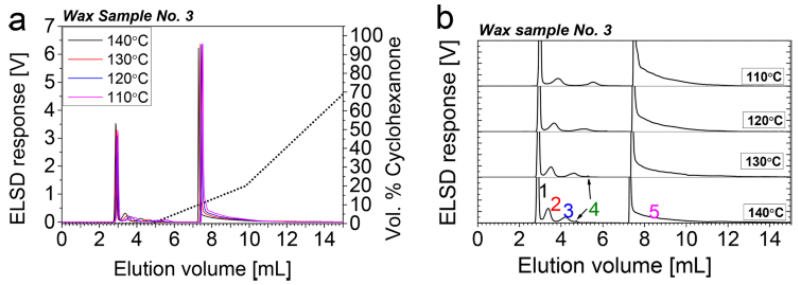


Figure 1. Overlays of the elugrams obtained from the gradient elution of wax No. 3 from a silica stationary phase at different column temperatures (a) and a stack plot of the same elugrams (b). The injection loop was maintained at 140 °C. Detector: ELSD. (The dotted line represents the gradient at the detector.)

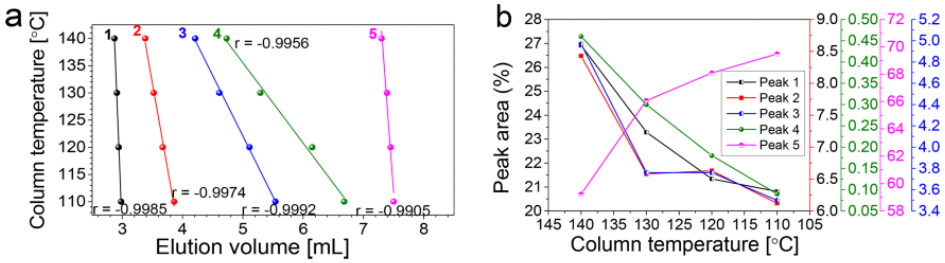


Figure 2. Relationship between the column temperature and the peak elution volumes of eluting fractions as detected by the ELSD detector (a); relationship between peak area and column temperature as obtained from the elugrams of wax No. 3 (b).

shall be used to separate the oxidized waxes according to the degree of oxidation. Most importantly, nonoxidized macromolecules shall be separated from oxidized macromolecules bearing different numbers of carbonyl groups.

Several solvent combinations were tested as mobile phases on a polar silica-based stationary phase at elevated temperature (up to 140 °C). It was found that low polarity solvents, which are good solvents for polyolefins, do not promote adsorption onto the silica stationary phase. These solvents include decalin, ODCB, and TCB, which have been used successfully with functionalized high molar mass polyolefins previously.[26,27] On the other hand, it was found that linear hydrocarbon solvents are better adsorption promoting solvents. Decane was particularly suitable when used in combination with 1-decanol or cyclohexanone. The combination of its low polarity and the high boiling point (174.1 °C) made it the solvent of choice for solvent gradient elution at high temperature.

Polar solvents are typically used to desorb the analyte macromolecules from the stationary phase. Prospective solvents which are thermally stable at high temperatures include alcohols (e.g., 1-decanol) and cyclic ketones (e.g., cyclohexanone). The use of 1-decanol in the solvent gradient resulted in an increase in backpressure at lower column temperatures (approximately 110 °C) due its high viscosity. Therefore, cyclohexanone remained a good alternative due to its lower viscosity as compared to 1-decanol.

Ideally, if a solvent gradient is used, the adsorption promoting solvent is allowed to flow in isocratic mode for at least one column volume so that any components that are not retained elute in SEC mode. However, this part of the solvent gradient method must be kept reasonably short to prevent very long experiments in cases where the development of a two-dimensional method is required. Usually, the column void volume and the system dwell volume of the chromatographic system provide sufficient delay for isocratic elution. This is a simple approach to separating a mixture of polar and nonpolar material in an analyte.

Wax No. 3 was subjected to the solvent gradient shown in Figure 1a. It was observed that at 140 °C, the analyte eluted in several peaks, with the majority of the sample being retained and eluting in the course of the gradient. Decreasing the temperature of the column resulted in a better separation of the early eluting peaks, see Figure 1b. Lowering the column temperature increases adsorptive interactions of polar material with the stationary phase leading to larger elution volumes.

The first eluting peak (peak 1) corresponds to nonpolar material that elutes in SEC mode which means that at the given column temperatures the separations are entropy-based and adsorption is not dominating. Lowering the column temperature increases the elution volume of the peak insignificantly but decreases the peak area because at lower column temperatures adsorption gets stronger and more material is adsorbed. The peak elution volumes and the peak areas are summarized in Tables S1 and S2 (Supporting Information).

For our system, a void volume of 2.90 mL was measured using a low molar mass PS (M_w = 0.707 kg mol^{-1}) which was dissolved in TCB. The dwell volume was determined by a linear gradient applied from pure TCB to TCB containing 0.3 mg mL^{-1} of PS (M_w = 0.707 kg mol^{-1}). This was found to be 1.9 mL. Therefore, the gradient reaches the detector at 4.8 mL. Thus, peak 2 does not elute in SEC mode, but the oligomers in this fraction are weakly adsorbed on the stationary phase. Accordingly, its elution volume increases with decreasing column temperatures as can be seen in Figure 2a. The increase in the V_e of peak 2 is accompanied by peak broadening as the

DOI: 10.1021/acs.analchem.8b01480
Anal. Chem. 2018, 90, 7626−7634

column temperature decreases. These changes are indicative of stronger polar interactions.

The most significant change in the V_e is observed for peaks 3 and 4. Both peaks also show some peak broadening although the resolution between these peaks increases. Peak 4 is the smallest fraction which becomes almost undetectable with the ELSD due to peak broadening. The elution of peak 5 to a large extend is influenced by the presence of cyclohexanone in the mobile phase. Therefore, the peak onset and V_e do not significantly change with a decrease in the column temperature. However, the slight shift in V_e can be linked to an increase in adsorption, which requires slightly more cyclohexanone to elute. In addition to these observations, it was found that the peak area of fraction 5 increases from approximately 59% to about 69%, see Figure 2b. The combination of a decrease in the peak areas of fractions 1–4, and an increase in the peak area of fraction 5 is a strong indication of more material being adsorbed as the column temperature is decreased. Decreasing the column temperature to below 110 °C can yield better separations, but this poses significant challenges when samples are mixtures of oligomers and higher molar mass polyolefins. Higher molar mass polyolefins require higher column temperatures to stay in solution, especially in poor solvents such as decane.

Two important observations are made for the present samples. First, the separation of fractions 1–4 is enhanced with a decrease in the column temperature. Second, the elution of fraction 5 is influenced mostly by the gradient, and only the manipulation of the gradient can enhance the separation. The manipulation of the gradient improves the separation of fraction 5. Reducing the slope of the second segment of the gradient (4.8–9.8 mL) to allow cyclohexanone to increase by 4% and then rapidly increasing the cyclohexanone content to 100% results in two more fractions being obtained. This effect of the gradient on the separation of wax No. 3 is illustrated in Figure 3.

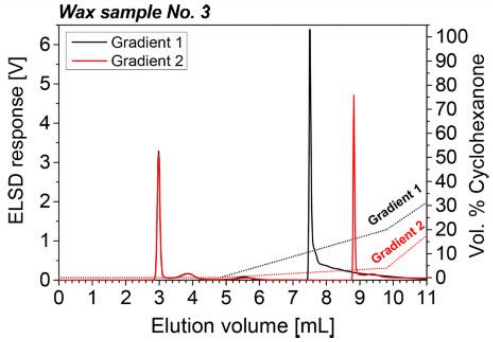


Figure 3. Overlays of elugrams of wax No. 3 at two different solvent gradients. The column temperature was kept at 110 °C in both experiments.

The established gradient and column conditions were used to analyze the three wax samples, and the elugrams are shown in Figure 4. The unmodified wax (No. 1) elutes mainly in SEC mode with the different molar mass fractions being visible at elution volumes of 1.8–4.0 mL. The small peak at approximately 8.6 mL is an artifact and due to the solvent gradient.

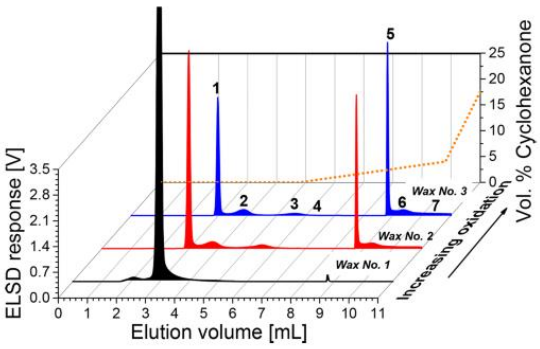


Figure 4. Overlays of chromatograms of waxes No. 1, No. 2, and No. 3 obtained using the optimized solvent gradient (see Figure 3) at a column temperature of 110 °C.

Waxes No. 2 and No. 3 elute with similar peak characteristics. However, subtle differences in the elution profiles of these samples can be seen when their elugrams are overlaid as shown in Figure 5a.

First, the first peak reduces as the oxidation level of the wax increases. This is expected as more wax molecules become oxidized and are retained longer due to stronger interactions with the stationary phase. To better illustrate the differences, the peak areas from the chromatograms of waxes No. 2 and 3 were integrated and expressed as a percentage of the total elugram area. The peak areas are compared in Figure 5b and Table S3 (Supporting Information). The most significant change is seen in peak 1, see Figure 5b, where the peak area decreases from 50.13 to 36.40%. This is attributed to the increase in the oxidized functionalities which results in a larger fraction of the wax being retained on the stationary phase.

In a next step, the fractions were identified as they eluted from the column. In the present case this was achieved via coupling of HPLC to FT-IR via the LC-transform interface. The analyses of fractions of wax No. 3 are shown in Figure S4 (Supporting Information). Although this is a very challenging approach, useful information can be obtained regarding the fractions' chemical compositions.

Figure S4 was generated automatically from a series of spectra obtained from scanning a germanium disc with deposited wax fractions. Correlation of the SGIC elution volume with the rotation time of the disc gives an orthogonal relationship which can be presented as a contour plot. Alternatively, spectra can be picked from the series at selected disc rotation angles to show the chemical composition of the material deposited at those locations, and such spectra are shown in Figure 6.

Of particular interest is the presence or absence of carbonyl functionalities or other functionalities that reflect oxidation. From Figure S4 (Supporting Information), it is observed that the first three eluting peaks appear to be not oxidized as seen by the absence of carbonyl functionalities. The elution of the first peak may be reasonable under these circumstances, but the elution of the second and third peak is well outside the total permeation volume of the column which implies there are some interactions of some sort. The oxidized functionalities within these fractions may go undetected due to their minute quantities. This would be particularly relevant for hydroxyl

DOI: 10.1021/acs.analchem.8b01480
Anal. Chem. 2018, 90, 7626–7634

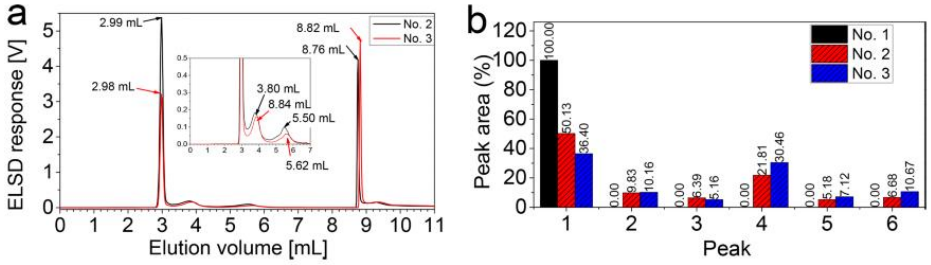


Figure 5. Comparison of the elugrams of waxes No. 2 and No. 3 (a) and graphical representation of the percentage peak areas of the samples including wax No. 1 (b).

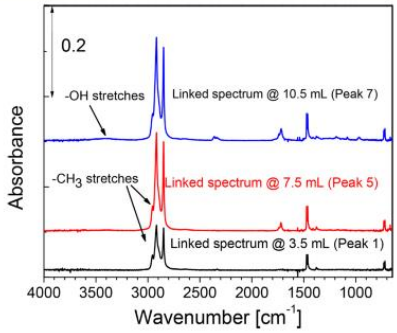


Figure 6. Stacked plots of linked FT-IR spectra at elution volumes of 3.5, 7.5, and 10.5 mL obtained from the coupling of HT-SGIC and FT-IR via the LC-transform interface for sample No. 3.

functionalities that have a significantly lower absorption coefficient than carbonyl functionalities.

Carbonyl functionalities only appear to be visible from the fourth peak, see Figure 6 and Figure S4 (Supporting Information). Later eluting peaks exhibit complex FT-IR spectra in the region of 1500–950 cm^{-1}. This is indicative of complex wax chain microstructures. Absorbances due to hydroxyl functional groups (3600–3250 cm^{-1}) become more visible. The hydroxyl functionalities are not seen in the bulk materials ATR-FTIR analyses as a result of their minute quantities.

High-Temperature Thermal Gradient Interaction Chromatography. The use of thermal gradient interaction chromatography (TGIC) based on using single solvents or isocratic binary mobile phases paves a way for the use of other sensitive detectors complementary to the ELSD, such as infrared (IR) detectors, refractive index detectors (RI), and differential viscometers that cannot be used in solvent gradient applications.[30] The application of TGIC on the silica stationary phase is particularly interesting for high temperature applications since the mechanisms of such separations are not quite yet understood. For the present study, the fundamentals of the adsorption/desorption mechanisms are not under investigation but rather the elution behavior of the oxidized waxes and the ability to separate them according to functionality.

Figure 7 shows the elution behavior of waxes No. 1, No. 2, and No. 3 as well as three PE standards (703, 1180, and 2030 g mol^{-1}) under TGIC conditions. The mobile phase used was a mixture of 90% decane and 10% cyclohexanone.

Nonoxidized wax No. 1 elutes in two peaks, the first being narrow in its elution profile. This was attributed to material which does not crystallize or adsorb onto the stationary phase after injection. This is indicative of material that is soluble in the decane/cyclohexanone mixture at 30 °C. Low molar mass oligomers are soluble even at temperatures below ambient. The second peak is broad and elutes at higher temperatures, which proves that the mechanism of separation is by precipitation/crystallization onto the stationary phase. Unlike porous graphitic carbon, used as Hypercarb, silica does not retain nonpolar polyolefins. However, if the injected solution is allowed to crystallize in a poor solvent such as in our case, the polymer is retained. At low temperatures, polyolefins rearrange from the linear (easy to adsorb form) to compact crystallized structures. It must also be noted that all solvents used in our TGIC method are poor solvents of polyolefins (i.e., 90% decane and 10% cyclohexanone).

The elution profiles of the samples exhibit two main elution regions at 40–45 min and 50–60 min. The first elution region shows three distinct peaks, peak 1 being characteristic for all three samples while peaks 2 and 3 only appear in the oxidized samples. Accordingly, peak 1 is tentatively assigned to nonoxidized material while peaks 2 and 3 are assigned to oxidized species, therefore, proving that HT-TGIC is capable of separation according to the degree of oxidation.

In the second elution region, all three samples exhibit elution peaks, see Figure 7c. This means that in this region separation is not according to oxidation. Here, it is suspected that crystallizable material is eluting that becomes soluble only at higher TGIC temperatures. The presence of crystallizable material has been indicated by the CRYSTAF and DSC results shown in Figure S2.

In order to verify the assumption that the fractionation is influenced by crystallization, three low molar mass PE standards were analyzed under similar conditions. Figure 7d shows the TGIC profiles of PEs 703, 1180, and 2030 g mol^{-1}, respectively. It is clear that some material is soluble at ambient conditions while higher molar mass components elute only at higher temperatures caused by the higher crystallizability of these components. A comparison of wax No. 1 to PEs 1180 and 2030 g mol^{-1} is made in Figure 7e. The influence of molar mass is evident; an increase in the molar mass of the PE materials (M_p for wax No. 1 = 800 g mol^{-1}) increases the elution temperature.

Wax No. 3 was used to verify the separation mechanism of the TGIC method. From the series of spectra obtained, four linked spectra are shown in Figure 8. A two-dimensional plot constructed from the HT-TGIC-FT-IR spectra is also shown in Figure S5 (Supporting Information). It is noticed that the

DOI: 10.1021/acs.analchem.8b01480
Anal. Chem. 2018, 90, 7626–7634

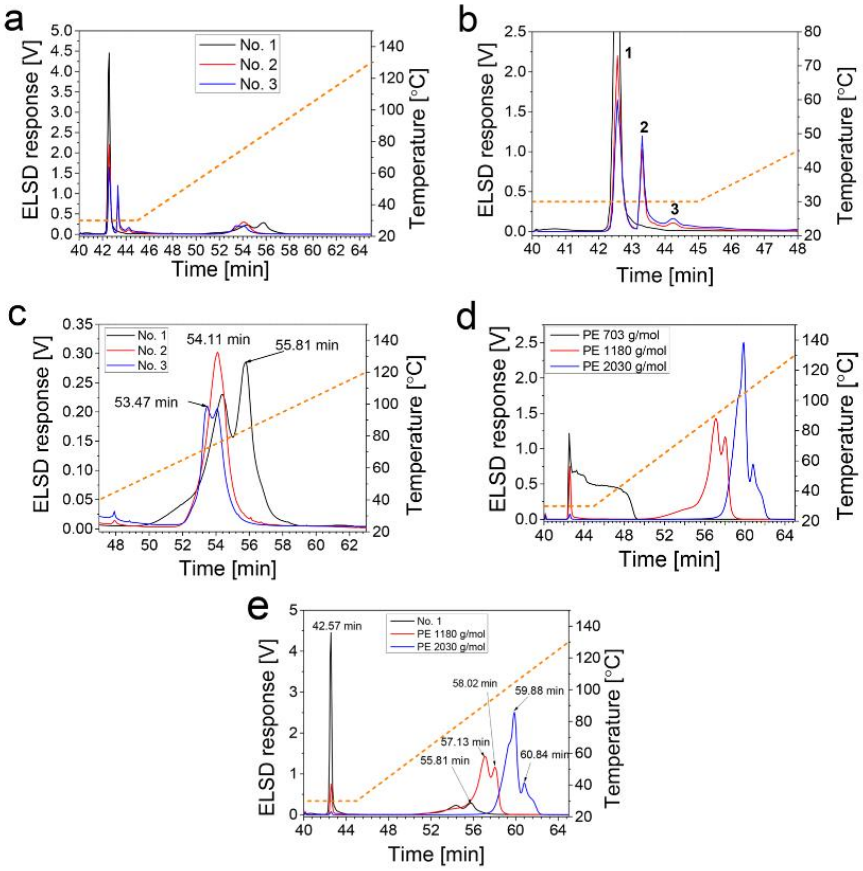


Figure 7. Elugrams of TGIC of waxes No. 1, 2, and 3, mobile phase 90/10% decane-cyclohexanone (v/v) (a); elution regions of 40–48 min and 47–63 min in (b and c); PEs 703, 1180, and 2030 g mol^{-1} standards (d); PEs 1180, 2030 g mol^{-1} compared to wax No. 1 (e).

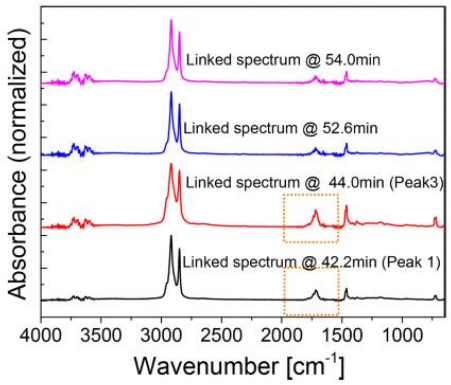


Figure 8. Stacked plots of linked FT-IR spectra at elution times of 42.2, 44.0, 52.6, and 54.0 min obtained from the coupling of HT-TGIC and FT-IR via the LC-transform interface for sample No. 3. The rectangles (dotted orange lines) indicate the carbonyl regions of fractions at 42.2 and 44.4 min.

highest intensity of carbonyl functionalities is observed for peaks 2 and 3 of the first elution region (see dotted orange rectangles in Figure 8 and circled area in Figure S5). Furthermore, methyl stretch absorbances (indicated by the arrow in Figure S5) confirm shorter oligomer chains. Carbonyl functionalities appear to be distributed over the complete elution range. The fact that they have different intensities indicates some functionality type separation. However, this separation is influenced by the crystallinity of the material that is a function of molar mass and functionality.

Two-Dimensional Liquid Chromatography. SGIC separates the samples according to functionality but not molar mass. Molar mass information on the different fractions, however, can be obtained by comprehensive 2D-LC where SGIC (or TGIC) are used in the first dimension and SEC is used in the second dimension. In Figure 9a,b, the contour plots obtained from the 2D-LC analysis of wax No. 1 with SGIC in the first dimension are presented.

Due to the fact that this sample is nonpolar and does not have any carbonyl functionalities, it elutes in SGIC mode in the first dimension before the solvent gradient starts. Therefore, a narrow elution range between 2.8 and 4.6 mL HPLC elution volume is seen (vertical direction). In the horizontal direction, the SEC separation is presented and it is seen that the sample exhibits a quite broad elution profile between 2.8 and 5.0 mL SEC elution volume.

