DEVELOPMENT OF HIGH TEMPERATURE TWO DIMENSIONAL LIQUID CHROMATOGRAPHY OF POLYOLEFINS

Vom Fachbereich Chemie
der Technischen Universität Darmstadt
zur
Erlangung des akademischen Grades eines

Doctor rerum naturalium
(Dr. rer. nat.)

genehmigte
Dissertation

vorgelegt von

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Tag der Einreichung: 02.11.2012
Tag der mündlichen Prüfung: 17.12.2012

Darmstadt 2013
D17

The research described in this thesis is part of the research program of the Dutch Polymer Institute (DPI), Eindhoven, the Netherlands.

Буду краток.

This dissertation would not have been possible without the guidance and the help of several individuals who in one way or another contributed in the preparation and completion of this work.

First of all, I would like to express my utmost gratitude to my scientific supervisors Prof. Dr. Matthias Rehahn, Dr. Robert Brüll and Dr. Wolfgang Radke who gave me an excellent opportunity to fruitfully work at DKI. I would like to specially thank Dr. Robert Brüll for guiding me throughout my PhD program. I will never forget your help, great input and extremely useful advices that helped me a lot in finding my scientific career path.

I would like to particularly thank my colleague Tibor Macko with whom I spent years working in the lab. I appreciate a lot his great contribution to this work, for his continuous enthusiasm, moral support and not letting me give up. I extremely value the knowledge and hands on that I got from him. With all this experience I am well prepared to tackle very challenging scientific problems.

I would like to acknowledge Dr. Klaas Remerie and Dr. Volker Dolle for the very fruitful collaboration, which ended up in some scientific publications and Prof. Dr. Vincenzo Busico who helped me to find an interesting way to go on with my scientific career and scientific development.

I would like to thank my friends, colleagues and staff who made my stay very comfortable and pleasant.

Особо хочу поблагодарить мою семью за терпение, поддержку и понимание на протяжении всех этих непростых лет. Все что я имею – все благодаря вам. Мама, твой вклад во все это просто бесценен и я всегда буду об этом помнить. Алиса, дорогая, огромное спасибо тебе за твою любовь, понимание и терпение. Можно сказать, что эта работа нас с тобой связала. Или это была музыка? ☺

Publications:

1. Ginzburg, A., Macko, T., Dolle, V., Brüll, R.; *High-temperature two-dimensional liquid chromatography of ethylene-vinyl acetate copolymers*, J. Chromatography A, 1217, 6867-6874, 2010.

2. Ginzburg, A., Macko, T., Dolle, V., Brüll, R.; *Characterization of polyolefins by comprehensive high-temperature two-dimensional liquid chromatography (HT 2D-LC)*, European Polymer J., 47, 319-329, 2011.

3. Ginzburg, A., Macko, T., Dolle, V., Brüll, R.; *High-Temperature Multidimensional Liquid Chromatography: A New Technique to Characterize the chemical Heterogeneity of Ziegler-Natta based Pipe Grade HDPE*, J. Polym. Sci., submitted.

4. Macko, T., Ginzburg, A., Remerie, K., Brüll, R.; *Separation of high impact polypropylene using interactive liquid chromatography*, Macromol. Chem. Phys., 213, 937–944, 2012.

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1. “Characterization of commercial EVA and LLDPE copolymers by high-temperature two-dimensional liquid chromatography’’, 11th international symposium on Hyphenated Techniques in Chromatography (HTC-11), 27-29 January 2010, Bruges, Belgium.

2. “Development of High-temperature Two-dimensional liquid chromatography for the Characterization of Polyolefins”, review presentation, DPI Polyolefin Cluster meeting, 3-4 March 2010, Amsterdam, The Netherlands.

3. “Characterization of polyolefins by high-temperature two-dimensional liquid chromatography”, World Forum on Advanced Materials (POLYCHAR-18), 7-10 April 2010, Siegen, Germany.