DOI: 10.1021/acs.analchem.8b01480
Anal. Chem. 2018, 90, 7626–7634

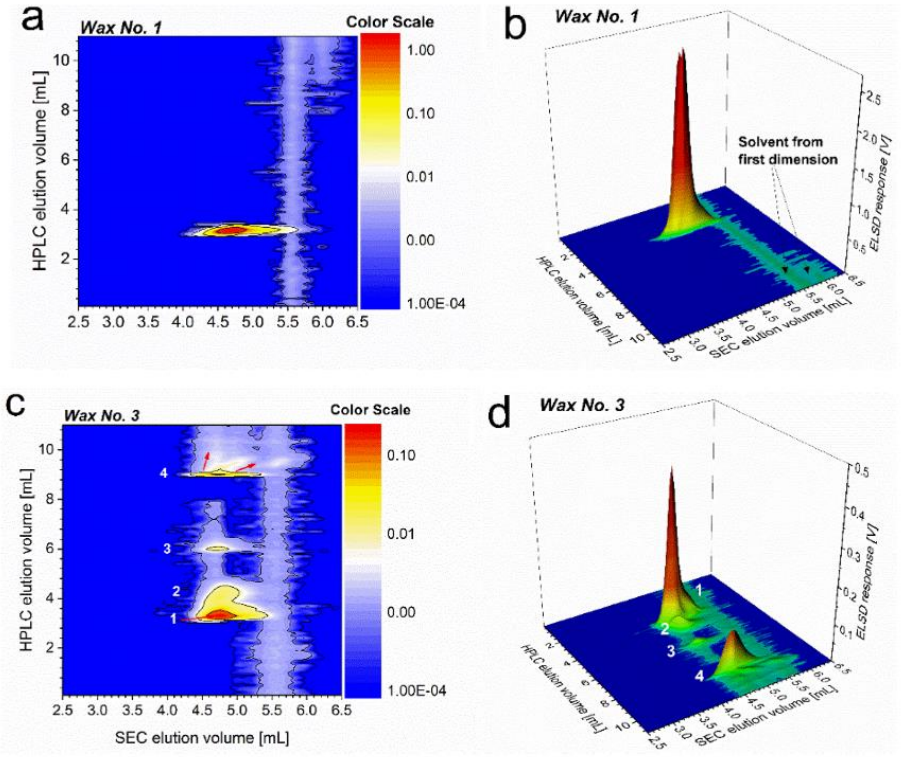


Figure 9. 2D and 3D contour plots for waxes No. 1 (a and b) and No. 3 (c and d) obtained by SGIC in the 1st dimension. 1st dimension flow = 0.05 mL min^{-1}; column temperature = 110 °C; 2nd dimension flow = 3.25 mL min^{-1}; 2D valve switching interval = 120 s; 2nd dimension column temperature = 140 °C; 2nd dimension solvent = 1,2-dichlorobenzene (ODCB).

Compared to the nonoxidized sample (Figure 9a,b), the 2D-LC results of oxidized sample No. 3 show a much more complex composition (Figure 9c,d). Four different components can be identified easily that agree well with peaks 1−4 in Figure 4. Peaks 5 and 6 cannot be seen due to their low intensities. These components correspond to nonoxidized species in peak 1 and species with different degrees of oxidation in all other peaks. For all those peaks molar mass information can be obtained from the SEC separation in the second dimension.

■ CONCLUSION

High-temperature liquid chromatography is presented as a unique and viable alternative to gas chromatography for the separation of oxidized/functionalized polyethylene waxes. For the first time, the separation of heterogeneous fractions in oxidized waxes with high-temperature solvent gradient interaction chromatography (SGIC) under tailored conditions of analysis was presented. The use of temperature gradient interaction chromatography (TGIC) as an additional method to SGIC in the fast characterization of oxidized waxes by liquid chromatography was also demonstrated.

Three waxes with different oxidation levels were studied. Separation and detection of heterogeneous fractions of increasing degree of oxidation was achieved using a SGIC instrument coupled to an evaporative light scattering detector. Under SGIC conditions, decane was found to be the solvent of choice to promote adsorption onto the silica stationary phase and cyclohexanone for analyte desorption. Lower column temperatures were shown to promote adsorption and improve separation of fractions in oxidized waxes when HT-SGIC is used. The mechanism of separation was shown to involve both the number and type of oxidized functionalities. This was verified by coupling HT-HPLC to FT-IR via the LC-transform interface.

HT-TGIC was also shown to be a viable alternative to HT-SGIC, with significant room for further development as far as solvents and instrumentation are concerned. The separation mechanism in HT-TGIC was shown to be influenced both by the oxidized functionalities as well as molar mass and crystallinity.

HT-SGIC (and HT-TGIC, not shown) can be coupled to fast HT-SEC in the second dimension to produce 2D contour plots which give more details on the differences between oxidized and nonoxidized waxes as far as heterogeneous fractions are concerned.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.8b01480.

Detailed experimental methods for size exclusion chromatography, Fourier-transform Infrared spectroscopy, differential scanning calorimetry, crystallization

DOI: 10.1021/acs.analchem.8b01480
Anal. Chem. 2018, 90, 7626−7634

analysis fractionation, diagram of temperature profile and flow rate used in TGIC, bulk analyses of the three waxes by DSC, CRYSTAF and SEC, tabular information for peak elution volumes and peak areas of wax No. 3 as influenced by column temperature, and peak area comparisons of wax Nos. 1, 2, and 3, ATR-FT-IR spectra of wax Nos. 1, 2, and 3, HT-SGIC-FT-IR, and HT-TGIC-FT-IR analysis of wax No. 3 (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: hpasch@sun.ac.za.

ORCID

Anthony Ndiripo: 0000-0003-4834-3101

Harald Pasch: 0000-0003-1132-3393

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to thank the National Research Foundation of South Africa (NRF) for funding.

REFERENCES

(1) Chung, T. *Prog. Polym. Sci.* **2002**, *27*, 39−85.
(2) Reynhardt, E. *J. Phys. D: Appl. Phys.* **1985**, *18*, 1185−1197.
(3) Deckers, A.; Weber, W.; Ebisch, D. *Preparation of oxidized polyolefin waxes*. U.S. Patent 6,169,148, January 2, 2001.
(4) Deckers, A.; Kingma, A. J.; Moll, U.; Weber, W. *Oxidized metallocene-polyolefin waxes*. U.S. Patent 6,348,547, February 19, 2002.
(5) Luyt, A.; Krupa, I.; Assumption, H.; Ahmad, E.; Mofokeng, J. *Polym. Test.* **2010**, *29*, 100−106.
(6) Krump, H.; Alexy, P.; Luyt, A. *Polym. Test.* **2005**, *24*, 129−135.
(7) Roberts, T. D.; Muhlestein, K. D.; Slemons, G. T. *Process for the maleation of polyethylene waxes*. U.S. Patent 5,420,303, May 30, 1995.
(8) Lawrence, J.; Iyengar, J.; Page, B.; Conacher, H. *J. Chromatogr. A* **1982**, *236*, 401−403.
(9) Czech, F.; Fuchs, R.; Antczak, H. *Anal. Chem.* **1961**, *33*, 698−704.
(10) O'Connor, J. G.; Burow, F. H.; Norris, M. S. *Anal. Chem.* **1962**, *34*, 82−85.
(11) Regert, M.; Langlois, J.; Colinart, S. *J. Chromatogr. A* **2005**, *1091*, 124−136.
(12) Heath, D. J.; Lewis, C.; Rowland, S. J. *Org. Geochem.* **1997**, *26*, 769−785.
(13) Lu, X.; Redelius, P. *Energy Fuels* **2006**, *20*, 653−660.
(14) Carbognani, L. *J. Chromatogr. A* **1997**, *788*, 63−73.
(15) Macko, T.; Pasch, H.; Wang, Y. *Macromol. Symp.* **2009**, *282*, 93−100.
(16) Macko, T.; Pasch, H.; Denayer, J. F. *J. Chromatogr. A* **2003**, *1002*, 55−62.
(17) Macko, T.; Pasch, H.; Denayer, J. F. *J. Sep. Sci.* **2005**, *28*, 59−64.
(18) Macko, T.; Pasch, H.; Kazakevich, Y. V.; Fadeev, A. Y. *J. Chromatogr. A* **2003**, *988*, 69−76.
(19) Arndt, J.; Macko, T.; Brüll, R. *J. Chromatogr. A* **2013**, *1310*, 1−14.
(20) Cheruthazhekatt, S.; Harding, G. W.; Pasch, H. *J. Chromatogr. A* **2013**, *1286*, 69−82.
(21) Cheruthazhekatt, S.; Pasch, H. *Anal. Bioanal. Chem.* **2013**, *405*, 8607−8614.
(22) Dreux, M.; Lafosse, M.; Morin-Allory, L. *LC-GC* **1996**, *9*, 148−156.
(23) Ginzburg, A.; Macko, T.; Dolle, V.; Brüll, R. *Eur. Polym. J.* **2011**, *47*, 319−329.
(24) Megoulas, N. C.; Koupparis, M. A. *Crit. Rev. Anal. Chem.* **2005**, *35*, 301−316.
(25) Schultz, R.; Engelhardt, H. *Chromatographia* **1990**, *29*, 517−522.
(26) Albrecht, A.; Brüll, R.; Macko, T.; Pasch, H. *Macromolecules* **2007**, *40*, 5545−5551.
(27) Albrecht, A.; Brüll, R.; Macko, T.; Sinha, P.; Pasch, H. *Macromol. Chem. Phys.* **2008**, *209*, 1909−1919.
(28) Albrecht, A.; Heinz, L. C.; Lilge, D.; Pasch, H. *Macromol. Symp.* **2007**, *257*, 46−55.
(29) Prabhu, K.; Macko, T.; Brüll, R.; Remerie, K.; Tacx, J.; Garg, P.; Ginzburg, A. *J. Chromatogr. A* **2016**, *1441*, 96−105.
(30) Alghyamah, A.; Soares, J. B. P. *Ind. Eng. Chem. Res.* **2014**, *53*, 9228−9235.
(31) Al-Khazaal, A. Z.; Soares, J. B. P. *Macromol. Chem. Phys.* **2014**, *215*, 465−475.
(32) Cong, R.; Degroot, W.; Parrott, A.; Yau, W.; Hazlitt, L.; Brown, R.; Miller, M.; Zhou, Z. *Macromolecules* **2011**, *44*, 3062−3072.
(33) Greibrokk, T.; Andersen, T. *J. Chromatogr. A* **2003**, *1000*, 743−755.
(34) Hlangothi, S.; Krupa, I.; Djoković, V.; Luyt, A. *Polym. Degrad. Stab.* **2003**, *79*, 53−59.
(35) Luyt, A.; Brüll, R. *Polym. Bull.* **2004**, *52*, 177−183.
(36) Hillman, D. *Anal. Chem.* **1971**, *43*, 1007−1013.
(37) Gulmine, J. V.; Akcelrud, L. *Polym. Test.* **2006**, *25*, 932−942.
(38) Lacoste, J.; Carlsson, D.; Falicki, S.; Wiles, D. *Polym. Degrad. Stab.* **1991**, *34*, 309−323.
(39) Gugumus, F. *Polym. Degrad. Stab.* **1999**, *65*, 5−13.
(40) Khabbaz, F.; Albertsson, A.-C.; Karlsson, S. *Polym. Degrad. Stab.* **1998**, *61*, 329−342.

DOI: 10.1021/acs.analchem.8b01480
Anal. Chem. 2018, 90, 7626−7634

4.3 Comparing solvent and thermal gradient interaction chromatography for the separation of olefin plastomers/elastomers

Chromatographic separations offer the most needed tool for the chemical composition distribution (CCD) analysis of non-crystallizing polyolefins. HT-HPLC can be operated in solvent or thermal gradient interaction modes (HT-SGIC and HT-TGIC, respectively). While the use of HT-SGIC is well established with regard to polyolefin analyses, HT-TGIC has only been recently introduced. Due to the fact that both HT-SGIC and HT-TGIC can separate non-crystallizing polyolefins, the major challenge that remains is understanding their application range and separation capabilities. The present study uses a set of well-defined elastomers to compare the application range of the two modes of HT-LC. It is clearly shown that HT-SGIC has a broader separation range (26 – 100 mol% comonomer) as compared to HT-TGIC (50 – 100 mol% comonomer). In addition, a linear dependency of elution volume on ethylene content is obtained with HT-SGIC in practically the whole ethylene range, see Fig. 4.3. In the case of HT-TGIC, a linear dependency is obtained within certain ethylene content limits.

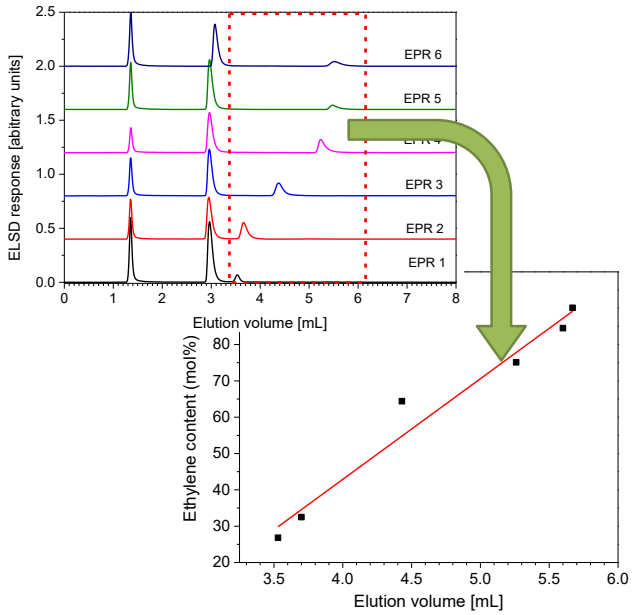


Figure 4.3 HT-SGIC elution profiles of ethylene-propylene elastomers showing the linear dependency of elution volume on ethylene content.

COMMUNICATION

Polyolefin Fractionation

Macromolecular Rapid Communications
www.mrc-journal.de

Chemical Composition Fractionation of Olefin Plastomers/Elastomers by Solvent and Thermal Gradient Interaction Chromatography

*Anthony Ndiripo, Andreas Albrecht, Benjamin Monrabal, Jingbo Wang, and Harald Pasch**

Olefin plastomers/elastomers are typically copolymers with high comonomer contents and low crystallinities. Therefore, the fractionation of these materials with crystallization-based methods is not feasible. On the other hand, solvent and temperature gradient interaction chromatography (SGIC and TGIC, respectively) are suitable techniques for the separation of olefin copolymers with regard to their chemical composition. In this study, the application ranges of both techniques are investigated and compared for ethylene–propylene (EP) copolymers. A linear dependency of ethylene content versus elution volume is obtained with SGIC in practically the whole ethylene range. In the case of TGIC, a linear dependency is obtained within certain ethylene content limits. The accessible ethylene content separation range for TGIC is 50–100 mol% ethylene, and a broader 26–100 mol% ethylene range is accessible for SGIC, the latter being the technique of choice in the analysis of EP rubbers.

1. Introduction

Typically, polyolefins with useful technical applications are semicrystalline thermoplastic materials that crystallize from melt or solution. They have distinct melting and crystallization temperatures that are a function of the molecular heterogeneity of the sample. High density polyethylene contains very small amounts of amorphous (noncrystallizable) fractions while in low and linear low density polyethylenes (LDPE and LLDPE, respectively) the amount of amorphous material depends on the degree of branching and the chemical composition. Plastomers/elastomers are typically olefin copolymers with high comonomer contents that have low crystallinities and high amounts of amorphous species.[1]

The chemical composition distribution (CCD) of complex polyolefins is typically measured by crystallization techniques such as temperature rising elution fractionation (TREF), crystallization elution fractionation or crystallization analysis fractionation. These techniques fractionate the macromolecules according to their crystallizability in solution and provide a predictable separation of the polymer fractions depending on the comonomer content, polymer chain irregularities, or tacticity differences. Such methods are still able to separate plastomers with densities between 902 and 910 kg m^{-3} according to their comonomer contents but are not suitable for elastomers with densities from 900 to 857 kg m^{-3}.[2–5]

The most significant contribution to the characterization of polyolefins with low crystallinities according to their CCDs has been achieved by interaction liquid chromatography at high temperatures (HT-IC), which works at operating conditions above crystallization and melting temperatures and separates complex polyolefins regarding chemical composition, irrespective of crystallinity.[6–10] HT-IC uses graphitized carbon black as stationary phase and the separation is based on the selective interaction of long uninterrupted ethylene sequences with the graphitic surface. For the first time, this stationary phase has been used by Macko and Pasch for the fractionation of polypropylene according to tacticity.[11] The authors used a solvent gradient technique (solvent gradient interaction chromatography, SGIC) that is based on adsorptive interactions and it has been demonstrated later that the method can be applied to olefin homopolymers, copolymers, and blends.[10,12–19] The technique has the drawback that for 1D separations only the evaporative light scattering detector (ELSD) can be used, which needs to be calibrated versus several polymer features to enable quantification.

As an alternative, thermal gradient interaction chromatography (TGIC) has been introduced where a single solvent is used as mobile phase enabling the usage of various detectors such as infrared (IR), light scattering (LS), and online viscometer.[20,21] This method has been used extensively for the chemical composition analysis of LLDPE.[22–24] While SGIC operates

A. Ndiripo, Prof. H. Pasch
Department of Chemistry and Polymer Science
University of Stellenbosch
Private Bag X1, Matieland 7602, South Africa
E-mail: hpasch@sun.ac.za
Dr. A. Albrecht, Dr. J. Wang
Borealis Polyolefine GmbH
St. Peter-Strasse 25, 4021 Linz, Austria
Dr. B. Monrabal
Polymer Char
Valencia Technology Park
Gustave Eiffel 8, 46980 Paterna, Spain
The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/marc.201700703.

DOI: 10.1002/marc.201700703

ADVANCED SCIENCE NEWS
www.advancedsciencenews.com

Macromolecular Rapid Communications
www.mrc-journal.de

at temperatures above melting, and thus, sample crystallinity does not influence the fractionation process, TGIC uses a temperature gradient starting at ambient temperature. At this temperature, most sample components have crystallized or precipitated onto the stationary phase, and a mixed fractionation mechanism may take place in the elution process during the heating ramp.[22–24] To determine the application ranges for both methods, it would have been necessary to fractionate the same sample set by SGIC and TGIC, which has never been done and it is addressed in this study.

For a selected set of ethylene–propylene copolymers with higher comonomer contents, SGIC and TGIC experiments were conducted, the application ranges for both methods determined and the suitability for CCD analysis discussed.

2. Experimental Section

2.1. Materials and Polymerization

The polymerization of the heterophasic polypropylene (Heco-PP) was carried out in a 20L stirred autoclave reactor, and performed in two steps. In the first step propylene (C3) was polymerized at 80 °C for 20 min at 36 bar, where in the second step copolymerization of ethylene (C2) and propylene (C3) was performed at 70 °C at pressures between 20 and 25 bars. H_2 was used to adjust the molar mass. For each run about 200 mg of catalyst were used. The details of polymerization parameters (e.g., monomer concentration, time) are listed in **Table 1**.

The selected ethylene–propylene (EP) copolymers are model EP rubbers (EPR), obtained by xylene fractionation of the heterophasic copolymers (Heco-PP1-4 and Heco-PP6), with low to high amounts of comonomer. The EPR is the xylene soluble fraction at 23 °C. For heco-PP5 a complete separation of the EPR and the homo-PP is not feasible due to the semicrystallinity of EPR5 (see **Table 2** and Table S2 (Supporting Information)). For all other xylene soluble fractions the average reactivity ratio r_1r_2 ($r_1r_2 = 4(EE)(PP)/(EP)^2$), calculated from the corresponded ethylene–ethylene (EE), propylene–propylene (PP), and ethylene–propylene (EP) diad concentration is between 1,5 and 1,8, where for EPR 5 is over 180, indicating blocky structures. The reactivity ratio slightly over 1 can be explained by the presence of low molar mass PP, which is also soluble in xylene at 23 °C.

2.2. SGIC

The separations were conducted on a high temperature SGIC using a Hypercarb column. The flow rate of the mobile phase was 0.5 mL min^{-1}. The column was placed in a column oven maintained at 160 °C. Separations were accomplished by applying a linear gradient from 1-decanol to 1,2,4-trichlorobenzene (TCB). Samples were injected at a concentration of 1–1.2 mg mL^{-1}, with 20 µL of each sample being injected. An ELSD was used for detection. Further details on the instrumentation and system conditions are given in Section 1 of the Supporting Information.

2.3. TGIC

The separations were conducted on a TGIC (Polymer Char, Valencia, Spain) using a Hypercarb column and ortho-dichlorobenzene as eluent. The samples were dissolved at 160 °C and injected with a 100 µL loop at a concentration of 1 mg mL^{-1}; the column was then cooled down to 40 °C for adsorption, at 20 °C min^{-1}. The elution step was performed with a flow rate of 0.5 mL min^{-1} and a heating rate of 2 °C min^{-1}. An infrared detector (IR5) was used to monitor the components concentration and composition when eluting from the Hypercarb column. Further details on the instrumentation and system conditions are given in Section 2 of the Supporting Information.

2.4. ^{13}C-Nuclear Magnetic Resonance Spectroscopy (^{13}C-NMR)

Quantitative ^{13}C {^1H} NMR spectra were recorded in solution-state using a Bruker Avance III 400 NMR spectrometer operating at 400.15 and 100.62 MHz for ^1H and ^{13}C, respectively. All spectra were recorded using a ^{13}C optimized 10 mm extended temperature probe head at 125 °C using nitrogen gas for all pneumatics. Approximately 200 mg of material was dissolved in 3 mL of *1,2*-tetrachloroethane-d_2 (TCE-d_2) along with chromium (III) acetylacetonate ($Cr(acac)_3$). A total of 6144 (6k) transients were acquired per spectrum. The quantification of the comonomer fraction and the corresponding triad distribution was performed using the method of Wang and Zhu.[25] Further details on the instrumentation and system conditions are given in literature[26–28] and in Section 3 of the Supporting Information.

Table 1. Polymerization conditions for EP copolymers.

Sample	1st step (homo)		2nd step (copolymerization)			
	Total H_2 [g]	Total C3 [g]	Time [min]	Total H_2 [g]	C3 feed [g]	C2 feed [g]
Heco-PP1	0,314	240	129	0	164	62
Heco-PP2	0,314	240	171	0	322	80
Heco-PP3	0,314	240	105	0	214	213
Heco-PP4	0,314	240	87	0	100	396
Heco-PP5	0,314	240	140	0	31	285
Heco-PP6	0,416	240	217	0	245	451

ADVANCED SCIENCE NEWS
www.advancedsciencenews.com

Macromolecular Rapid Communications
www.mrc-journal.de

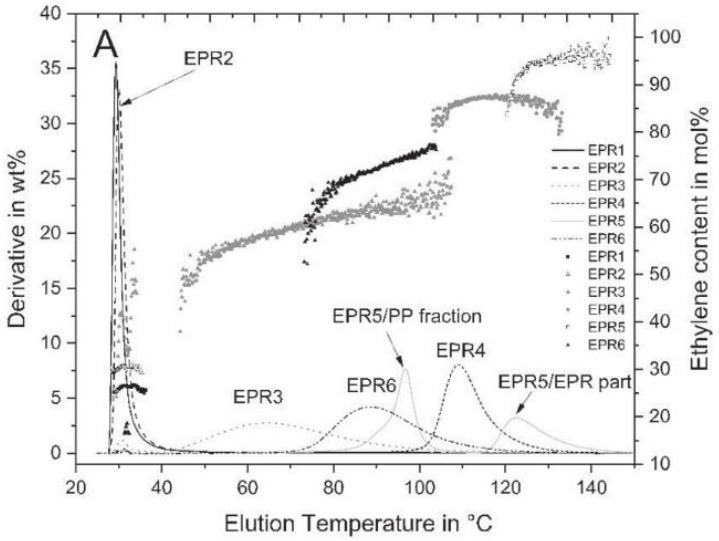
Table 2. Summary of EP copolymers, their melt flow indexes, molar masses, and comonomer contents.

Sample	MFI (g/10 min)	Ethylene (mol% by NMR)	M_n [kg mol^{-1}]	M_w [kg mol^{-1}]
EPR 1	17	26.8	106.0	235.0
EPR2	20	32.5	86.0	194.0
EPR3	15	64.5	76.8	176.0
EPR4	3	84.5	127.0	337.0
EPR5[a)]	7	38.7[a)] (90,1[b)])	52.4	261.0
EPR6	15	75.1	106.0	235.0

[a)]EPR5 is apparently a blend of homo-PP and EPR (semicrystalline); [b)]Calculated ethylene content of EPR in EPR5 from the weight fraction of EPR in the reactor blend Heco-PP5 and the NMR result of the reactor blend.

2.5. Size Exclusion Chromatography Coupled to Infrared Spectroscopy (SEC-IR)

A high temperature gel permeation chromatograph (Polymer Char, Valencia, Spain) equipped with a five band infrared detector (IR5) using PLgel Olexis columns as stationary phase was used for the determination of the molar mass distribution and the ethylene content as a function of molar mass. As sample solvent and mobile phase TCB was used. The chromatographic system was operated at 160 °C at a constant flow rate of 1 mL min^{-1}. 200 µL of sample solution was injected with a concentration of 1 to 1.2 mg mL^{-1}. Further details on the instrumentation and system conditions are given in literature[29,30] and in Section 4 of the Supporting Information.



3. Results and Discussion

In the first part of the experiments the EPRs are analyzed by ^{13}C-NMR and SEC-IR showing that samples EPR1-4 and EPR6 are homogenous regarding chemical composition as a function of molar mass (see Figure S1, Supporting Information). The PPP and EEE triads obtained from NMR are as expected for homogeneously distributed copolymers with varying ethylene contents (see Table S1, Supporting Information). With increasing ethylene content, the concentration of EEE triads increases. For sample EPR5 a clear bimodality is observed in the SEC-IR profile, with low ethylene content in the low molar mass fraction and high ethylene content in the high molar mass fraction. NMR indicates that this fraction contains a number of different species, a propylene-rich copolymer or polypropylene and an ethylene-rich copolymer.

The EPR copolymers were then analyzed by TGIC. As is seen in **Figure 1**A, for all samples except sample EPR5 unimodal

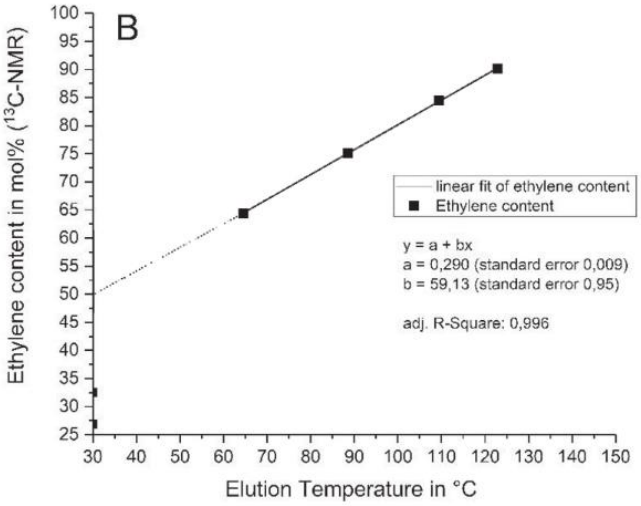


Figure 1. A) TGIC separations of the EP copolymers EP1-6, ethylene content as a function of elution temperature is obtained via IR detector and B) plot of ethylene content as a function of elution temperature.

ADVANCED SCIENCE NEWS
www.advancedsciencenews.com

Macromolecular Rapid Communications
www.mrc-journal.de

elution profiles in the elution temperature range of 40–140 °C are obtained. At elution temperatures >40 °C, components elute in the order of increasing ethylene content. Proper separation is seen in the comonomer content range between 50 and 100 mol% ethylene. Components that contain between ≈20 and 50 mol% ethylene (15–30 wt% ethylene) elute in the temperature range between 30 and 40 °C. This means that these polymer fractions are coeluting irrespective of the ethylene content and no separation according to CCD takes place. EP copolymers with lower ethylene contents have semicrystalline fractions, which will elute at higher elution temperatures as it can be seen for EPR5 which contains (most probably) isotactic-PP eluting at ≈100 °C (see Tables S1 and S2, Supporting Information).[26]

For EPR1 and EPR2 (26.8 and 32.5 mol% ethylene, respectively) complete coelution is observed indicating that these polymers are not adsorbed on the stationary phase in ODCB at 40 °C or higher. By plotting the ethylene contents of the EP rubbers obtained from ^{13}C-NMR (in mol%) versus the corresponding elution temperature at peak maximum, a linear correlation of the ethylene content and the elution temperature is obtained for EP copolymers with 50 to 100 mol% ethylene in the copolymer, see Figure 1B.

This observation leads to the conclusion that TGIC is not the method of choice to determine the CCD of EP rubbers and most industrially relevant heterophasic polypropylenes, where the ethylene content of the xylene soluble fraction which corresponds to the rubber phase is between 18 and 50 wt%. This becomes even more evident when blends of polypropylene and EPR are analyzed by TGIC without previous separation of the xylene soluble fraction (see Figure S2, Supporting Information). Here, heterophasic polypropylenes containing reactor blends of homo-PP and EPR are analyzed. For the samples PP/EPR3-6, coelution of the PP matrix with the EP rubber is observed. Homo-PP eluting between 95 and 100 °C indicates a separation according to crystallinity. This is in good agreement with TREF analyses. Similar observations were made in systematic studies by Monrabal et al.[31,32] where mixed mechanisms of adsorption/desorption were proposed for EP copolymers with ethylene contents of 60 mol% and more and crystallization for ethylene contents below 15 mol%. For the region between 20 and 60 mol% ethylene, no systematic study has been conducted yet.

One option to increase the separation range of TGIC would be to start the experiments at subambient temperatures instead of 30 °C. The expectation is that samples that are not separated at 30 °C or higher, e.g., samples EPR1 and EPR2, will be separated at lower temperatures. Figure S3 of the Supporting Information shows the elution profile of EPR2 that was obtained by starting the fractionation at subambient temperature as compared to the standard protocol starting at 30 °C. The elution of the sample starts at that subambient temperature and a narrow elution profile is obtained similar to the one from the standard protocol. This proves that for the analyzed sample even at lower temperatures (–20 °C) no adsorption takes place and the complete polymer is eluting at –20 °C. Due to the fact that EPR1 has an even lower ethylene content, which means less adsorption on the stationary phase, it can be expected that EPR1 and EPR2 cannot be separated according to chemical composition by applying lower elution temperatures.

Different from TGIC, the separation in SGIC is based on the modulation of the interactions between macromolecules and the stationary phase by the solvent strength of the mobile phase which is adjusted through changing the composition (binary

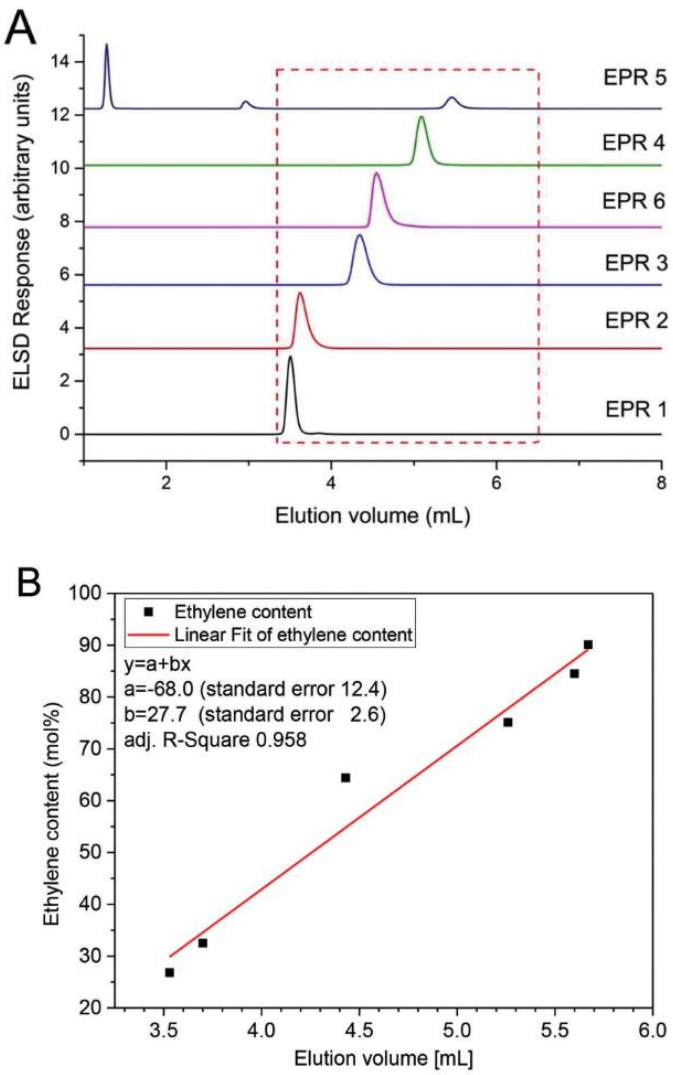


Figure 2. A) SGIC separations of samples EP1-6, and B) plot of ethylene content as a function of elution volume. EP components elute at 3.5–6.2 mL, as indicated by the dotted box.

ADVANCED SCIENCE NEWS
www.advancedsciencenews.com

Macromolecular Rapid Communications
www.mrc-journal.de

solvent mixture) of the mobile phase over time. Elution starts at low solvent strength with a weak mobile phase and continues toward higher solvent strengths by adding a good solvent to the mobile phase. Elution occurs in the direction of decreasing comonomer contents, PE being the latest eluting component.

The same EPR copolymers as well as the corresponding heterophasic PP containing the EP copolymers listed in Table S2 of the Supporting Information were analyzed. The chromatograms of samples EPR1-6 are presented in **Figure 2**. For the present experiments a linear solvent gradient is used starting from 100% decanol and going to 100% TCB. Decanol is a weak solvent while TCB is a strong solvent for polyolefins and by increasing the percentage TCB in the mobile phase its solvent strength increases.

Unimodal elution peaks were obtained for EPR1-4 and EPR6 while a complex elution pattern is obtained for EPR5 as well as for EPR-PP blends (see Figure S4, Supporting Information). The first two elution peaks at 1.5 mL and at 3–3.2 mL can be assigned to low molar mass (1.5 mL) and high molar mass homo-PP (3 mL), respectively. PP shows very weak adsorptive interactions with the stationary phase and elutes, therefore, before or at the start of the solvent gradient. The SGIC result confirms the findings from NMR, SEC-IR, and TGIC that EPR5 is a blend of EP copolymer with high comonomer content and a homo-PP.

The following peaks (indicated by the box) can be assigned to the EP copolymer fractions produced during the 2nd polymerization stage of the reactor blend preparation. The elution of the copolymer fractions corresponds to the copolymer composition, components with low comonomer contents eluting earlier and components with high comonomer contents eluting later. Different elution volumes are obtained for varying ethylene contents of the copolymer fractions, see **Table 3**. Separation corresponds to the ethylene content of the EPRs or more precisely to the ethylene amount and the length of the ethylene sequences.

By plotting the elution volume at peak maximum as a function of the corresponding ethylene content a linear correlation is obtained, see Figure 2B and Equation (1). An R-square value of 0.958 was obtained, indicating a strong linear dependence of elution volume on the ethylene content

$$y = a + bx \quad (1)$$

where a = –68.0 (standard error 12.4) and b = 27.7 (standard error 2.6).

Table 3. Summary of SGIC elution volumes of the EPR copolymer fractions.

Sample	Elution volume [mL]	Ethylene [mol%]
EPR1	3.53	26.8
EPR2	3.70	32.5
EPR3	4.43	64.4
EPR4	5.60	84.5
EPR5	5.67	90.1
EPR6	5.26	75.1

As can be seen, a range of ethylene contents of 26.8–90.1 mol% is covered. Compared to the ethylene range for TGIC, the accessible ethylene range for SGIC is significantly larger.

4. Conclusions

SGIC and TGIC are suitable techniques for the separation of ethylene–propylene copolymers with regard to their chemical composition. In both cases, linear dependencies of ethylene content versus elution volume (SGIC) or elution temperature (TGIC), respectively, are obtained. The accessible ethylene content separation ranges are 50–100 mol% ethylene for TGIC and 26.8–100 mol% ethylene for SGIC. Accordingly, the accessible ethylene content range is significantly broader for SGIC.

For EP rubbers as well as for PP-EPR reactor blends, TGIC remains insensitive for some compositions even if improved experimental protocols are applied. It will be interesting to see if a change in mobile phase broadens the accessible ethylene content range.[22–24] This will be the subject of forthcoming investigations and will be of significant interest due to the fact that all industrially relevant EP rubbers have comonomer contents below 60 mol% ethylene. This is particularly true for PP-EPR reactor blends. With SGIC, all analyzed EP copolymers between 18 and 100 mol% ethylene can be separated according to the chemical composition.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

chemical composition distribution, polyolefins, solvent gradient interaction chromatography, thermal gradient interaction chromatography

Received: October 17, 2017
Revised: December 4, 2017
Published online: January 15, 2018

[1] S. Bensason, J. Minick, A. Moet, S. Chum, A. Hiltner, E. Baer, *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 1301.
[2] S. Cheruthazhekatt, N. Mayo, B. Monrabal, H. Pasch, *Macromol. Chem. Phys.* **2013**, *214*, 2165.
[3] R. Chitta, A. Ginzburg, T. Macko, R. Brull, G. van Doremaele, *LC-GC Eur.* **2012**, *25*, 352.
[4] T. Macko, A. Ginzburg, K. Remerie, R. Bruell, *Macromol. Chem. Phys.* **2012**, *213*, 937.
[5] B. Monrabal, P. Del Hierro, *Anal. Bioanal. Chem.* **2011**, *399*, 1557.

[6] T. Macko, H. Pasch, J. F. Denayer, *J. Chromatogr. A* **2003**, *1002*, 55.
[7] T. Macko, H. Pasch, Y. Kazakevich, A. Fadeev, *J. Chromatogr. A* **2003**, *988*, 69.
[8] T. Macko, J. Denayer, H. Pasch, L. Pan, J. Li, A. Raphael, *Chromatographia* **2004**, *59*, 461.
[9] M. J. Phiri, S. Cheruthazhekatt, A. Dimeska, H. Pasch, *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *53*, 863.
[10] S. Cheruthazhekatt, H. Pasch, *Macromol. Symp.* **2014**, *337*, 51.
[11] T. Macko, H. Pasch, *Macromolecules* **2009**, *42*, 6063.
[12] T. Macko, A. Ginzburg, K. Remerie, R. Bruell, *Macromol. Chem. Phys.* **2012**, *213*, 937.
[13] T. Macko, R. Brüll, R. G. Alamo, F. J. Stadler, S. Losio, *Anal. Bioanal. Chem.* **2011**, *399*, 1547.
[14] S. Cheruthazhekatt, T. F. J. Pijpers, G. W. Harding, V. B. F. Mathot, H. Pasch, *Macromolecules* **2012**, *45*, 2025.
[15] A. Ndiripo, H. Pasch, *Anal. Bioanal. Chem.* **2015**, *407*, 6493.
[16] A. Ndiripo, D. Joubert, H. Pasch, *J. Polym. Sci., Part A: Polym. Chem.* **2016**, *54*, 962.
[17] S. Cheruthazhekatt, T. F. J. Pijpers, V. B. F. Mathot, H. Pasch, *Anal. Bioanal. Chem.* **2013**, *405*, 8995.
[18] S. Cheruthazhekatt, H. Pasch, *Anal. Bioanal. Chem.* **2013**, *405*, 8607.
[19] L.-C. Heinz, H. Pasch, *Polymer* **2005**, *46*, 12040.
[20] R. Cong, W. Degroot, A. Parrott, W. Yau, L. Hazlitt, R. Brown, M. Miller, Z. Zhou, *Macromolecules* **2011**, *44*, 3062.
[21] D. Mekap, T. Macko, R. Brüll, R. Cong, A. W. deGroot, A. R. Parrott, *Ind. Eng. Chem. Res.* **2014**, *53*, 15183.
[22] B. Monrabal, N. Mayo, R. Cong, *Macromol. Symp.* **2012**, *312*, 115.
[23] A. Alghyamah, J. B. P. Soares, *Ind. Eng. Chem. Res.* **2014**, *53*, 9228.
[24] A. Z. Al-Khazaal, J. B. P. Soares, *Macromol. Chem. Phys.* **2014**, *215*, 465.
[25] W.-J. Wang, S. Zhu, *Macromolecules* **2000**, *33*, 1157.
[26] H. Cheng, *Macromolecules* **1984**, *17*, 1950.
[27] Z. Zhou, R. Kümmerle, X. Qiu, D. Redwine, R. Cong, A. Taha, D. Baugh, B. Winniford, *J. Magn. Reson.* **2007**, *187*, 225.
[28] V. Busico, P. Carbonniere, R. Cipullo, R. Pellecchia, J. R. Severn, G. Talarico, *Macromol. Rapid Commun.* **2007**, *28*, 1128.
[29] T. Kawai, S. Teramachi, S. Tanaka, S. Maeda, *Int. J. Polym. Anal. Charact.* **2000**, *5*, 381.
[30] D. Suwanda, R. Lew, S. Balke, *J. Appl. Polym. Sci.* **1988**, *35*, 1033.
[31] B. Monrabal, E. López, L. Romero, *Macromol. Symp.* **2013**, *330*, 9.
[32] B. Monrabal, *Macromol. Symp.* **2015**, *356*, 147.

4.4 Characterization of complex multimodal ethylene-1-hexene copolymers using advanced analytical techniques *(Ready for submission)*

Multimodal ethylene-1-alkene copolymers often referred to as bi- or multimodal high density polyethylenes (HDPEs) are complex materials due to their blend nature. Typical Ziegler-Natta catalyzed bimodal HDPE resins for e.g. pipe grades have broad MMDs and CCDs. These resins are composed of low molar mass polyethylene, low and high comonomer content high molar mass poly (ethylene-1-hexene) copolymers, see Fig. 4.4. In order to fully understand the microstructure of these materials, it is necessary to couple multiple fractionation techniques. In addition, the complexity of the resin must simplified by preparative fractionation followed by further analysis. In the present work, two bimodal HDPE resins with 0.5 mol% 1-hexene comonomer are studied together with a PE homopolymer produced with the same catalyst. The multiple fractionation concept is shown to provide very detailed information regarding the samples' microstructure. It is illustrated that preparative temperature rising elution (p-TREF) followed by offline analysis of the fractions is a feasible approach for the microstructure analysis of complex multimodal ethylene-1-hexene copolymer.