4. “High-temperature Two-dimensional liquid chromatography - a new tool for the Characterization of Polyolefins”, visit of the group of Prof. J.P.B Soares, 9 July 2010, University of Waterloo, Waterloo, Canada.

5. “Development of High-temperature Two-dimensional liquid chromatography for the Characterization of Polyolefins”, review presentation, DPI Polyolefin Cluster meeting, 2-3 March 2011, Amsterdam, The Netherlands.

6. “High-temperature Two-dimensional liquid chromatography of polyolefins”, DKI Colloquium, 1 April 2011, Darmstadt, Germany.

7. “Development of High-temperature Two-dimensional liquid chromatography for the Characterization of Polyolefins”, final account presentation, DPI Polyolefin Cluster meeting, 7-8 March 2012, Amsterdam, The Netherlands.

Posters:

1. A. Ginzburg, T. Macko, R. Brüll, Characterization of commercial EVA and LLDPE copolymers by high-temperature two-dimensional liquid chromatography, Annual meeting, Dutch Polymer Institute, November 18-19, 2009, Eindhoven, The Netherlands.

2. R. Brüll, A. Ginzburg, R. Chitta, T. Macko, Characterization of functionalized polyolefins using high-temperature two-dimensional liquid chromatography, 238th ACS meeting, Division of Analytical Chemistry, August 16-20, 2009, Washington, USA

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Content

Diese Arbeit wurde am Deutschen Kunststoff-Institut unter Leitung von Prof. Dr. M. Rehahn in der Zeit von September 2008 bis Dezember 2011 durchgeführt.

German Summary

Polyolefine sind, gemessen am Volumen, mit einer globalen Produktion von mehr als 100 Millionen Tonnen die bedeutendsten synthetischen Polymere. Ihre Produktion hat in den letzten Jahren kontinuierlich zugenommen und es ist zu erwarten, dass sich dieser Trend in Zukunft weiter fortsetzen wird. Treibende Kraft dabei sind neue Verarbeitungstechnologien und Syntheseverfahren, welche entwickelt werden, um den Anforderungen des Marktes nachzukommen.

Wie alle Polymere können Polyolefine unterschiedliche Arten molekularer Heterogenität zeigen, deren Bestimmung der Schlüssel ist, um Struktur↔Eigenschafts-Beziehungen zu erarbeiten und Anwendungseigenschaften maßzuschneidern. Die Molmassenverteilung und die Verteilung der chemischen Zusammensetzung sind die beiden grundlegenden molekularen Parameter, die im Fall von Polyolefinen von entscheidendem Interesse sind, da sie den größten Einfluss auf die Eigenschaften des Endprodukts haben. Zur Bestimmung der Molmassenverteilung und der daraus resultierenden durchschnittlichen Molmassen wird die Hochtemperatur-Größenausschlusschromatographie (HT-SEC) eingesetzt. TREF (Temperature Rising Elution Fractionation) und CRYSTAF (Crystallization Analysis Fractionation) werden zur Fraktionierung von Polyolefinen nach der chemischen Zusammensetzung verwendet. Zur Analyse der bivariaten Verteilung nach Zusammensetzung und Molmasse wird TREF mit der Größenausschlusschromatographie (SEC) gekoppelt (TREF x SEC).

Grundsätzlich kann die Zusammensetzungsverteilung einer Polymerprobe mittels Hochleistungsflüssigschromatographie (HPLC) bestimmt werden und die bivariate Verteilung durch Kopplung der HPLC mit der SEC (HPLC x SEC). Methodisch war dies jedoch bisher lediglich bei Raumtemperatur bekannt.