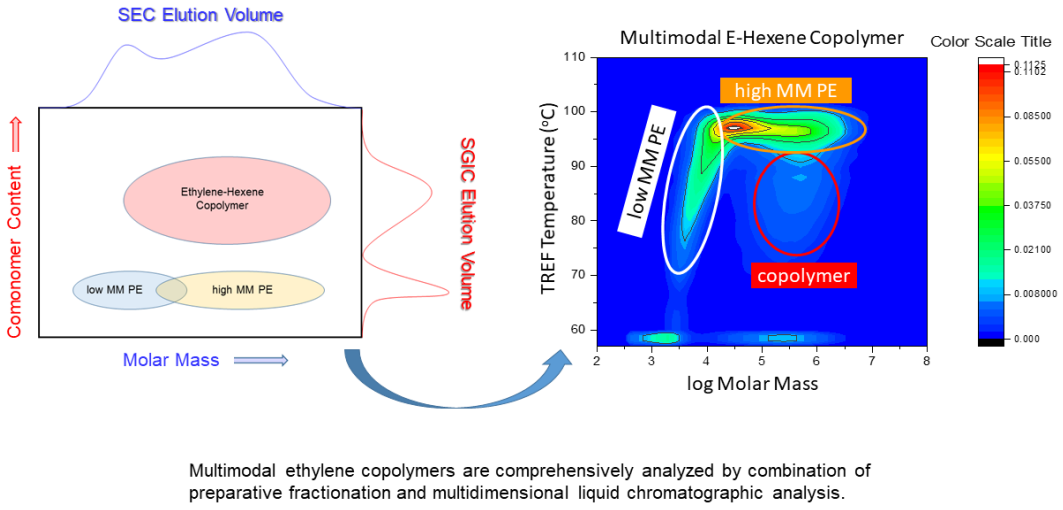


Figure 4.4 Schematic representation of the complex microstructural nature of a multimodal ethylene-1-hexene copolymer.

Journal Name

ARTICLE

Comprehensive Characterization of Multimodal Ethylene-1-Hexene Copolymers by Multiple Fractionation and Advanced Analysis

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Andreas Albrecht[b], Anthony Ndiripo[a], Elena Pomakhina[b], Harald Pasch[a,b]*

Typically, multimodal polyethylenes (PE) used in pipe applications are ethylene-1-olefin copolymers with very low comonomer contents. Accordingly, such materials contain polyethylene as the majority phase while the copolymer components have rather low concentrations. Still, their bulk materials' properties are determined by the molar mass balance of the PE homopolymer species and the molar mass and chemical composition of the copolymer fractions. To address the multimodality in molecular properties, multiple fractionation and analysis methods are developed for ethylene-1-hexene copolymers with bulk comonomer contents of about 0.5 mol.% of 1-hexene. Chromatographic cross-fractionation of the bulk samples provides molar mass information for the low and high molar mass PE homopolymers. Due to the low concentration of the copolymer fraction and overlapping elution profiles, the comonomer content and the molar mass of the copolymer fraction can only be estimated and not accurately determined. For more detailed molecular information on all sample components preparative temperature rising elution fractionation is used, the resulting fractions being analyzed by SEC-IR, solvent gradient interaction chromatography and comprehensive two-dimensional liquid chromatography.

INTRODUCTION

To a large extent the final and application properties of olefin copolymers are determined by their molecular structure. The in-depth understanding of the correlation between molecular parameters and application properties is the key to product optimization and commercial success. For olefin copolymers, the comonomer incorporation, comonomer distribution along and across the different polymer chains and the correlation to the molar mass distribution determines important physical properties such as crystallinity, toughness and long term stability. Therefore, the comprehensive analysis of different molecular parameters such as chemical composition distribution (CCD) and molar mass distribution (MMD) is an integral part of any materials' development and optimization.

Up to now, polyolefin characterization frequently addresses the analysis of single parameters (molar mass, average comonomer content, crystallization and melting temperatures) of bulk samples by specific methods. MMD is typically analysed by high-temperature size exclusion chromatography (SEC)[1-3] using multidetector setups with chemical composition (infrared, IR), absolute molar mass (light scattering, LS) and intrinsic viscosity (on-line viscometer) detectors.[4-9] CCD is determined using crystallization-based fractionation methods (temperature rising elution fractionation, TREF, crystallization analysis fractionation, CRYSTAF) where a copolymer composition may be obtained for the crystallisable components of the material.[10-14] These techniques, however, are of limited value for materials with high comonomer contents (plastomers, low amounts of crystallizable fractions) and materials with very low comonomer contents and broad MMD, such as multimodal ethylene copolymers. This is due to coelution of low molar mass polyethylene (PE) and copolymer fractions with low comonomer contents.

The most significant advancement in characterising polyolefins regarding their CCD irrespective of crystallinity/crystallization has been achieved by interaction chromatography at high temperatures (HT-IC) using spherical graphitized carbon black as stationary phase as described by Macko and Pasch[5, 15-18] and patented by Dow.[19-21] One current approach to HT-IC is thermal gradient interaction chromatography (TGIC), where isocratic solvent conditions are applied enabling the usage of a variety of information-rich detectors. Another technique using a solvent gradient approach which has become known as solvent gradient interaction chromatography (SGIC) has been also developed and applied to a large number of different polyolefin systems.[5] This technique has the drawback that for one-dimensional separation only the evaporative light scattering detector can be used which needs to be calibrated versus several polymer features to enable quantification.

A more comprehensive approach for the evaluation of the molecular heterogeneity in terms of CCD and/or MMD in heterogeneous systems is to perform fractionations on a preparative scale as in preparative TREF (pTREF)[11, 13, 22, 23], solvent gradient fractionation[24] and preparative molar mass fractionation (pMMF).[25] These techniques produce fractions in

[a] *Department of Chemistry and Polymer Science, University of Stellenbosch, Private bag X1, 7602, Matieland, South Africa. email: hpasch@sun.ac.za.*
[b] *Borealis Polyolefine GmbH, St. Peter-Strasse 25, Linz 4021, Austria.*

mg or g quantities that differ in chemical composition (pTREF) and molar mass (pMMF) which can then be subjected to further analysis by spectroscopic methods (NMR, FTIR) to provide in-depth information on chemical composition and molar mass. Although all these techniques have their limitations, combining them in multiple fractionation schemes and hyphenated techniques is the key to providing comprehensive microstructural information on complex polyolefins.

For comprehensive information at an analytical scale, different fractionation methods are coupled such as in chromatographic cross-fractionation (CFC) and in two-dimensional liquid chromatography (2D-LC). In CFC, an analytical TREF (aTREF) experiment is conducted in the 1st dimension and the fractions transferred to SEC in the 2nd dimension to provide molar mass information on all fractions.[26-28] In contrast to CFC, 2D-LC is not based on any crystallization-based processes. In this case SGIC is used in the 1st dimension to separate the sample according to CCD which is then coupled to SEC in the 2nd dimension for molar mass analysis.[5, 29-32]

The present study aims at presenting the feasibility of the multiple preparative fractionation concept for the analysis of multimodal ethylene-hexene copolymers. Typical Ziegler-Natta catalyzed materials for e.g. pipe grades exhibit broad MMDs and CCDs. Such materials may be composed of fractions of high and low molar mass polyethylene along with copolymer fractions (ethylene-1-hexene in the present case). The total comonomer content of these materials is typically very low making it extremely challenging to detect and analyze the copolymer fraction.

The application of liquid chromatography for the analysis of bimodal HDPE has been proposed by Ginzburg et al.[33] They analysed a set of TREF fractions of ethylene-butene copolymers by SGIC and 2D-LC and found that the TREF pre-fractionation enhanced the detectability of separated components. Albrecht et al. used a CRYSTAF-based approach to analyse the CCD of ethylene-1-olefin copolymers polymerized with different Ziegler-Natta catalysts.[28]

In the present study, multiple fractionations and analyses of a set of selected ethylene-1-hexene copolymers are conducted to prove that specific microstructural information can be obtained from each method. The multiple fractionation approach has been presented schematically and applied to a low density polyethylene sample in a recent work by Bungu and Pasch.[34] This approach is compared to the bulk analysis of the samples. The focus of the present study is on combining pTREF fractionation with other advanced techniques such as HT-HPLC, HT-SEC, ^{13}C NMR, CFC and 2D-LC to map the distributions of both chemical composition and molar mass. The main text of the article should appear here with headings as appropriate.

EXPERIMENTAL SECTION

Samples

In this study, two multimodal ethylene-1-hexene copolymers with similar comonomer contents but different melt flow indexes are used. These samples are compared to a multimodal polyethylene. All polymers were synthesized by Borealis using Borstar® Technology. The physical properties of the samples are presented in **Table 1**.

Table 1. Physical properties of the ethylene-1-hexene copolymers.

Sample	C6 [mol.%]	Pellet MFR5 (g/10min)
Sample 1	0	n.a
Sample 2	0.52	0.25
Sample 3	0.50	0.17

NMR Analysis

Quantitative $^{13}C[^{1}H]$ NMR spectra were recorded in melt-state using a Bruker Avance III 500 NMR spectrometer operating at 500.13 and 125.76 MHz for ^{1}H and ^{13}C, respectively. All Spectra were recorded using a ^{13}C optimized 7 mm magic-angle spinning (MAS) probe head at 150 °C using nitrogen gas for all pneumatics. Approximately 200 mg of polymer sample was packed into a 7 mm outer diameter zirconia MAS rotor and spun at 4 kHz. A total of 1024 (1k) transients were acquired per spectrum. The quantification of the comonomer fraction and the corresponding triad distribution was performed as described by Parkinson et al.[35, 36]

SEC-IR analysis

A high temperature chromatograph GPC-IR (Polymer Char, Valencia, Spain) equipped with a five band infrared detector (IR5) was used for the determination of the molar mass distribution and the ethylene content along the molar mass.[37] The chromatographic separation was carried out by using three PLgel Olexis columns and 1 × PLgel Olexis guard column (Agilent Technologies, Church Stretton, UK). As sample solvent and mobile phase 1,2,4-trichlorobenzene (TCB) stabilized with 250 mg/L 2,6-di-tert-butyl-4-methyl-phenol (BHT) was used. The chromatographic system was operated at 160 °C and at a constant flow rate of 1 mL/min. 200 µL of sample solution was injected per analysis. The column set was calibrated using universal calibration with narrow molar mass polystyrene (PS) standards in the range of 0.5 kg/mol to 11 500 kg/mol. Mark-Houwink constants for PS (K= 0.00019 and α=0.655) and PE (K= 0.00039 and α=0.725) are used for converting the PS equivalent molar masses into PE equivalent molar masses. The IR5 detector was calibrated with narrow distributed ethylene-hexene, ethylene-butene and ethylene-octene copolymer standards having SCB contents between 0 and 85 SCB/1000TC. The SCB/1000TC content of the GPC-IR standards were determined by ^{13}C NMR as described in the **NMR Analysis Section**. Data collection was performed by using the Polymer Char GPC-IR control software.

CFC Analysis

All samples were analysed using a fully automated Cross-Fractionation Chromatography (CFC) device to determine the chemical heterogeneity and to be able to determine the molar mass distributions and the corresponded molar mass averages (M_n, M_w and M_v) at certain elution temperatures. A CFC instrument (PolymerChar, Valencia, Spain) was used to perform the cross-fractionation (TREF × SEC).[27] An IR5 infrared detector (PolymerChar, Valencia, Spain) was used to monitor the

concentration. Around 50 mg of the polymer sample was dissolved in 40 mL TCB in a stainless steel vessel for 180 min at 160 °C. Once the sample was completely dissolved an aliquot was loaded into the TREF column and stabilised for a while at 110 °C. The following analytical parameters were chosen for analysing the samples, see **Table 2**.

Table 2 Experimental parameters for the CFC analysis

Dissolution temperature [°C]	Dissolution time [min]	Cooling rate [°C/min]	Elution steps
160	180	0.07	24 steps from 30 to 140 °

A discontinuous elution process was performed using the temperature profile given in **Figure 1**.

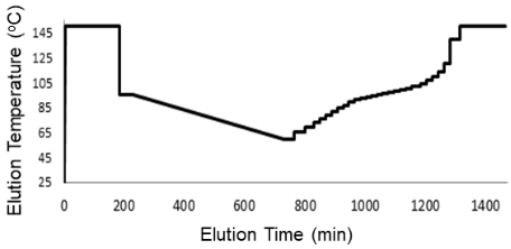


Figure 1. Temperature profile of CFC analysis.

In the 2nd dimension (SEC), three PL Olexis columns and an Olexis guard column from Agilent (Church Stretton, UK) were used as the stationary phase. As eluent 1,2,4-trichlorobenzene (TCB, stabilized with 250 mg/L 2,6-di-tert-butyl-4-methyl-phenol) at 150 °C and a constant flow rate of 1 mL/min were applied. The column set was calibrated using universal calibration (according to ISO 16014-2:2003) with at least 15 narrow molar mass PS standards in the range of 0.5 kg/mol to 11 500 kg/mol. Mark-Houwink constants for PS, PE were used in the same manner as described in the **SEC-IR Analysis Section**.

p-TREF

Preparative fractionations of the samples were performed using a semi-automated fractionation instrument PREP-MC² (PolymerChar, Valencia, Spain). Around 1 g of the polymer samples was dissolved in 180 mL TCB, stabilized with 250 mg/L 2,6-di-tert-butyl-4-methyl-phenol at 160 °C for 90 min under discontinuous gentle stirring (discontinuously at 200 rpm, 30 sec on, 5 sec off). The solution was cooled down to 95 °C (20 °C/min cooling rate) for stabilization for 45 min and afterwards the solution was cooled down to 30 °C with a cooling rate of 0.1 °C/min. The elution temperature was obtained by increasing the temperature with a heating rate of 20 °C/min and after 30 min of stabilization the polymer solution was taken out by pressing it through a filter placed inside the vessel using nitrogen overpressure. This step was repeated for each individual p-TREF fraction.

After adding 200 mL of acetone to each of the obtained fraction solutions, they was allowed to precipitate overnight at 7 °C and filtrated thereafter through 5 µm PTFE filters by vacuum filtration. After drying under vacuum at 55 °C, the fractions were weighed on a precision scale.

SGIC Analysis

High temperature chromatographic experiments were performed using a solvent gradient interaction chromatograph (SGIC) constructed by Polymer Char (Valencia, Spain). For solvent gradient elution, a high-pressure binary gradient pump (Agilent, Waldbronn, Germany) was utilised. A evaporative light scattering detector (ELSD, model PL-ELS 1000, Polymer Laboratories, Church Stretton, England) was used with the following parameters: gas flow rate of 1.5 SLM, 160 °C nebuliser temperature and an evaporative temperature of 270 °C. A Hypercarb column (Hypercarb®, Thermo Scientific, Dreieich, Germany) with dimensions of 100 × 4.6 mm² (l × i.d.) packed with porous graphite particles which had an average particle diameter of 5 µm (making a surface area of 120 m^2g^{-1}) and a pore size of 250 Å was used for all HT-HPLC experiments. The column was placed in an oven and the temperature maintained at 160 °C. The flow rate of the mobile phase during analysis was 0.5 mL/min. To achieve separation, a linear gradient was applied from 100 % 1-decanol to 100 % TCB within 10 min after sample injection. These conditions were held for 20 min before re-establishing 1-decanol to 100 %. For all HT-SGIC analyses a concentration of 1.0 – 1.2 mg/mL was used (approximately 4 mg in 4 mL of 1-decanol) with 50 µL of each sample being injected.

2D-LC Analysis

HT-SGIC and HT-SEC were coupled with the aid of an electronically controlled eight-port valve system (VICI Valco instruments, Houston, Texas) equipped with two 100 µL sample loops. Injection into the first dimension (HT-HPLC) was carried out using a 110 µL sample loop and the flow rate was 0.05 mL/min. A linear gradient was applied from 100% 1-decanol to 100% TCB within 5 mL (100 mins). A flow rate of 2.75 mL/min was used in the second dimension (HT-SEC) with TCB being used as the mobile phase. In the second dimension, a PL Rapide H [Polymer Laboratories (Now Agilent), Church Stretton, UK.] 100 × 10 mm² (l × i.d.) column with an average particle diameter of 10 µm was used at 160 °C. The column was kept in an oven at this temperature during the analysis. The evaporative light scattering detector (ELSD, model PL-ELS 1000, Polymer Laboratories, Church Stretton, England) was used with the following parameters: gas flow rate of 1.5 SLM, 160 °C nebulizer temperature and an evaporative temperature of 270 °C.

RESULTS AND DISCUSSION

The samples of interest for this study are multimodal ethylene-1-hexene copolymers with average comonomer contents of 0.5 mol.%. It is known for these types of samples that they contain significant amounts of low molar mass PE, large amounts of high molar mass PE and rather low amounts of

copolymer species.[33, 38] Limited information on the amounts and molar masses of the PE homopolymers and the copolymer as well as the copolymer composition is available since (typically) most of the analytical work is done only on bulk samples. Here, more subtle and selective fractionation techniques will provide distinctively more detailed molecular information and open a way for the correlation of the molecular composition with the materials' properties. From an analytical point of view, method development is required for comprehensive chemical composition and molar mass fractionation of bulk samples and the analysis of the molecular heterogeneity (chemical composition and molar mass) of the copolymer fraction.

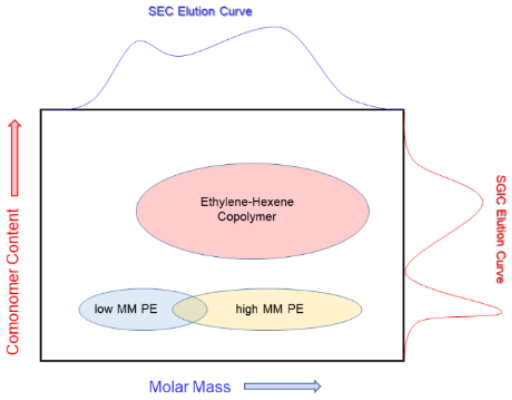


Figure 2 Schematic presentation of the complexity of multimodal PE.

The molecular complexity of multimodal PE is schematically presented in **Figure 2**. Plotting the chemical composition (comonomer content) vs. molar mass in a two-dimensional diagram it becomes obvious that one single fractionation method cannot comprehensively address the composition of the sample. If fractionation is conducted according to chemical composition, e.g. using solvent gradient interaction chromatography (SGIC), PE and the copolymer might be separated, however, low and high molar mass PE will co-elute. Alternatively, if a molar mass fractionation is carried out, co-elution of homo- and copolymer fractions will take place. Only the combination of different fractionation methods in multidimensional schemes will be able to address both the chemical composition and the molar mass distribution

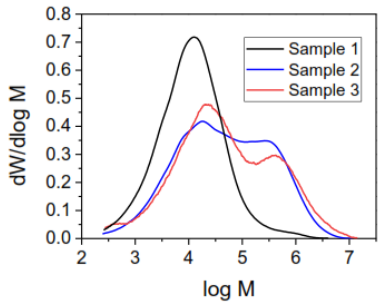


Figure 3. Molar mass distributions of the bulk samples as obtained by HT-SEC.

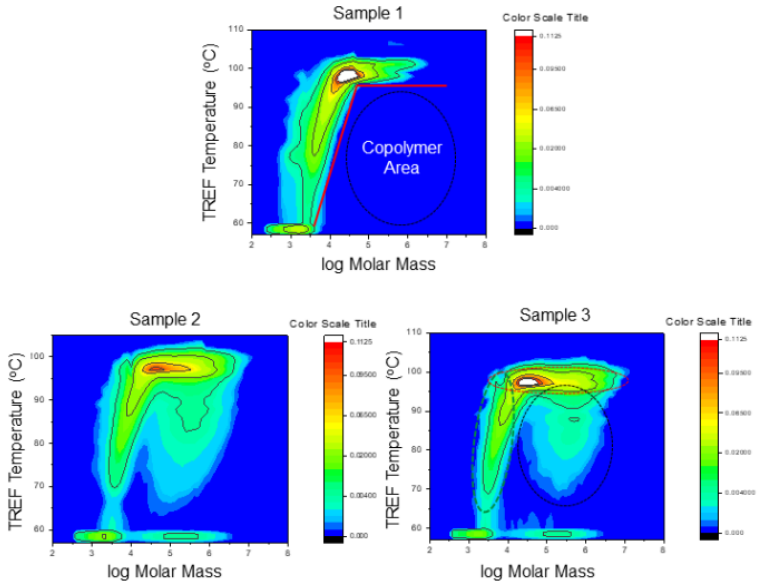


Figure 4. CFC plots of the samples, 1st dimension (vertical) aTREF, 2nd dimension HT-SEC, colour code indicates concentration profile (see color scale title); - - - - low molar mass PE, - - - - high molar mass PE, - - - - copolymer fraction

The molar mass analysis of the bulk samples by high temperature size exclusion chromatography (HT-SEC) is shown in **Figure 3** and summarized in **Table 3**. The samples clearly exhibit bimodal molar mass distributions (MMDs) that are

caused by components with different molar masses including low and high molar mass PE produced in different reactors (low molar masses in a loop reactor and high molar masses in a gas phase reactor). As expected, sample 1 that was produced in a loop reactor exhibits a monomodal MMD. This sample does not contain comonomer. Using the present HT-SEC experimental setup, specific copolymer fractions in samples 2 and 3 could not be identified. These fractions co-elute with PE homopolymers with similar molar masses.

Table 3. Bulk molar masses of the samples given as PE equivalents.

Sample	Mn [kg/mol]	Mw [kg/mol]	Mz [kg/mol]	Đ
Sample 1	4.4	35.8	466.0	8.2
Sample 2	8.0	234.0	1390.0	29.3
Sample 3	9.0	307.0	2109.0	33.3

The ^{13}C NMR analysis of the bulk samples provides average monomer contents and corresponding triad distributions, see **Table 4**. Average 1-hexene contents between of 0.52 and 0.50 mol.% were obtained for samples 2 and 3, respectively. The average comonomer content, however, does not allow to conclude how much copolymer has been formed and, accordingly, what the copolymer composition is. To obtain this kind of information, dedicated multiple fractionations are required.

Table 4. ^{13}C NMR results of the bulk samples including average comonomer contents (C6 content in mol.%) and triad distributions, E - ethylene, X – hexene.

Sample	C6 [mol.%]	EEE	EEX	XEX	EXE	EXX
1	0.52	98.11	1.33	0.02	0.54	0.00
2	0.50	98.37	1.08	0.05	0.50	0.00

The ^{13}C NMR results show very clearly that the average chain structure of the samples is made predominantly of EEE triads. Considering the very low comonomer contents it is obvious that the majority fractions of the samples are low and high molar mass PE and the concentration of ethylene-1-hexene copolymer species is rather low.