Ziel dieses Forschungsvorhabens war es, die HPLC bei hohen Temperaturen (HT-HPLC) mit der HT-SEC zur zweidimensionalen Flüssigchromatographie (HT 2D-LC) zu koppeln. Dazu wurde in Zusammenarbeit mit der Firma *PolymerChar* (Valencia, Spanien) ein Chromatograph entwickelt, in dem beide chromatographischen Trenndimensionen über ein Schaltventil miteinander verbunden sind. HT 2D-LC Untersuchungen wurden sowohl an Copolymeren aus Olefinen und polaren Comonomeren als auch an unpolaren Polyolefinen und Olefincopolymeren durchgeführt.

Zur HT 2D-LC von Ethylen-Vinylacetat (EVA) Copolymeren wurde in der ersten Trenndimension Kieselgel als stationäre Phase und ein Lösungsmittelgradient 1,2,4-Trichlorbenzol (TCB)→Cyclohexanon eingesetzt. Beide Achsen wurden mittels geeigneter Standards hinsichtlich des VA-Gehaltes (HPLC) und der Molmasse (SEC) kalibriert. Zu diesem Zweck wurde eine Methodik zur Bestimmung des sog. Void- und Dwell-Volumens erarbeitet. Ein Vergleich der Ergebnisse aus HT 2D-LC mit denen aus TREF x SEC zeigte die Überlegenheit der HT 2D-LC aufgrund ihrer Möglichkeit amorphe Proben zu trennen. Der Einfluss experimenteller Parameter auf die HT 2D-LC von Polyolefinen wurde untersucht: Eine Erhöhung der Flussrate in der SEC-Dimension führte zu höheren Elutionsvolumina und Peakverbreiterung. Auch eine Erhöhung des Injektionsvolumens führt zu Peakverbreiterung. Durch Wahl geeigneter experimenteller Parameter gelang es, die Zeit für eine HT 2D-LC Analyse ohne signifikanten Verlust an Auflösung von 200 auf ca. 100 min zu reduzieren. Dieses Versuchsprotokoll wurde eingesetzt, um industriell relevante EVA-Copolymere zu charakterisieren. Diese Methode ermöglicht es jedoch nicht, mit Methylmethacrylat gepfropftes Ethylen/1-Buten-Copolymer bzw. Polyropylen aufzutrennen. Dies gelang, indem Graphit (Hypercarb®) als stationäre Phase und ein Lösungsmittelgradient 2-Ethyl-1-hexanol→TCB als mobile Phase eingesetzt wurde. Zur chromatographischen Retention tragen bei dieser Trennung sowohl die unpolare Hauptkette (Ethylen/1-Buten-Copolymer bzw. Polypropylen) als auch das gepfropfte polare Comonomer bei

Die HT 2D-LC von unpolaren Polyolefinen und Olefincopolymeren wurde ebenfalls mit Hypercarb® in der ersten Dimension durchgeführt. Bei dieser Trennung beeinflusst die mobile Phase der ersten Dimension die Molmassentrennung in der zweiten Dimension. Eine Kalibrierung der zweiten Dimension gelang mittels PE-Standards. Dieses experimentelle Protokoll wurde zur Trennung einer großen Bandbreite von Polyolefinblends eingesetzt. Erstmals wurde der Effekt der Temperatur auf die Trennung linearer PE-Standards auf Hypercarb® als stationärer Phase und einem Lösungsmittelgradienten 1-Decanol→TCB als mobiler Phase untersucht. Das Elutionsvolumen am Peakmaximum steigt für hochmolekulare PE-Standards abrupt, wenn die θ- Temperatur erreicht wird, während es für niedermolekulare Standards linear ansteigt. Gleichzeitig wird für die hochmolekularen Standards eine Peakverbreiterung beobachtet. Ein bimodales PE wurde mittels HT 2D-LC aufgetrennt. Beide Trenndimensionen wurden mit hinsichtlich ihrer Zusammensetzung eng verteilten Ethylen/1-Buten-Copolymeren und linearen

PE-Standards kalibriert. Eine Vorfraktionierung der Probe mittels TREF und nachfolgende Analyse der Fraktionen mittels HT 2D-LC erhöht die Informationstiefe der chromatographischen Analyse signifikant.