The ^{13}C NMR results show very clearly that the average chain structure of the samples is made predominantly of EEE triads. Considering the very low comonomer contents it is obvious that the majority fractions of the samples are low and high molar mass PE and the concentration of ethylene-1-hexene copolymer species is rather low.

Chromatographic Cross-Fractionation

The separation of such samples with very low comonomer contents regarding their molecular complexity is possible by chromatographic cross-fractionation (CFC) where in a 1st step fractionation takes place according to crystallizability which is related to chemical composition. Typically, analytical temperature rising elution fractionation (aTREF) is used for this step. The TREF fractions are subsequently analyzed by HT-SEC in the 2nd dimension providing the molar mass information for the TREF fractions. The CFC plots of the samples are presented in **Figure 4** showing the separation into three different components that can be assigned tentatively to low and high molar mass PE and a copolymer fraction.

Using this analytical approach, the main components of these complex samples – low and high molar mass PE and copolymer – can be identified. As one would expect from the bulk compositions, samples 2 and 3 containing rather similar amounts of comonomer might give an indication of the presence and amount of copolymer. Sample 1 does not contain any comonomer and its CFC plot just shows polyethylene. On the other hand, this sample contains a fraction with a very high molar mass that appears at a TREF temperature of 110 °C. In all samples, small fractions are detected that appear at TREF temperatures below 60 °C. These fractions have very low molar masses and, hence, do not properly crystallize in the TREF experiment. The material that is appearing in this region is termed 'soluble fraction' (SF) and is assumed to be low molar mass PE and/or copolymer.

Assuming that the detector response in CFC reflects relative concentrations, the relative amounts of the homo- and copolymer fractions can be calculated, see **Table 5**. As is seen in **Figure 4**, the different fractions are overlapping in the CFC plots and, therefore, only semiquantitative information can be provided. For more precise quantification the selectivity of CFC fractionation must be enhanced or multiple fractionations using different fractionation principles must be conducted.

Table 5. Bulk sample compositions obtained from CFC.

Sample	PE homopolymer (%)	Copolymer (%)	Soluble fraction (%)
Sample 1	100.0	0.0	0.1
Sample 2	74.0	26.0	1.9
Sample 3	83.0	17.0	1.5

An alternative method to fractionate ethylene copolymers according to chemical composition is SGIC. This method does not rely on the crystallizability of the components (as in TREF) but purely on chemical composition because the fractionation is conducted above the melting and crystallization temperatures of all sample components. This has the major advantage that the co-crystallization occurring in TREF[39, 40] and (therefore) also in CFC does not occur in SGIC separation. At the present experimental conditions, separation occurs in the direction of longer ethylene sequences meaning that linear PE elutes last while copolymer fractions with high comonomer contents elute first. For pure ethylene copolymers separation is in the direction of decreasing comonomer contents.

The SGIC profiles of the samples are shown in **Figure 5A**. The main elution peak is caused by PE being the majority fraction of the samples. This is in alignment with the CFC results that indicate 74 to 100 % of PE homopolymer in the samples. The shoulder at lower elution volume is probably due to the presence of copolymer fractions and/or low molar mass PE fractions, however, the selectivity of the separation for the different components is not sufficient for a conclusive analysis.

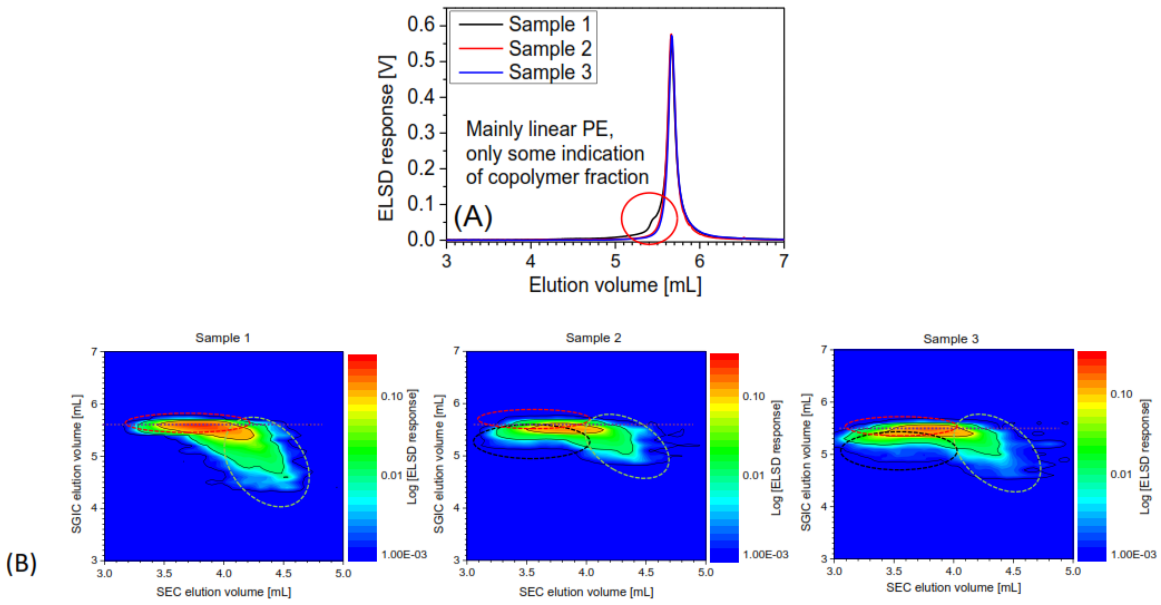


Figure 5. SGIC profiles of three samples (A) and 2D-LC fractionation of these samples (B), 1st dimension (vertical) SGIC, 2nd dimension SEC, colour code indicates concentration profile; - - - - low molar mass PE, - - - - high molar mass PE, - - - - copolymer fraction.

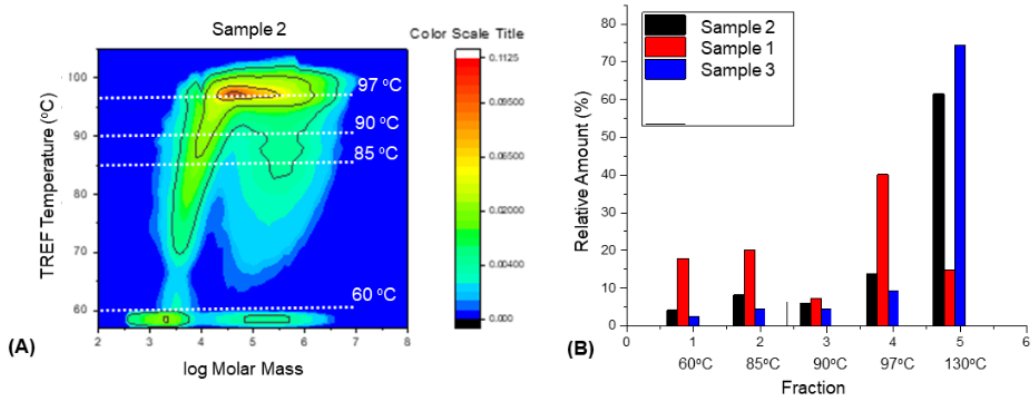


Figure 6. CFC plot of sample 2 with TREF collection temperatures indicated (A) and concentration distributions of the p-TREF fractions of the fractionated samples (B).

Comprehensive 2D-LC operates similar to CFC the only difference being that SGIC comprises the 1st dimension instead of aTREF (as in CFC). Accordingly, 2D-LC fractionates samples in the coordinates chemical composition (comonomer content) vs. molar mass. As can be seen in **Figure 5B**, similar to CFC analysis three components can be identified in the bulk samples. These components are (1) a high molar mass PE fraction which appears at HPLC elution volumes of 5.5 – 6.0 mL, (2) a high molar mass copolymer fraction which is eluting at 4.8 – 5.5 mL HPLC elution volume and a SEC elution volume below 3.8 mL and (3) a low molar mass PE or copolymer region eluting below a HPLC elution volume of 5.0 mL and a SEC elution volume higher than 3.9 mL. From the 2D-HPLC analysis it seems that for sample 3 a broader chemical composition distribution (CCD) compared to sample 2 is observed. The extended profile along the molar mass axis (SEC elution volume 3.0 – 5.0 mL) indicates that the low and high molar mass PE components co-elute in SGIC. Similar to CFC, the copolymer fraction (circled in black) can be identified but quantification in terms of copolymer composition and MMD is challenging due to the complex ELSD response and the poor resolution of 2D-LC for the present samples. On the other hand, in CFC co-crystallization influences the quantification of the copolymer composition and, therefore, none of the two methods (CFC or 2D-LC) is able to provide comprehensive molecular information when conducted on the bulk samples.

Preparative TREF Fractionation and Fraction Analysis

For a more comprehensive analysis of the samples, prep TREF fractionations were conducted. Since TREF fractionates according to crystallizability which is a function of composition it was expected that preparative fractions with different chemical compositions will be obtained. The samples were fractionated into 5 fractions each, the collection temperatures were 60, 85, 90, 97 and 130 °C, respectively. As shown in **Figure 6A**, those fractions should contain different sample components. The distributions of the preparative fractions as obtained by p-TREF fractionation are presented in **Figure 6B**.

As a first analysis step the TREF fractions were investigated by HT-SEC and in some cases by HT-SEC-IR. As presented in **Figure 6**, the fractions exhibit different elution profiles that indicate that at different TREF elution temperatures different components were separated. Particularly interesting were the fractions collected at 85 and 90 °C because they were assumed to be blends of low molar mass PE and high molar mass copolymer, which could be confirmed by HT-SEC-IR and NMR analyses of these fractions.

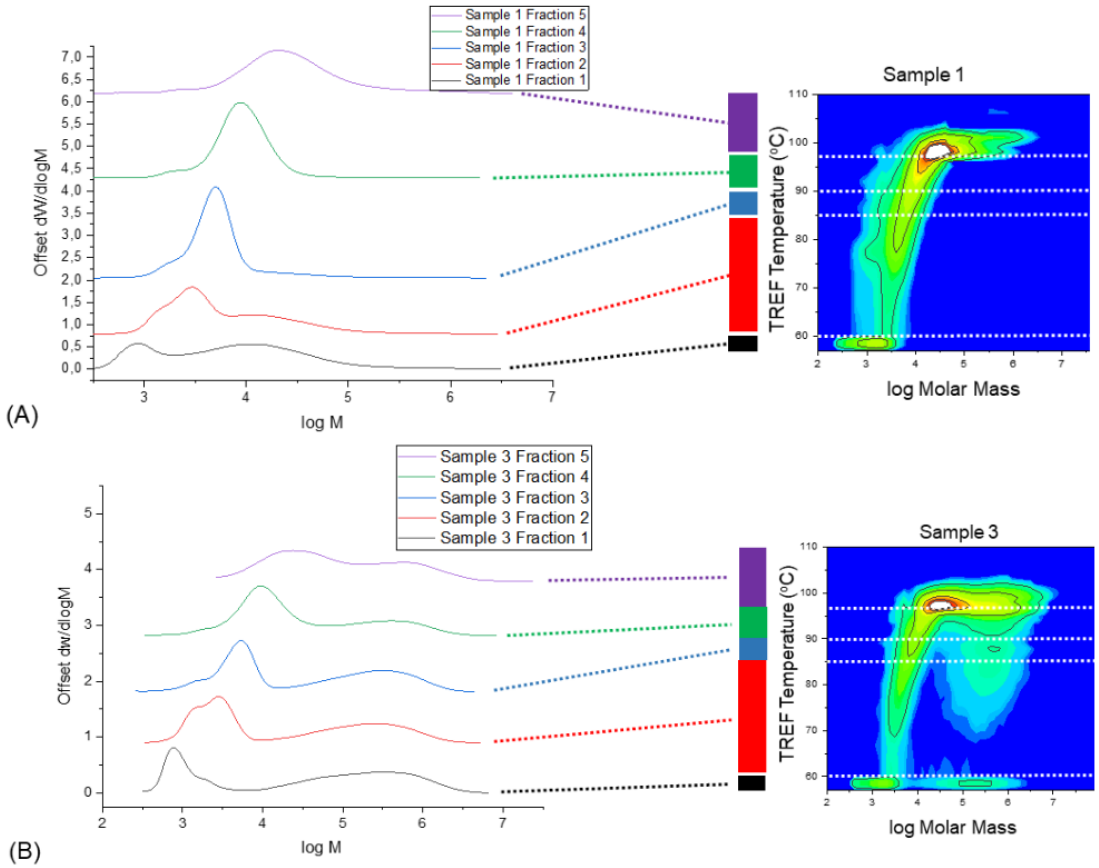


Figure 7. Molar mass distributions of TREF fractions of samples 1 (A) and 3 (B) as obtained by HT-SEC, TREF collection temperatures were 60 (fraction 1), 85 (fraction 2), 90 (fraction 3), 97 (fraction 4) and 130 °C (fraction 5).

The HT-SEC results for the TREF fractions of samples 1 and 3 are summarized in **Figures 7A** and **7B**. As has been explained before, sample 1 is a PE homopolymer and, accordingly, does not contain copolymer fractions. As has been found by CFC, this sample consists of lower and higher molar mass components that are eluting at increasing TREF temperatures with regard to their increasing molar masses. Fractions 1 and 2 exhibit bimodal MMDs which could be a result of co-crystallization occurring in the TREF process.

Sample 3 presented in **Figure 7B** has a bulk comonomer content of 0.50 mol.%) and shows copolymer fractions in the CFC plot. The MMDs of the TREF fractions as obtained by HT-SEC show nicely that the sample contains a lower molar mass PE fraction with a molar mass that increases with increasing TREF elution temperature and a high molar mass PE fraction that elutes at the highest TREF temperature (above 100 °C). In addition, copolymer fractions are found particularly in TREF fractions 2 and 3 that correspond to the high molar mass components in the SEC profiles.

The TREF fractions containing comonomer were investigated by HT-SEC-IR. In the present application the comonomer content is expressed as SCB/1000C. **Figure 8** summarizes the results for sample 3 having a comonomer content of 0.5 mol.% of 1-hexene. The HT-SEC-IR results for sample 3 show clearly that different TREF fractions exhibit different compositions. Fractions 1-3 exhibit bimodal MMDs with a low molar mass component that does not contain comonomer. Accordingly, this component can be assigned to low molar mass PE. The high molar mass components contain comonomer and it is seen that the comonomer content decreases with increasing molar mass. At the same time, the comonomer content decreases with increasing TREF elution temperature (increasing fraction number). This confirms that TREF fractionates the copolymer according to the comonomer content from higher to lower comonomer content with increasing TREF temperature.

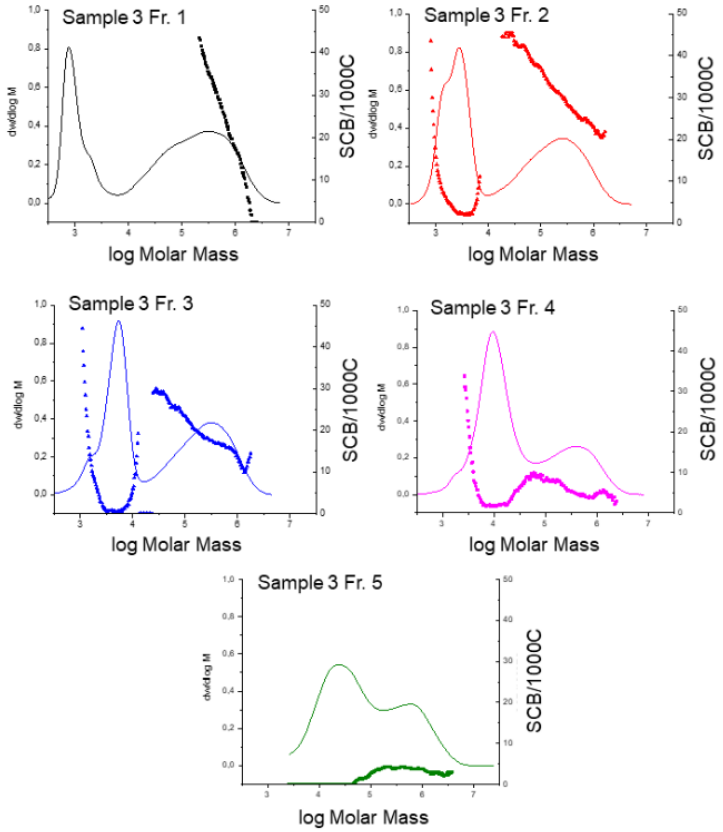


Figure 8. Molar mass distributions and SCB as a function of molar mass of TREF fractions of sample 3 as obtained by HT-SEC-IR, TREF collection temperatures were 60 (fraction 1), 85 (fraction 2), 90 (fraction 3), 97 (fraction 4) and 130 °C (fraction 5).

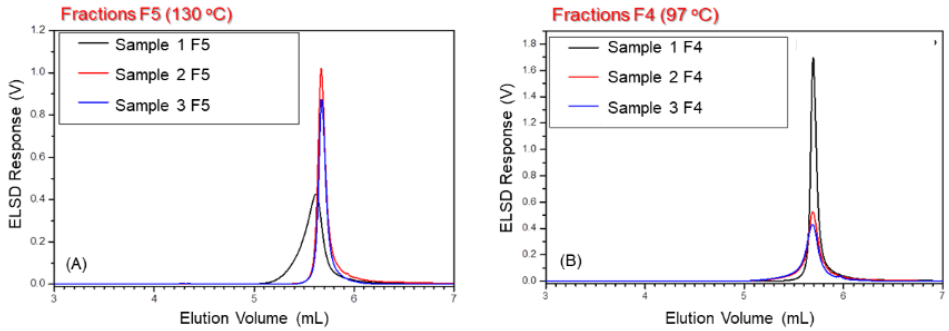


Figure 9. Chemical composition separations of TREF fractions of samples 1, 2 and 3 as obtained by SGIC, fractions 5 (A) and 4 (B).

Journal Name

ARTICLE

At the same time it is seen that the molar mass of the lower molar mass homopolymer increases with increasing TREF temperature which is in agreement with the findings for sample 1. In fractions 4 and 5 very low comonomer contents are detected. It is assumed that the high molar mass parts in the MMDs are composed of co-eluting high molar mass PE and copolymer. This, again, is in perfect agreement with the CFC results as presented in **Figure 4**.

The results of HT-SEC-IR are in excellent agreement with the NMR data for the fractions which show a decrease of the calculated C6 content in the high molar mass fractions with increasing TREF temperature. The molar masses, comonomer contents and triad distributions for the pTREF fractions of samples 2 and 3 are presented in **Table 6**. For some of the fractions the quantities were too low to be analyzed by ^{13}C NMR. For those that provided NMR results it can be seen that the fractions eluting at pTREF temperatures of around 90 – 100 °C which contain the highest amounts of copolymer, the C6 content was quite low. For sample 3 the copolymer-rich fraction at 88 °C had a comonomer content of 1.06 mol.%. This result explains why it is so difficult to obtain selective compositional information on the copolymer fractions.

In the next step, the TREF fractions were analyzed by SGIC. As was mentioned before, this technique separates according to chemical composition (comonomer content) in the direction of decreasing comonomer contents. The fractionation in SGIC is not influenced by crystallinity or crystallizability and provides, therefore, direct chemical composition information.

The last eluting SGIC fractions (elution volume ~5.7 mL) can be assigned to PE homopolymer. The SGIC experiments convincingly confirm the HT-SEC results. As was suspected, fractions F4 (97 °C) and F5 (130 °C) consist mainly of PE homopolymer (see **Figure 9**) which is also confirmed by the HT-SEC-IR and NMR analyses. From a chemical composition point of view, the most interesting fractions are Fr. 2 eluting at a TREF temperature of 85 °C, see **Figure 10**. For these fractions bimodal HPLC profiles are obtained with elution ranges of 4.0 – 5.0 mL and 5.0 – 6.0 mL. The later eluting fractions can be assigned to high molar mass PE (for sample 1) and high molar mass, low comonomer content copolymer (for samples 2 and 3). For the early eluting fractions the assignment is more challenging. Sample 1 does not contain any comonomer and, therefore, the early eluting part must be due to low molar mass PE.

The fact that in this fraction low and high molar mass PE are found indicates, that co-crystallization took place during the TREF fractionation. From CFC it is known that samples 2 and 3 also contain low molar mass PE. The early eluting SGIC fractions of these samples could, therefore contain both low molar mass PE and high molar mass copolymer. From the SGIC profiles molar mass information cannot be obtained since this method fractionates mainly according to chemical composition. Therefore, low and high molar mass PEs are not separated from each other by SGIC unless the molar mass is below 20 kg/mol.

Table 6. SEC and NMR results for the pTREF fractions of samples 2 and 3.

Sample	T_{TREF} [°C]	M_n [kg/mol]	M_w [kg/mol]	M_z [kg/mol]	C6 [mol.%]	EEE	EEX	EXE
2	60	2.6	260.0	1300.0	1.33	95.1	3.5	1.3
	85	4.4	161.0	876.0	1.54	95.0	3.4	1.6
	90	7.4	174.0	902.0	1.15	96.2	2.6	1.2
	97	11.3	181.0	1020.0	0.52	98.2	1.3	0.5
	130*	--	--	--	n.m*	--	--	--
3	60	2.4	273.0	1230.0	0.60	97.0	2.1	0.8
	85	3.7	170.0	1540.0	1.06	96.5	2.3	1.2
	90	6.1	204.0	1500.0	0.83	97.1	1.9	0.9
	97	9.5	181.0	1100.0	0.43	98.5	1.1	0.5
	130	22.0	332.0	1570.0	n.m*	--	--	--

*Fraction insufficient for further analyses.

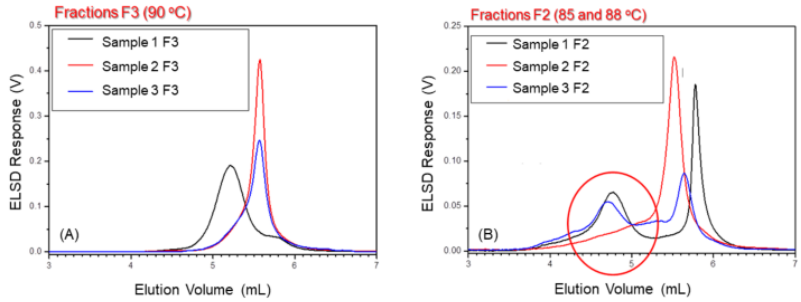


Figure 10. Chemical composition separations of TREF fractions of samples 1, 2 and 3 as obtained by SGIC, fractions 3 (A) and 2 (B).

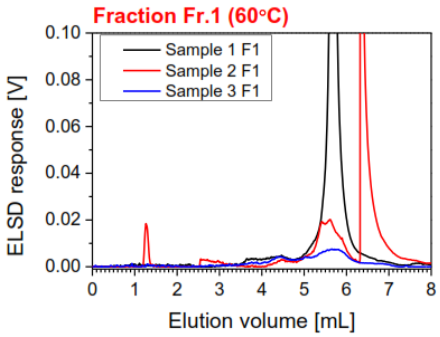


Figure 11. Chemical composition separations of TREF fractions 1 of samples 1, 2 and 3 as obtained by SGIC.

As has been found by HT-SEC, TREF fractions Fr.1 are rather ill-defined and require further investigations. The late elution of these fractions suggests that they consist of low molar mass PE and copolymer fractions with broad comonomer and molar mass distributions, see **Figure 11**.

Unfortunately, all obtained TREF fractions contain some low molar mass PE fractions (see **Figure 8** for the HT-SEC-IR analysis of the TREF fractions). By applying only one-dimensional separation techniques like SGIC or TREF it is very challenging or even impossible to comprehensively analyze the chemical composition of such highly bimodal TREF fractions. For such samples two-dimensional separation techniques are more feasible, which are capable of separating molecules with similar PE sequence lengths according to molar mass. The method of choice here is comprehensive 2D-LC that separates the samples according to composition in the 1st dimension and according to molecular size in the 2nd dimension. Fractions that are generated in the 1st dimension are temporarily collected in two sample loops and subsequently injected into the 2nd dimension (refer to the experimental part for more details).

The results of the 2D-LC separations are summarized in **Figures 12** and **13**. As was already indicated by the SGIC experiments, fractions Fr.5 is mainly due to PE homopolymer. The position and shape of the profile of sample 2/Fr.5 is characteristic for high molar mass PE while the position and shape of the profile of sample 1/Fr.5 indicates that this is a blend of higher and lower molar mass PE. The broader elution profile that is seen for sample 1/Fr.5 (see **Figure 12A**) as compared to sample 2/Fr.5 can now be explained by the presence of this lower molar mass PE. The same interpretation is valid for sample 1/Fr.4 while for sample 2/Fr.4 it seems that a small portion of polymer elutes below the red line as indicated in **Figure 12B**. The red line indicates a critical elution volume of ~5.3 – 5.4 mL: above this line PE elutes while below this line high molar mass copolymer fractions elute.

As compared to the 2D-LC plots of fractions Fr.5 and Fr.4, the 2D-LC plots of fractions Fr.3 and Fr.2 indicate a significantly more complex composition, see **Figure 13**. This is expected because it was shown previously that these fractions contain PE homopolymer along with copolymer fractions.

This is particularly obvious for the fractions Fr.2 of sample 2 but also for Fr.3 of sample 3 which exhibit a clear bimodality. The components that elute at a HPLC elution volume of 4.0 – 5.3 mL and an elution volume below 4 mL in SEC mode can be assigned to copolymer fractions while the components eluting at HPLC elution volumes larger than 5.5 mL are due to PE homopolymer. These findings are in perfect agreement with the SGIC experiments. In addition to the separation according to chemical composition the 2D-LC experiments provide separation according to molar mass. The higher SEC elution volume of the 'copolymer' fractions show that they have lower molar masses compared to the PE fractions seen at SEC elution volumes of 3.0 – 4.0 mL. A much more conclusive assignment of the different components can be achieved when the separation of the homo- and copolymer fractions is improved. In future work the selectivity of the SGIC dimension needs to be improved to be able to get a clear fractionation into high and low molar mass PE and the copolymer fractions.

Conclusions

The present study has shown clearly that very complex polyolefins such as multimodal ethylene copolymers exhibit complex and multimodal molecular properties. These include the molar mass distributions of the low and high molar mass PE homopolymer fractions as well as the chemical composition and molar mass distributions of the copolymer fractions. To address these multiple distributions in molecular properties, advanced preparative fractionation (pTREF) combined with a variety of analysis methods must be used. It is demonstrated that most detailed molecular information is obtained by combining CFC,

pTREF, SGIC and comprehensive 2D-LC. For future studies it is important to enhance the selectivity of the fractionation methods and to combine pTREF with preparative molar mass fractionation as a complementary method.

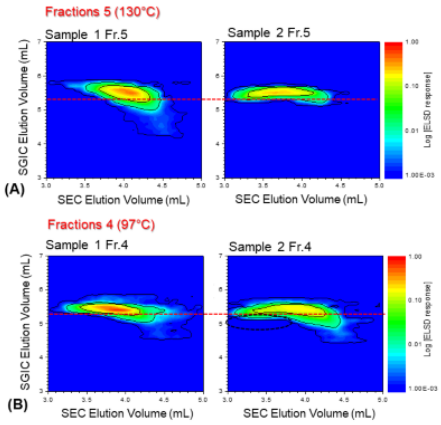


Figure 12. 2D-LC (SGIC × SEC) separations of TREF fractions 5 (A) and 4 (B) of samples 1 and 2; . . . . . copolymer fraction.

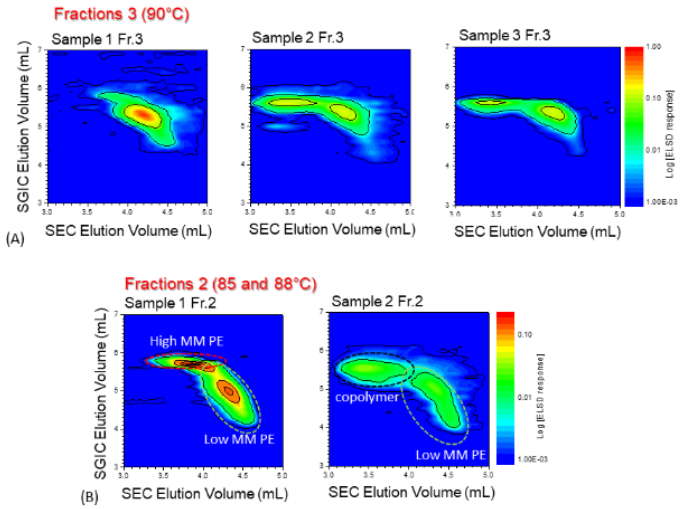


Figure 13. 2D-LC (SGIC × SEC) separations of TREF fractions 3 (A) and 2 (B) of samples 1-3.

Conflicts of interest

There are no conflicts of interest to declare.

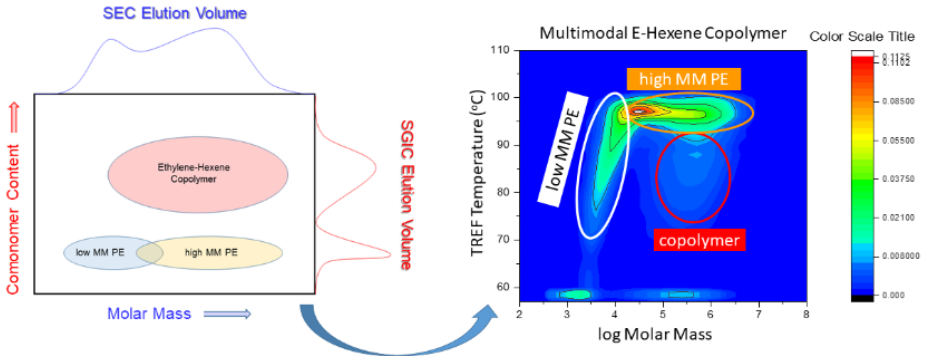
Acknowledgements

Notes and references

1. Z. Dobkowski, *Fluid Phase Equilib.*, 1998, **152**, 327–336.
2. H. Pasch, *Polym. Adv. Technol.*, 2015, **26**, 771–784.
3. Y.-h. Xue, S.-q. Bo and X.-l. Ji, *Chin. J. Polym. Sci.*, 2015, **33**, 508–522.
4. H. Benoit and P. Doty, *J. Phys. Chem.* , 1953, **57**, 958–963.
5. H. Pasch and M. I. Malik, *Advanced separation techniques for polyolefins*, Springer, 2016.
6. P. Tackx and J. Tacx, *Polymer*, 1998, **39**, 3109–3113.
7. P. M. Wood-Adams and J. M. Dealy, *Macromolecules*, 2000, **33**, 7481–7488.
8. W. W. Yau, *Polymer*, 2007, **48**, 2362–2370.
9. S.-H. Yoo and J.-l. Jane, *Carbohydr. Polym.*, 2002, **49**, 307–314.
10. B. Monrabal, L. Romero, N. Mayo and J. Sancho-Tello, *Macromol. Symp.*, 2009, **282**, 14–24.
11. M. J. Phiri, S. Cheruthazhekatt, A. Dimeska and H. Pasch, *J. Polym. Sci., Part A: Polym. Chem.*, 2015, **53**, 863–874.
12. C. L. P. Shan, L. G. Hazlitt and D. Gillespie, *Polymer*, 2005, **46**, 11755–11767.
13. Y. Xue, S. Bo and X. Ji, *J. Polym. Res.*, 2015, **22**, 160.
14. B. Monrabal and P. del Hierro, *Anal. Bioanal. Chem.*, 2011, **399**, 1557–1561.
15. A. Albrecht, R. Brüll, T. Macko and H. Pasch, *Macromolecules*, 2007, **40**, 5545–5551.

16. T. Macko and H. Pasch, *Macromolecules*, 2009, **42**, 6063–6067.
17. H. Pasch, L. C. Heinz, T. Macko and W. Hiller, *Pure Appl. Chem.*, 2008, **80**, 1747–1762.
18. H. Pasch, M. I. Malik and T. Macko, *Adv. Polym. Sci.*, 2013, **251**, 77–140.
19. R. Cong, A. W. deGroot, A. Parrott, W. Yau, L. Hazlitt, R. Brown, M. Cheatham, M. D. Miller and Z. Zhou, 2012.
20. R. Cong, W. Degroot, A. Parrott, W. Yau, L. Hazlitt, R. Brown, M. Miller and Z. Zhou, *Macromolecules*, 2011, **44**, 3062–3072.
21. US 8318896 B2 2011.
22. A. Krumme, M. Basiura, T. Pijpers, G. Vanden Poel, L. C. Heinz, R. Bruell and V. BF Mathot, *Mater Sci.*, 2011, **17**, 260–265.
23. Y.-h. Xue, S.-q. Bo and X.-l. Ji, *Chin. J. Polym. Sci.*, 2015, **33**, 1000–1008.
24. Y. Xue, S. Bo and X. Ji, *J. Polym. Res.*, 2016, **23**, 1–8.
25. J. K. Jørgensen, A. Larsen and I. Helland, *e-Polymers*, 2010, **10**, 1596–1612.
26. A. Ortin, B. Monrabal and P. del Hierro, *LC GC EUROPE*, 2010, 35–36.
27. A. Ortin, B. Monrabal and J. Sancho-Tello, *Macromol. Symp.*, 2007, **257**, 13–28.
28. A. Albrecht, K. Jayaratne, L. Jeremic, V. Sumerin and A. Pakkanen, *J. Appl. Polym. Sci.*, 2016, **133**.
29. S. Cheruthazhekatt, G. W. Harding and H. Pasch, *J. Chromatogr. A*, 2013, **1286**, 69–82.
30. S. Cheruthazhekatt, T. F. J. Pijpers, G. W. Harding, V. B. F. Mathot and H. Pasch, *Macromolecules*, 2012, **45**, 2025–2034.
31. A. Ginzburg, T. Macko, V. Dolle and R. Brüll, *Eur. Polym. J.*, 2011, **47**, 319–329.
32. A. Ginzburg, T. Macko, V. Dolle and R. Brüll, *J. Chromatogr. A*, 2010, **1217**, 6867–6874.
33. A. Ginzburg, T. Macko, V. Dolle and R. Brüll, *J. Appl. Polym. Sci.*, 2013, **129**, 1897–1906.
34. P. Eselem Bungu and H. Pasch, *Polym. Chem.*, 2017, **31**, 4565–4575.
35. K. Klimke, M. Parkinson, C. Piel, W. Kaminsky, H. W. Spiess and M. Wilhelm, *Macromol. Chem. Phys.*, 2006, **207**, 382–395.
36. M. Parkinson, K. Klimke, H. W. Spiess and M. Wilhelm, *Macromol. Chem. Phys.*, 2007, **208**, 2128–2133.
37. A. Ortin, B. Monrabal, J. Montesinos and P. Del Hierro, 2009.
38. Y. Fan, Y. Xue, W. Nie, J. Xiangling and S. Bo, *Polym. J.*, 2009, **41**, 622–628.
39. S. Cheruthazhekatt, T. F. J. Pijpers, V. B. F. Mathot and H. Pasch, *Anal. Bioanal.Chem.*, 2013, **405**, 8995–9007.
40. S. Cheruthazhekatt, N. Mayo, B. Monrabal and H. Pasch, *Macromol. Chem. Phys.*, 2013, **214**, 2165–2171.

Entry for the Table of Contents



Multimodal ethylene copolymers are comprehensively analyzed by combination of preparative fractionation and multidimensional liquid chromatographic analysis.

Chapter 5

Conclusions and recommendations

Overall conclusions from the studies conducted in the present thesis work are presented and recommendations for future work based on the findings are proposed.

5.1 Conclusions

The present study demonstrated the unique capabilities of high-temperature liquid chromatography as a characterization platform for polyolefin materials that are challenging to characterize with other established methods. The capabilities of HT-HPLC are further enhanced when coupled to pre-fractionation techniques such as preparative temperature rising elution fractionation (p-TREF) and preparative solution crystallization (p-SCF).

Major conclusions from the various studies are summarized as follows:

In the first part of the study, it was shown that both oxidized and non-oxidized waxes can be separated into their constituent oligomers with porous graphitic carbon as the stationary phase. This was successfully demonstrated by HT-SGIC on two oxidized waxes and a non-oxidized wax using. The separations in the first dimension were successfully coupled to fast HT-SEC in the second dimension to relate CCD to MMD via HT-2D-LC. The findings show that oligomers in oxidized and non-oxidized waxes can be separated irrespective of their oxidation levels. Chromatographic separations in HT-2D-LC showed a broadening of the molar mass distributions of shorter oligomers for oxidized waxes. This was attributed to oligomer chain modification. This also reveals that the oxidation process mainly affects low molar mass oligomers as compared to those with higher molar masses. To get the best of the HT-HPLC system, the ELSD detector had to be optimized. It was shown that for low molar mass waxes, better detection is achieved with the ELSD when both the evaporator temperature and the nebulizing gas flow are lowered. Pre-fractionation techniques were shown to be necessary for the complete microstructural unravelling of the waxes. These enable the pre-concentration of specific oligomer fractions from the bulk waxes resulting in more sophisticated chromatograms which indicated the presence of overlooked oligomers. Even shorter and possibly odd-numbered oligomers were identified which have not been detected in bulk wax analysis.

For the first time, heterogeneous fractions in oxidized waxes were separated using HT-SGIC under tailored conditions of analysis. This method serves as a viable alternative to GC with the capability of handling even higher molar masses or highly oxidized waxes. Low viscous solvents such as decane and cyclohexanone were found to be the best combination of

adsorption and desorption promoting solvents, respectively. In addition, lower column temperatures were both effective at promoting adsorption and improving separation.

As an alternative to HT-SGIC, HT-TGIC on silica was applied for the fast characterization of oxidized waxes by liquid chromatography. Through this technique, separation and detection of heterogeneous fractions of increasing degree of oxidation was achieved. In addition, the separation mechanism in HT-TGIC was shown to be influenced by the oxidized functionalities, molar mass and crystallinity. It was demonstrated that the coupling of HT-SGIC to fast HT-SEC in the second dimension to produce 2D contour plots gives more details on the differences in the retention of components of oxidized and non-oxidized waxes.

In the second part of the study a comparison of HT-SGIC and HT-TGIC was done using a set of ethylene-propylene copolymers. For both techniques, linear dependencies of elution volume (HT-SGIC) or elution temperature (HT-TGIC) and copolymer composition were obtained. From the set of samples studied, it was established that the accessible ethylene content separation ranges are 50 – 100 mol% ethylene for HT-TGIC and 26.8 – 100 mol% ethylene for HT-SGIC. This shows that HT-SGIC has a significantly broader accessible ethylene content range as compared to HT-TGIC.

The third part of the study shows that multidimensional analytical approaches are required to address the complex molecular properties of multimodal ethylene-1-hexene copolymers. In addition to the broad MMDs where low and high molar mass PE homopolymer fractions are present, significant amounts of copolymer with low and high comonomer contents make the materials very complex in their CCD. In order to address the multiple distributions in microstructure, p-TREF combined with a variety of subsequent analytical methods was used. It was demonstrated that most detailed molecular information is obtained by combining CFC, p-TREF, HT-SGIC and comprehensive HT-2D-LC.

5.2 Recommendations for future work

Characterization of polyolefins serves two purposes, the first being continuous monitoring of online processes. The second is a more detailed and thorough approach aimed at understanding the complete microstructure of a given sample.

Different types of waxes for different purposes are available on the market from different producers. For future work, it is possible to obtain and create detailed libraries of the different types of waxes regarding their microstructure. However, if libraries of microstructural properties are to be created, a even more detailed and thorough approach as the one used in the present study is required. This will enable for the better tailoring of the waxes to specific applications based on microstructure rather than conventional titration and saponification methods.

To add to the present work, other fractionation techniques with better fraction recovery can be coupled to HT-SGIC to confirm the presence of odd-numbered oligomers and to monitor the effect of oxidation on chain microstructure. Simple laboratory setups can be used to fractionate the waxes. In addition, preparative fractionation based on oxidation level rather than molar mass/crystallinity can be applied. However, this is easier said than done since the mentioned microstructural properties are interdependent.

For EP rubbers as well as for PP-EPR reactor blends, HT-TGIC remains insensitive for some compositions even if improved experimental protocols are applied. To improve the accessible separation range of HT-TGIC, the use of other weaker solvents/binary solvent mixtures can be investigated. It will be interesting to see if a change in the mobile phase broadens the accessible ethylene content range. The interest stems from the fact that all industrially relevant EP rubbers have comonomer contents below 60 mol% ethylene such as in the case of PP-EPR reactor blends.

With regard to elastomers and bimodal HDPE resins it is important to enhance the selectivity of the fractionation methods. Therefore, instead of crystallization-based fractionation methods such as p-TREF, preparative molar mass fractionation (p-MMF) can be used as alternative preparative fractionation method. This solves the major challenge of co-elution of low molar mass PE with high comonomer content copolymer fractions as the components are separated according to molar mass rather than crystallizability.

Appendix A: Supporting information to Section 4.1

A Multidimensional Fractionation Protocol for the Oligomer Analysis of Oxidized Waxes

Anthony Ndiripo, Harald Pasch*

Department of Chemistry and Polymer Science, University of Stellenbosch, 7602 Matieland, South Africa

*Corresponding author: Prof. Harald Pasch, e-mail: hpasch@sun.ac.za

Table 1s. Average molar masses values and molar mass dispersities (*Đ*) of polystyrene standards used for SEC calibration.

Vail Code*	M_n (g/mol)	M_w (g/mol)	*Đ*	M_p	Mass/vial
RED	540 5000	5 680 000	1.05	6 035 000	0.8
	419 300	430 900	1.03	436 200	1.6
	19 740	20 260	1.03	19 920	2.4
	1 080	1 170	1.08	1 150	3.2
YELLOW	2777000	2 996 000	1.08	3 187 000	0.8
	197900	204 000	1.03	202 100	1.6
	9370	9 580	1.02	9 590	2.4
	540	605	1.11	580	3.2
GREEN	1 013 000	1 059 000	1.05	1 074 000	0.8
	68 100	69 350	1.02	70 500	1.6
	4 550	4 690	1.03	4 730	2.4
	-	-	1.00	162	3.2

*Polystyrene High EasiVials (4mL)

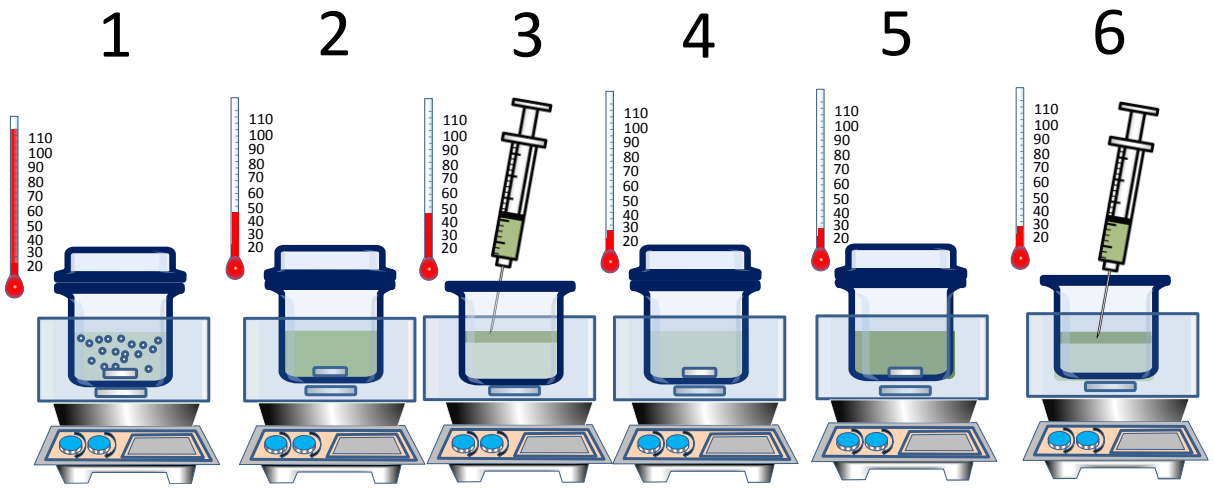


Fig. 1s. Illustration of the solution crystallisation fractionation process.