1. Introduction

With a global production reaching over 100 million tons per annum, polyolefins are of enormous importance in the materials market. During the past 60 years, they have become the highest volume commercial class of synthetic polymers due to their versatility with respect to physical and mechanical properties, non-toxicity, and their competitive monomer costs. To tailor the application properties and thus produce high quality products the characterization of the chemical heterogeneity of polyolefins has always been vital in both research and production control. The remarkable versatility of polyolefins arises from the fact that ethylene, propylene and 1-olefins can be copolymerized to yield polymer chains with microstructures that lead to very different macroscopic properties. The latter are ultimately defined by the way the monomers are linked to form linear and branched chains with different degree of regularity. It mainly includes the distribution of comonomer-units and microstructural parameters (Chemical Composition Distribution-CCD) along or across the molar mass distribution (MMD). To establish structure↔property relationships requires separations according to both, molar mass and chemical composition. At the time being, the characterization of these interlinked chemical heterogeneities is not straightforward and needs a multidisciplinary laborious approach. Even then, interpretation of results is not an easy task and often speculative.

The aim of the work presented in this thesis was to develop and elaborate experimental protocols capable to unravel the chemical heterogeneities of non polar olefin copolymers as well as polar modified ones using high-temperature two-dimensional liquid chromatography (HT 2D-LC).

The thesis consists of two main parts. The first one (Chapter 2) provides a general introduction to polyolefins, including their properties, synthesis and modern analytical techniques used for their characterization. The objectives and motivations are explained. The second part compiles results, discussions and conclusions (Chapter 3 - Chapter 5).

2. Theoretical Considerations

2.1. Polyolefin types: microstructural classification

2.1.1. Polyethylene types

Polyethylene (PE) is normally classified into three main types: low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE) and high-density polyethylene (HDPE). The traditional classification distinguishes PE according to its density range: approximately 915–0.935 g/cm^3 for LDPE, 0.915–0.94 g/cm^3 for LLDPE and 0.945–0.97 g/cm^3 for HDPE and the method of synthesis. LDPE is produced through high pressure (200 - 300 bar) and high temperature (150 - 260 °C) polymerization, initiated by radical starters. HDPE and LLDPE are made via transition metal catalyzed coordination polymerization. Owing to the free radical mechanism of polymerization, LDPE is a statistically branched polymer having both short chain branches (SCB) generated by chain backbiting and long chain branches (LCB) resulting from chain transfer to polymer. These render LDPE the distinctive combination of clarity, flexibility, impact resistance, and processability. LDPE is mainly used in film applications, including for example heavy-duty sacks, refuse bags or carrier bags.

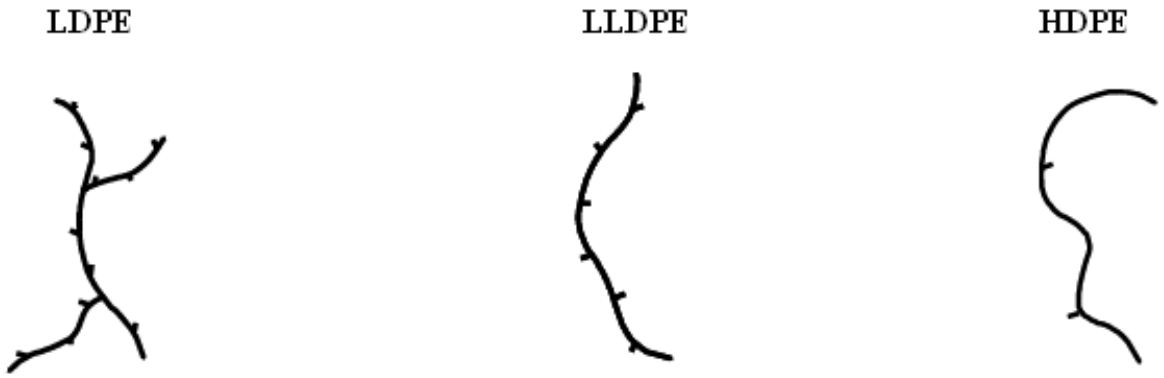


Fig. 1 Classification of polyethylenes according to branching structure.

LLDPE represents a large segment of the PE blown and cast film market. The resins are synthesized by copolymerizing ethylene with a 1-olefin such as 1-butene, 1-hexene or 1-octene. The incorporation of the comonomer results in ethyl-, butyl- or hexyl- branches, respectively, along the polymer backbone. LLDPE is replacing LDPE in certain film applications due to its higher impact and tensile strength. However, LLDPE also exhibits some undesirable properties,

such as lower gloss, greater haze, and a narrow heat sealing range. HDPE is an ethylene homopolymer which is linear in nature with no or very low levels of SCB. It has been commercially available since the mid 1950's. Compared to LDPE and LLDPE, HDPE is far more crystalline and consequently has a higher density. It also has increased tensile strength, stiffness, chemical resistance and upper heat sealing temperature range. However, HDPE has a reduced temperature impact strength, elongation, permeability, and resistance to stress cracking.

2.1.2. Polypropylene types

Polypropylene (PP) was first synthesized by Natta, following the discovery of Ziegler, by transition metal catalyzed polymerization of propylene in 1954 [1, 2]. The main molecular parameters that influence the properties of the homopolymer are stereoregularity of the monomer linkage (tacticity), the molar mass distribution (MMD) and the corresponding average molar mass. There are three extreme steric arrangements of the methyl groups linked to every second carbon atom in the chain: In the isotactic form, the methyl groups are placed on the same side of the backbone while in syndiotactic polypropylene they alternate sides; the structure where the pendant groups are located in a random manner on the polymer backbone is the atactic form. Fig. 2 depicts the stereochemical configurations of PP.

The main influence of the tacticity is on the degree of crystallinity. Atactic polypropylene (aPP) was the only form available before the development of stereospecific Ziegler-Natta catalysts. The amorphous and waxy material is used as an additive or it can be blended with other polymers. Isotactic polypropylene (iPP) is a relatively low cost material, especially on a volume basis, and due to its inherent low density attractive for many applications in packaging, transport, appliances, furniture, and textile. It has the lowest density of all commercially available thermoplastics (0.905 g/ml), a high melting temperature (≈165 °C), and good ensile strength, but at the same time the impact strength is low. Syndiotactic polypropylene (sPP) was developed more recently [2]. It is the development of metallocene catalysts which enabled a commercially viable route for sPP, and it is still at a relatively early stage of its commercial development. Compared to iPP, sPP exhibits a lower melting point (130 °C), lower stiffness, slower crystallization, and improved clarity and impact properties. Higher stiffness at a lower density (0,89 g/ml) and good resistance to higher temperatures when not subjected to mechanical stress

(particularly in comparison to HDPE and LDPE) are the key advantages over many other polymers for potential future applications. In addition to this sPP offers good resistance towards fatigue and environmental stress cracking and is relatively inert towards aggressive chemicals. These advantageous application properties are paired with ease of machining and good processability by for example injection moulding or extrusion.

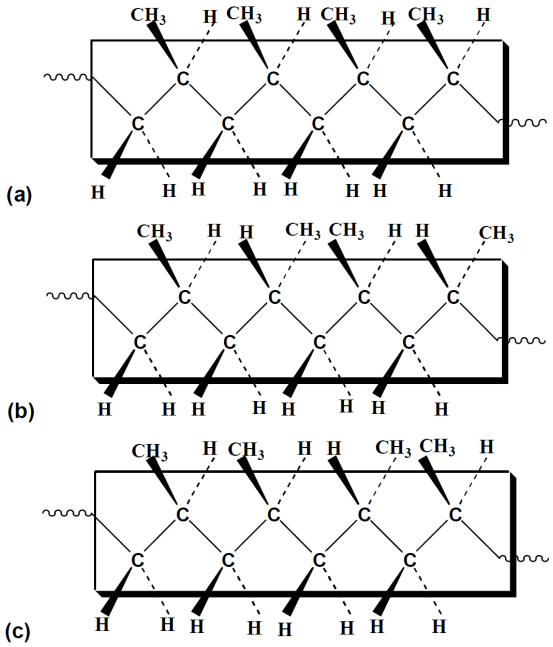


Fig. 2 Stereochemical configurations of PP: a) isotactic, b) syndiotactic, c) atactic.