Table 2s. A summary of the retention volumes (V_r), separation between peaks $(V_r\text{-}x)$, and widths at half peak maximum of wax No. 1 peaks obtained from column temperatures of 140, 120 and 100 °C.

Peak	140 °C			120 °C			100 °C		
	V_r (mL)	$(V_r–x)^a$	FWHM *	V_r (mL)	$(V_r–x)^a$	FWHM *	V_r (mL)	$(V_r–x)^a$	FWHM *
1	3.48	-	0.060	3.63	-	0.050	3.90	-	0.049
2	3.58	0.10	0.054	3.73	0.10	0.049	3.99	0.09	0.051
3	3.67	0.09	0.052	3.81	0.08	0.049	4.08	0.09	0.053
4	3.75	0.08	0.050	3.89	0.08	0.049	4.16	0.08	0.054
5	3.83	0.08	0.049	3.97	0.08	0.050	4.25	0.09	0.055
6	3.90	0.07	0.049	4.04	0.07	0.050	4.33	0.08	0.055
7	3.97	0.07	0.047	4.11	0.07	0.050	4.41	0.08	0.056
8	4.04	0.07	0.049	4.18	0.07	0.051	4.49	0.08	0.055
9	4.10	0.06	0.045	4.25	0.07	0.048	4.57	0.08	0.058
10	4.16	0.06	0.053	4.32	0.07	0.052	4.64	0.07	0.055
11	4.22	0.06	0.042	4.38	0.06	0.046	4.72	0.08	0.059
12	4.27	0.05	0.048	4.44	0.06	0.047	4.80	0.08	0.056
13	4.33	0.06	0.042	4.50	0.06	0.044	4.87	0.07	0.057
14	4.38	0.05	0.040	4.56	0.06	0.041	4.95	0.08	0.057
15	4.43	0.05	0.037	4.61	0.05	0.036	5.03	0.08	0.056
16	4.48	0.05	0.024	4.67	0.06	0.028	5.10	0.07	0.051

*Full width at half maximum

[a] $(V_r–x)$ = separation from last peak where x is the V_r of previous peak.

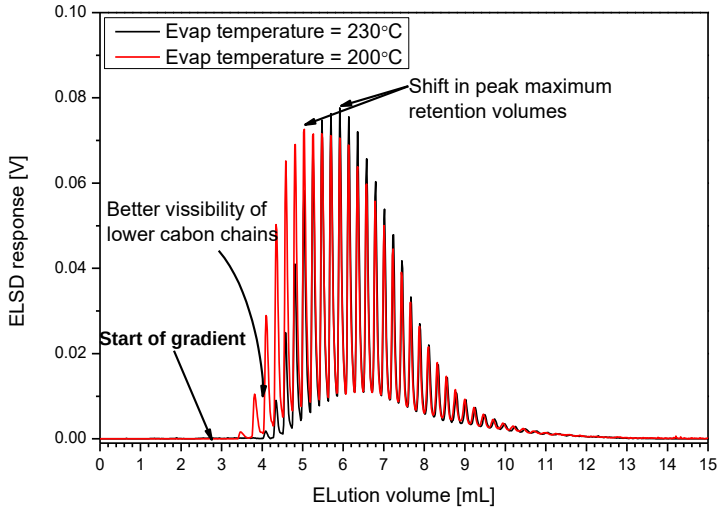


Fig. 2s. Comparison of chromatograms obtained using different evaporator temperatures for the analysis of wax No. 1 using a decane → ODCB gradient. The visibility of lower carbon chains present in the wax improves when the evaporator temperature is decreased from 230 °C (black line) to 200 °C (red line).

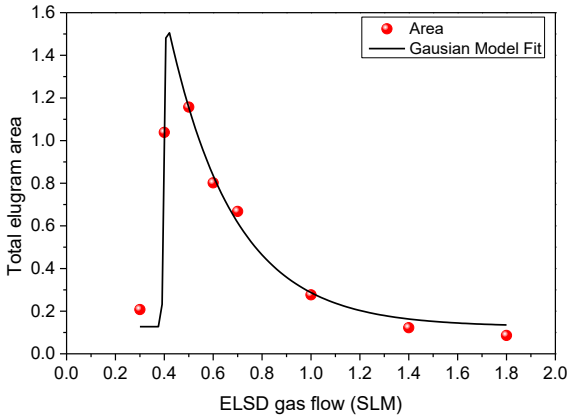


Fig. 3s. Relationship between ELSD gas flow and elugram area for wax (No. 1). A Gaussian Model fit was used to illustrate the trend. The detector conditions kept constant were as follows: Nebuliser = 140 °C; Evaporator = 200 °C. The mobile phase flow was 0.5 mL min^{-1}.

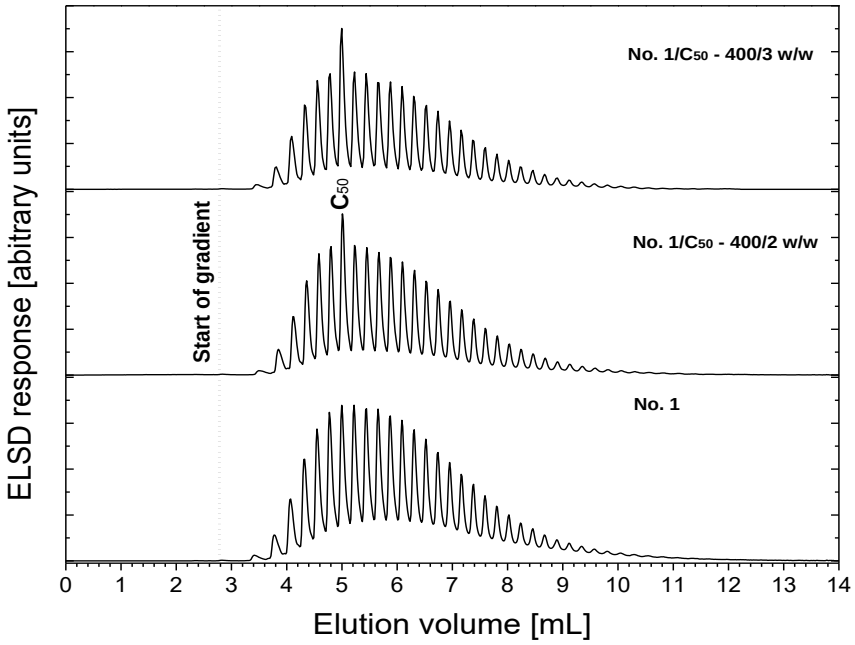


Fig. 4s. Stack plots of No. 1 before and after doping with 400/2 and 400/3 (w/w) C_{50}. The system conditions were as follows: column temperature = 100 °C; system temperature = 140 °C; flow rate = 0.5 mL min^{-1}.

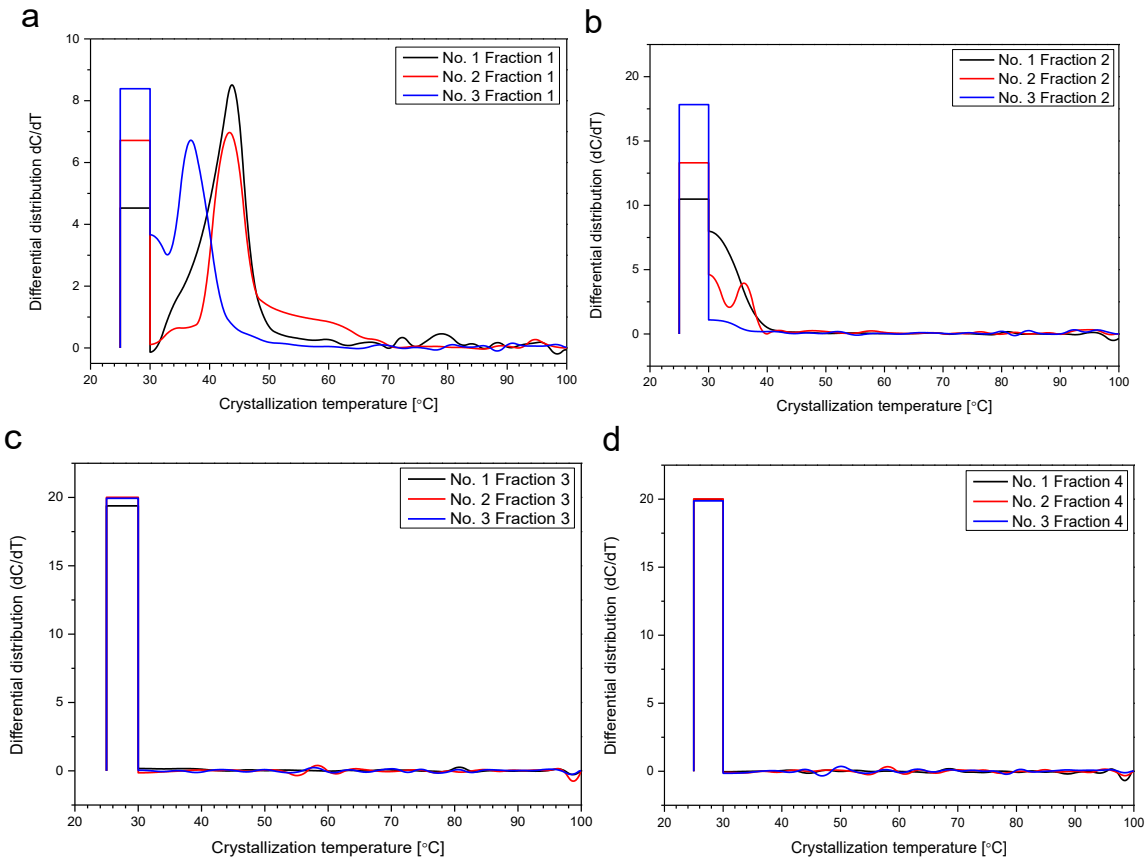


Fig. 5s. Overlays of CRYSTAF profiles of wax fractions obtained at 45, 25, 0 and below 0 °C in (a-d) respectively.

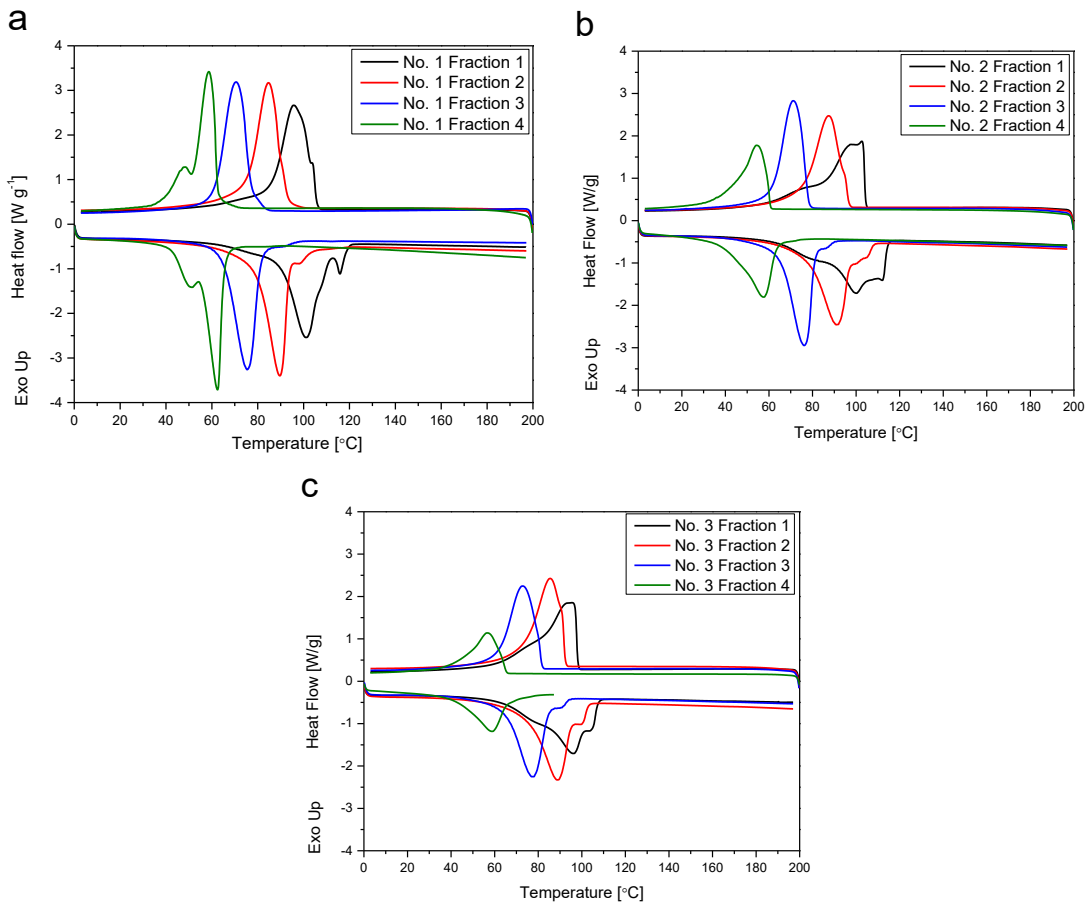


Fig. 6s. Overlays of DSC thermograms obtained from the analyses of the solution crystallisation fractions of waxes No. 1, No. 2 and No. 3. The heating and cooling rates were set at 10 °C min^{-1} for a 0 – 200 °C temperature range.

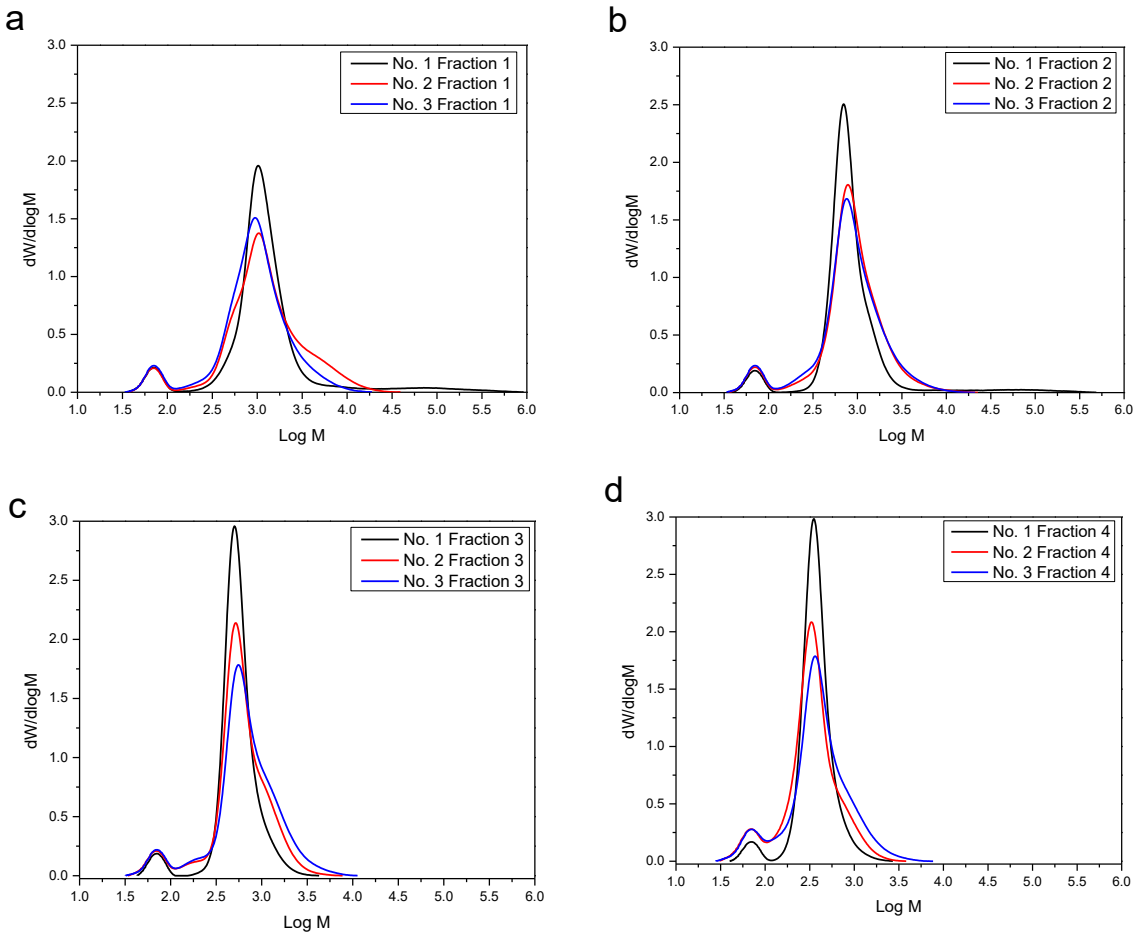


Fig. 7s. Overlays of molar mass distributions of wax fractions obtained at 45, 25, 0 and below 0 °C in (a-d) respectively.

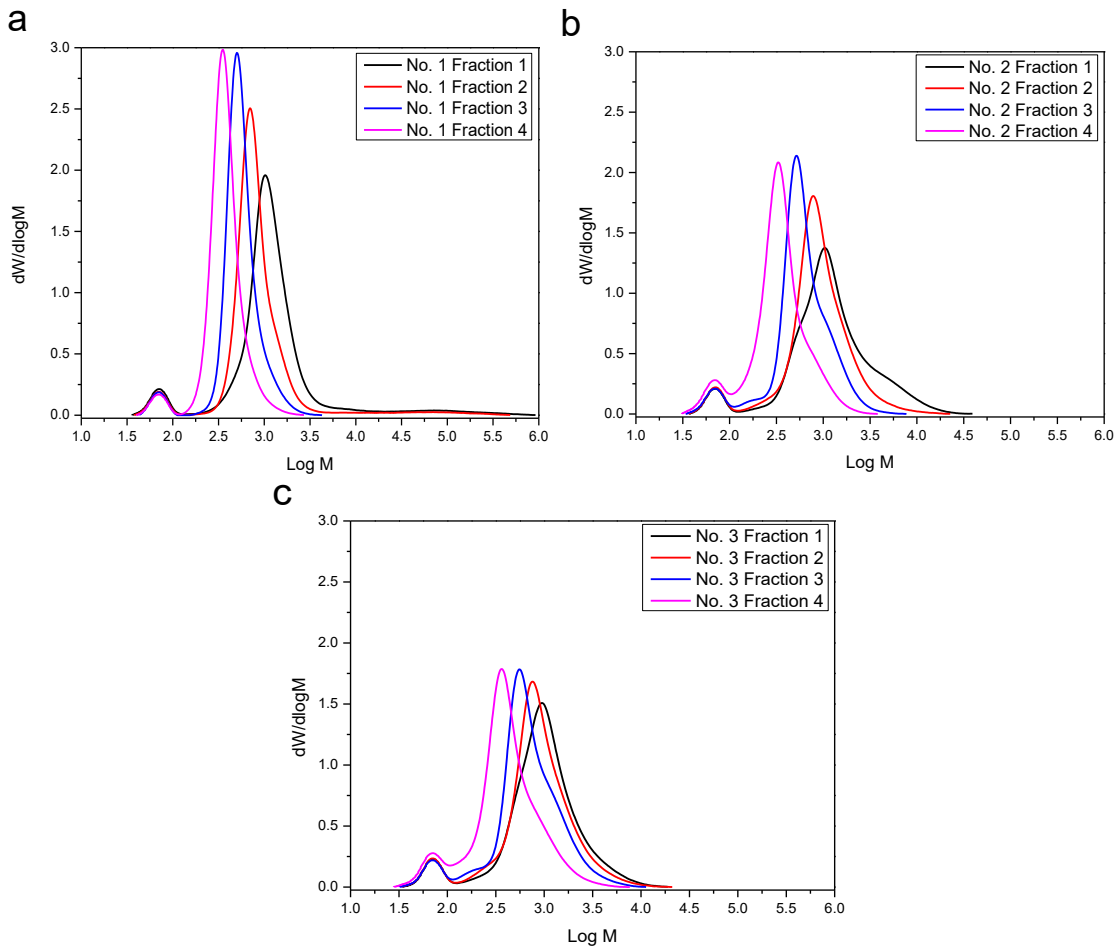


Fig. 8s. Overlays of molar mass distribution curves of SCF fractions of waxes No.1, No. 2 and No. 3 in (a-c) respectively.