As mentioned above iPP has a poor impact resistance, especially at low temperatures. One way to overcome this is to copolymerize propylene with a small amount (0,5 – 5 %) of ethylene, yielding random copolymers (PP-R). An alternative approach, which has received particular attention in the past decade is high impact PP (hiPP). HiPP is produced using at least two reactors in series with heterogeneous Ziegler–Natta (Z-N) or supported metallocene catalysts [2, 3]. The first reactor is used to make iPP (semicrystalline phase), while in the second reactor a fraction of amorphous copolymer (rubber phase) is produced by adding ethylene. The rubber phase is usually an ethylene/propylene (EP)- rubber although ethylene-propylene-diene terpolymers (EPDM) are also often used [4]. The result is an elastomeric rubber phase dispersed in a semicrystalline matrix of iPP. Du to the consecutive synthesis the amorphous copolymer is finely

dispersed in the homopolymer phase, even though the two phases are thermodynamically immiscible. The copolymer phase dissipates mechanical energy during impact and thereby greatly increases the impact resistance of the semicrystalline matrix. Various parameters influence the performance of hiPP, including, among others, the amount of elastomer, the size of the rubber particles and the chemical affinity of the elastomer for the PP, which in turn is a function of the CCD and the MMD, in particular of the elastomer [4].

Incorporating functional moieties in PE or PP is a well established route to obtain functionalized olefins, which have, in contrast to the non polar PE or PP alone, good adhesion and compatibility with other materials. The polar functionality allows these products to function as compatibilizer in blends of dissimilar materials or as adhesive. Such copolymers may be prepared either by grafting a polar group like maleic acid anhydride or acrylic acid onto PE as a side chain or by copolymerizing the polar monomer with ethylene or propylene. [15, 16].

2.2. Polyolefin polymerization chemistry: A brief overview

Olefin polymerization emerged in the 1950s as a principal area of organometallic research when Ziegler and Natta discovered that titanium tetrachloride in the presence of alkyl aluminum compounds is an efficient catalyst to polymerize ethylene and propylene [5, 6]. Today there are four major families of catalysts for olefin polymerization: Ziegler-Natta, Phillips, metallocene and late-transition metal catalysts.

Heterogeneous Ziegler-Natta (Z-N) catalysts have been the workhorse of polyolefin industry since their discovery. Typically, these include a titanium halide (for example - $TiCl_4$) (see Fig. 3), a cocatalyst, usually a trialkyl aluminium compound (AlR_3) and magnesium dichloride as a support. Additional suitable components of the Z-N catalyst composition may include an internal electron donor, dispersants, surfactants, diluents, inert supports such as silica or alumina, binding agents and antistatic compounds.

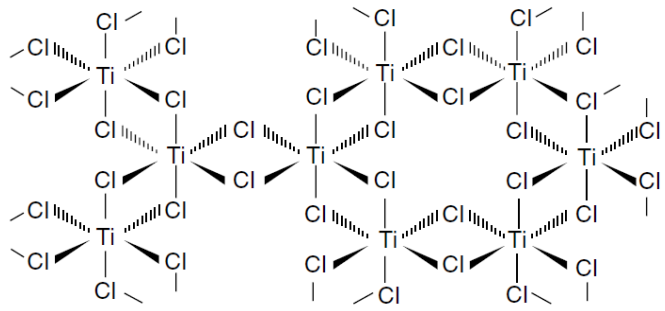


Fig. 3 Structure of $TiCl_4$.