Appendix B: Supporting information to Section 4.2

Supporting Information

Comprehensive Analysis of Oxidized Waxes by Solvent and Thermal Gradient Interaction Chromatography and Two-Dimensional Liquid Chromatography

Anthony Ndiripo, Harald Pasch*

Department of Chemistry and Polymer Science, University of Stellenbosch, 7602 Matieland, South Africa

*Corresponding author: Prof. Harald Pasch, e-mail: hpasch@sun.ac.za

Table of Contents

Supplementary Experimental methods

Size Exclusion Chromatography (SEC). Molar masses and molar mass dispersities of the wax samples were determined on a PL-GPC 220 High Temperature Chromatograph [Polymer Laboratories, Church Stretton, UK (now part of Agilent)] equipped with a differential refractive index (RI) detector. The samples (4 mg) were dissolved in 2 mL of TCB for 0.5 hr together with 0.025 % butyl-hydroxy-toluene (BHT) which acted as a stabilizer to prevent sample oxidative decomposition/degradation. TCB with 0.0125 % BHT was used as the mobile phase at a flow rate of 1 mL min^{-1}. Three 300 × 7.5 mm^2 PLgel Olexis columns (Agilent Technologies, UK) were used together with a 50 × 7.5 mm^2 PLgel Olexis guard column and 200 µL of each sample was injected. All experiments in HT-SEC were carried out at 150 °C.

Fourier Transform Infrared Spectroscopy (FTIR). Attenuated total reflectance (ATR) measurements of the waxes and their fractions were recorded on a Thermo Nicolet iS10 spectrometer. Solid samples were used in all the analyses with no prior modifications (except drying in the case of fractions). Spectra recorded from 4000 to 650 cm^{-1} were obtained from a collection of 64 scans at a resolution of 4 cm^{-1} with automatic background subtraction. Thermo Scientific OMNIC software (version 8.1) was used for data collection and processing.

Differential Scanning calorimetry. The wax samples were analyzed using the Q100 DSC system (TA Instruments, Delaware, USA) at a heating and cooling rate of 10 °C min^{-1} across a temperature range of 0 – 200 °C. An aluminum pan and lid folded and pressed were used as a reference and approximately 5 mg of each sample were used.

Crystallization Analysis Fractionation (CRYSTAF). A commercial CRYSTAF apparatus Model 200 (PolymerChAR, Valencia, Spain) was used for crystallization analysis

fractionation experiments. Approximately 20 mg of each sample were dissolved in 35 mL of TCB. Crystallization was carried out under constant stirring in stainless steel reactors which are equipped with automatic agitation and filtration devices. The samples were dissolved for 90 min. After dissolution, the temperature was decreased from 100 °C to approximately 30 °C at a rate of 0.2 °C min^{-1}. The concentration of the solution was determined automatically using an infrared detector operating at a fixed wavelength of 3.5 µm. Five samples were analyzed simultaneously and the experiment took approximately 15 hrs.

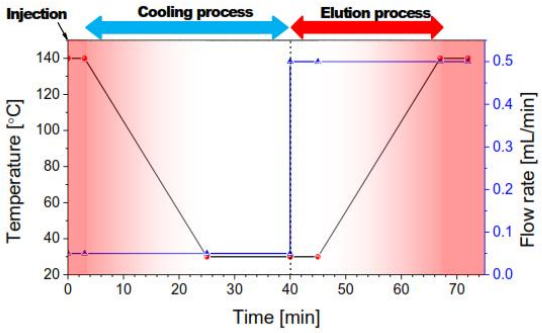
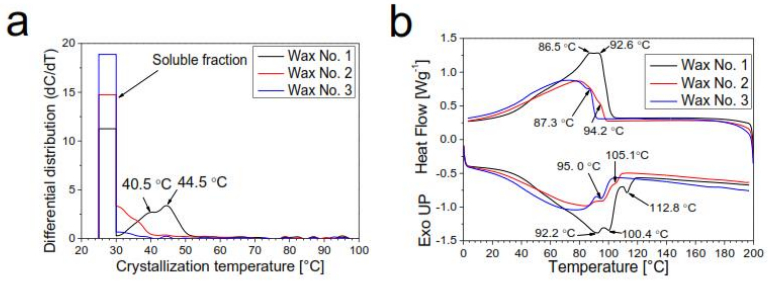


Figure S1. Temperature profile (black line with red spheres) and flow rate (blue line with triangles) used in TGIC.



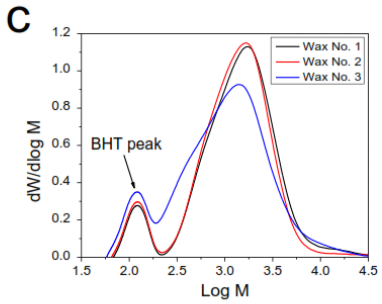


Figure S2. CRYSTAF profiles of waxes No. 1, 2 and 3, solvent: 1,2-dichlorobenzene, cooling rate 0.2 °C min^{-1} (a); DSC thermograms showing first crystallization and second melting curves, heating and cooling rates 10 °min^{-1} (b); SEC molar mass distribution curves (c).

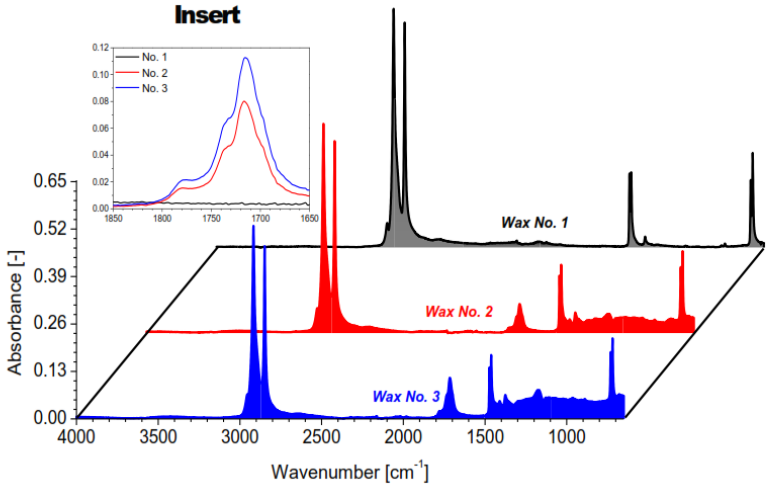


Figure S3. Overlays of ATR-FTIR spectra of waxes No. 1, 2 and 3 and enlargement of the carbonyl regions.

Table S1. Peak elution volumes of wax No. 3 as influenced by column temperature.

Column temperature [°C]	V_e [mL]				
	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5
140	2.87	3.38	4.21	4.73	7.30
130	2.91	3.52	4.61	5.29	7.39
120	2.94	3.67	5.11	6.15	7.45
110	2.98	3.86	5.54	6.68	7.50

Table S2. Peak areas of wax No. 3 as influenced by the column temperature.

Column temperature [°C]	Area %				
	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5
140	26.92	8.43	4.97	0.46	59.22
130	23.29	6.58	3.76	0.30	66.07
120	21.34	6.63	3.76	0.18	68.09
110	20.81	6.12	3.50	0.09	69.48

Table S3. Peak area comparisons of waxes No. 1, 2 and 3.

Wax	Area %					
	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6
No. 1	100.00*	0.00	0.00	0.00	0.00	0.00
No. 2	50.13	9.83	6.39	21.81	5.18	6.68
No. 3	36.40	10.16	5.16	30.46	7.12	10.67

*Saturated detector signal.

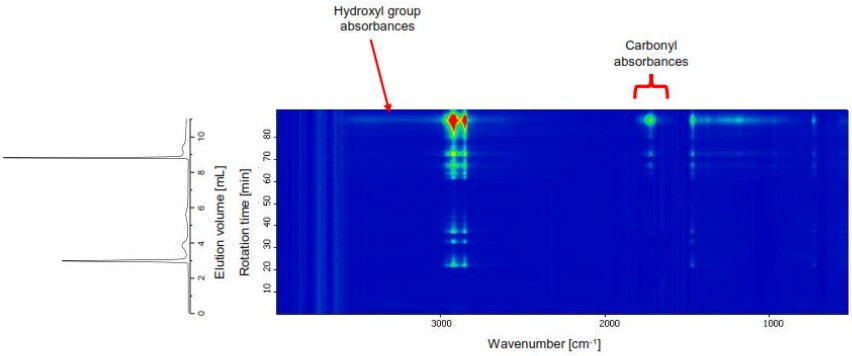


Figure S4. 2D contour plot of HT-SGIC-FTIR analysis of wax No. 3. FTIR was coupled to HPLC via the LC-transform interface.

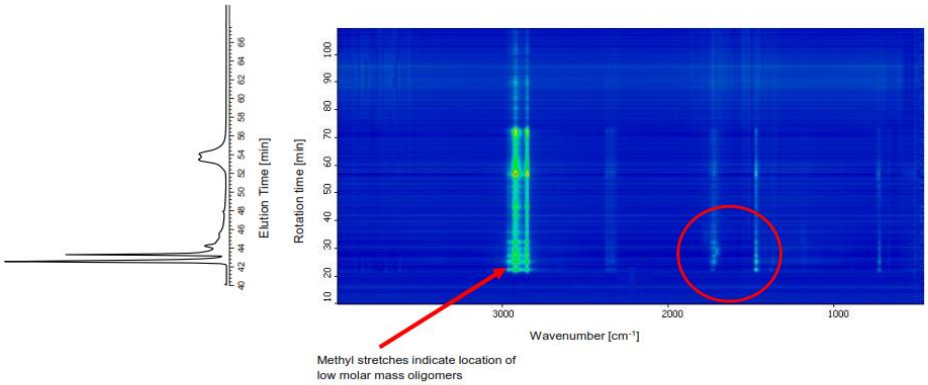


Figure S5. 2D contour plot of HT-TGIC-FTIR analysis of wax No. 3. FTIR was coupled to HPLC via the LC-transform interface.

Appendix C: Supporting information to Section 4.3

Supporting Information

for *Macromol. Rapid Commun.*, DOI: 10.1002/marc.201700703

Chemical Composition Fractionation of Olefin Plastomers/ Elastomers by Solvent and Thermal Gradient Interaction Chromatography

Anthony Ndiripo, Andreas Albrecht, Benjamin Monrabal, Jingbo Wang, and Harald Pasch*

Supporting Information

Chemical Composition Fractionation of Olefin Plastomers/Elastomers by Solvent and Temperature Gradient Interaction Chromatography

Anthony Ndiripo, Andreas Albrecht, Benjamin Monrabal, Jingbo Wang, Harald Pasch*

Section 1: SGIC

SGIC experiments were performed using a chromatographic system for high-temperature two-dimensional liquid chromatography constructed by Polymer Char (Valencia, Spain), comprising of an autosampler, two separate ovens, switching valves, and two pumps equipped with vacuum degassers (Agilent, Waldbronn, Germany). A high-pressure binary gradient pump was used for HPLC in the first dimension. One oven kept at 160 °C was used to house the HPLC column, while the second oven is the location of the injector and the switching valves. The autosampler is a separate unit connected to the injector through a heated transfer line. (Hypercarb®, Thermo Scientific, Dreieich, Germany) with the following parameters: 100 × 4.6 mm^2 i.d., packed with porous graphite particles with a particle diameter of 5 µm, a surface area of 120 $m^2 g^{-1}$, and a pore size of 250 Å was used for the SGIC experiments. The volume fraction of TCB was linearly increased to 100% from 1-decanol within 10 min after the sample injection and then held constant for 25 min. Finally, the initial chromatographic conditions were re-established with 100% 1-decanol. The gradient delay in reaching the detector was determined to be 2.8 mL. An evaporative light scattering detector [ELSD, model PL-ELS 1000, Polymer Laboratories (now Agilent), Church Stretton,

England] was used with the following parameters: A gas flow rate of 1.5 L min^{-1}, a nebuliser temperature of 160 °C, and an evaporator temperature of 270 °C.

Section 2: TGIC

TGIC experiments were performed using a crystallization elution fractionation (CEF) instrument from Polymer Char (Valencia, Spain). The instrument was equipped with a Hypercarb® column, from Thermo Scientific, to be used as a thermal gradient interaction chromatograph (TGIC). The column was similar to the one used in the SGIC experiments above. An autosampler was used to dissolve and inject all samples in a fully automated mode. The samples were dissolved for 60 min at 160 ºC with ortho-dichlorobenzene (DCB), containing 300 ppm of BHT, in 10 mL vials purged with nitrogen. The sample concentration was 1 mg mL^{-1}, and 100 µL were injected into the Hypercarb® column at 160 ºC, followed by a cooling ramp of 20 ºC min^{-1} down to 40 ºC to adsorb/precipitate all the components. Some experiments were performed with cooling ramps down to minus 20 ºC to promote adsorption of the most amorphous resins. Elution begins, isothermally, at the lowest temperature during five minutes at a flow rate of 0.5 mL min^{-1} of DCB, followed by a heating ramp at 2 ºC min^{-1} to desorb/dissolve the various components.

Section 3: ^{13}C-NMR

Quantitative $^{13}C\{^{1}H\}$ NMR spectra were recorded in solution-state using a Bruker Avance III 400 NMR spectrometer operating at 400.15 and 100.62 MHz for ^{1}H and ^{13}C, respectively. All spectra were recorded using a ^{13}C optimised 10 mm extended temperature probe head at 125 °C using nitrogen gas for all pneumatics. Approximately 200 mg of material was dissolved in 3 mL of *1,2*-tetrachloroethane-d_2 (TCE-d_2) along with chromium (III) acetylacetonate ($Cr(acac)_3$) resulting in a 65 mM solution of relaxation agent in the solvent.

Upon insertion into the magnet the tube was spun at 10 Hz. Standard single-pulse excitation was employed without NOE, using an optimised tip angle, a 1 s recycle delay and a bi-level WALTZ16 decoupling scheme.[27, 28] A total of 6144 (6k) transients were acquired per spectra. All chemical shifts were indirectly referenced to the central methylene group of the ethylene block (EEE) at 30.00 ppm using the chemical shift of the solvent. Characteristic signals corresponding to the incorporation of ethylene were observed[25] and the comonomer fraction calculated as the fraction of ethylene in the polymer with respect to all monomer in the polymer: fE = E / (P + E). The comonomer fraction was quantified using the method of Wang et al. through integration of multiple signals across the whole spectral region in the $^{13}C\{^{1}H\}$ spectra. The mole percent comonomer incorporation was calculated from the mole fraction: E [mol%] = 100 × fE. The weight percent comonomer incorporation was calculated from the mole fraction: E [wt.%] = 100 × (fE × 28.06) / ((fE × 28.06) + ((1-fE) × 42.08))

Section 4: SEC-IR

A high temperature chromatograph GPC-IR (Polymer Char, Valencia, Spain) equipped with a four band infrared detector (IR5) was used for the determination of the molar mass distribution and the ethylene content along the molar mass. The chromatographic separation was carried out by using 3 × Agilent-PLgel Olexis columns and 1× Agilent-PLgel Olexis Guard column (Agilent Technologies, Church Stretton, UK). As sample solvent and mobile phase 1,2,4-trichlorobenzene (TCB) stabilized with 250 mg L^{-1} 2,6-di-tert-butyl-4-methyl-phenol (BHT) was used. The chromatographic system was operated at 160 °C and at a constant flow rate of 1 mL min^{-1}. 200 µL of sample solution was injected per analysis. The column set was calibrated using universal calibration with narrow molar mass polystyrene (PS) standards in the range of 0.5 kg mol^{-1} to 11 500 kg mol^{-1}. Mark-Houwink constants for PS (K= 0.00019 dL g^{-1} and α= 0.655) and PP ((K= 0.00019 dL g^{-1} and α= 0.725) [29, 30] are

used for converting the PS equivalent molar mass into PP equivalent molar mass. The IR5 detector was calibrated with EP standards having ethylene contents between 0 and 80 wt.%. Data collection was performed by using the Polymer Char GPC-IR control software.

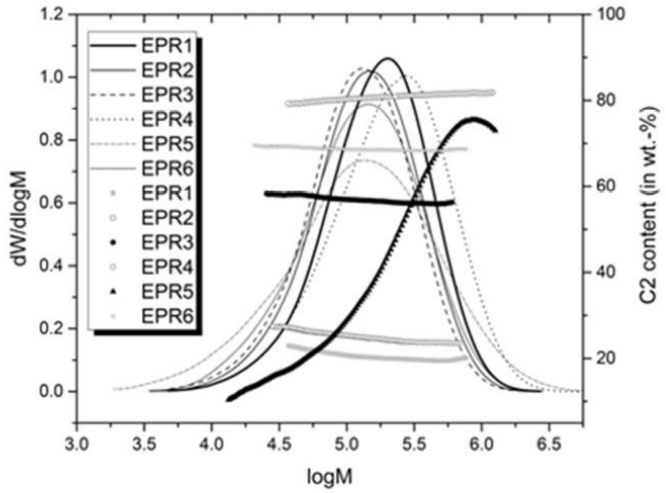


Figure S1 SEC-IR analysis of samples EPR1-6.

Table T1 NMR analysis of samples EPR1-6

Sample	Ethylene (mol%)	PPP triads	EEE triads	PP	EP	EE	r_1r_2
EPR 1	26.8	42.1	3,9	55,7	34,8	9,6	1,8
EPR2	32.5	34.0	6.4	47,60	38,80	13,60	1,7
EPR3	64.4	7.4	30.7	15,21	41,25	43,54	1,6
EPR4	84.5	1.6	59.9	3,65	25,10	71,25	1,6
EPR5*	38.7	57.1*	32.3*	57,89	6,67	35,44	184,5
EPR6	75.1	3.5	42.8	8,37	34,84	56,79	1,6

* seems to contain homo-PP, high PPP and high EEE triads in respect to the average ethylene content in mol%.

Table T2 Summary of heterophasic PP/EPR reactor blends

Sample	Description	MFI (2.16 g/10 min)	Ethylene (wt.% by IR)
PP/EPR1	Blend containing EPR1	17	1.5
PP/EPR2	Blend containing EPR2	20	7.4
PP/EPR3	Blend containing EPR3	15	15.6
PP/EPR4	Blend containing EPR4	3	27.0
PP/EPR5	Blend containing EPR5	7	23.1
PP/EPR6	Blend containing EPR6	15	24.8

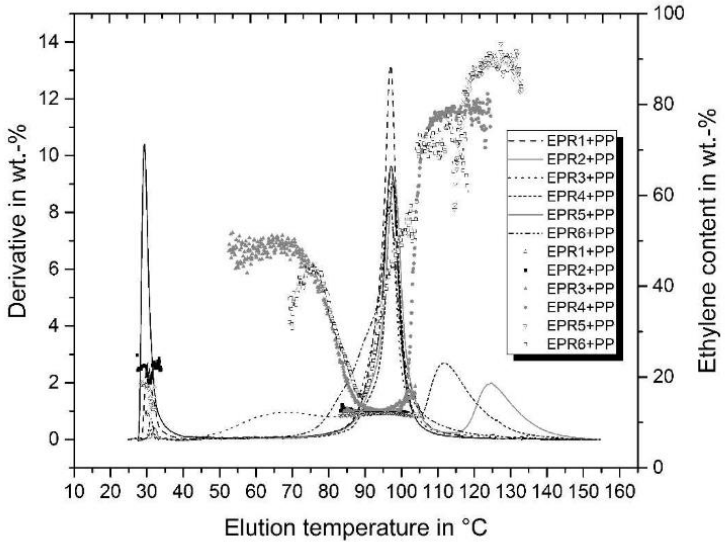


Figure S2 TGIC separations of samples of reactor blends of polypropylene and EPR1-6

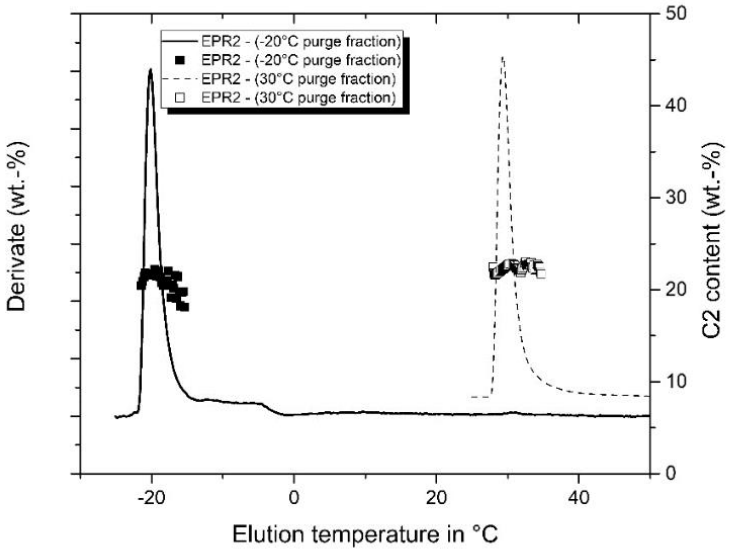


Figure S3 Comparison of TGIC results for EPR2 without xylene extraction using cooling to sub-ambient temperature (solid line) and 30 °C (dotted line).

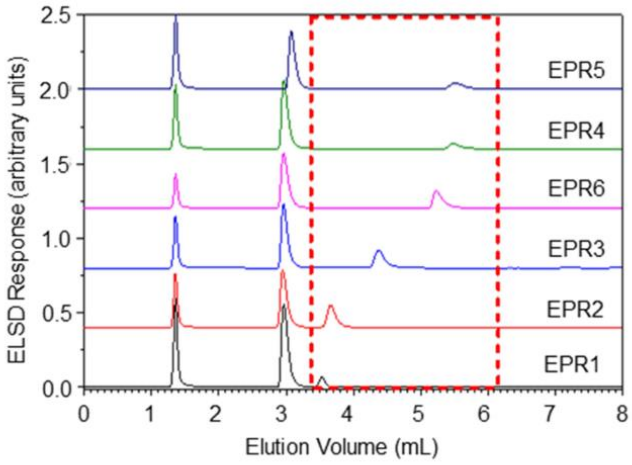


Figure S4 SGIC separations of reactor blends of polypropylene and EPR1-6