AlR_3 acts as an alkylating and reducing agent, extracting two halogen atoms (X) from, and transferring one alkyl group to, the catalyst. Cossee and Arlman elaborated [7] the commonly accepted model for the reaction pathway of 1-olefin insertion in Z-N catalysts (Fig. 4).

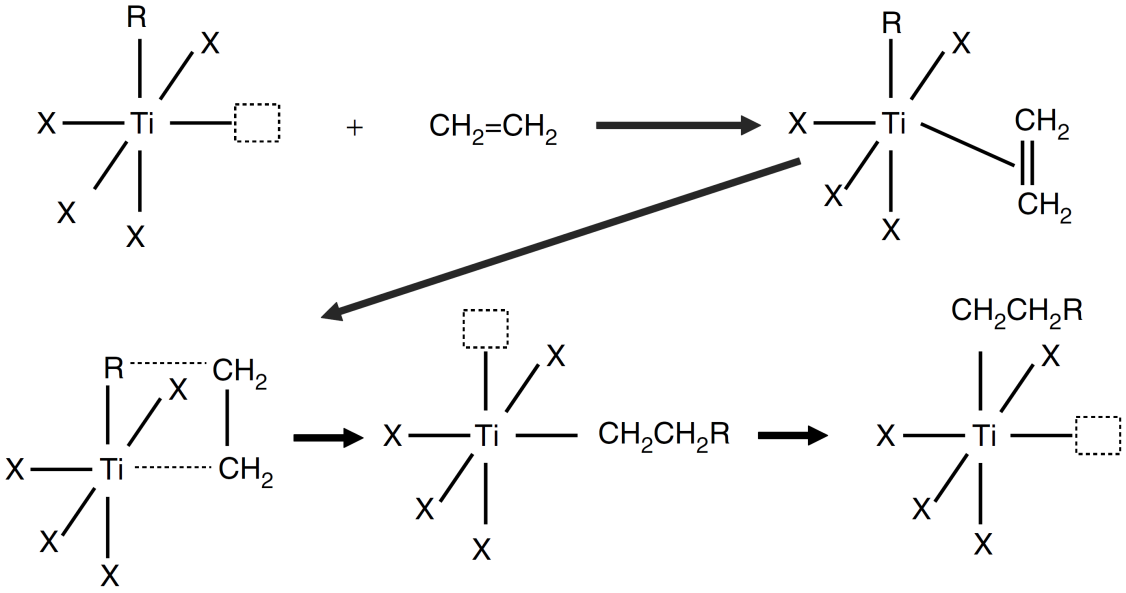


Fig. 4 Cossee-Arlman mechanism: X are ligands and R is the growing polymer chain.

In this, an octahedrally coordinated transition metal ion with one vacant coordination position and one alkyl group in its coordination sphere forms the active site. The role of the cocatalyst is solely to alkylate the active site and act as a scavenger. The π-bond of the olefin monomer coordinates to the vacant position, weakening the transition metal–carbon bond, and the olefin is inserted between the transition metal and carbon. The insertion proceeds via a four-membered

transition state involving the Ti-C bond and the carbons of the olefin double bond. The polymer chain then grows through successive monomer insertion until a transfer reaction - transfer to hydrogen and β-hydride elimination – takes place. In case that H_2 is present the molecule will react with the living chain, one hydrogen atom binding to the active site forming a metal hydride and the other one being transferred to the end of the living chain, thereby creating a saturated chain end. Thus hydrogen can be used to regulate chain growth and the molar mass of the polyolefin. The metal hydride can also result from β-hydride elimination, during which the hydrogen atom is abstracted from the β-carbon of the living polymer chain thereby generating a terminal vinyl group.

Although Z-N catalysts have very important advantages over the more recently developed homogeneous olefin polymerization catalysts (metallocene, late-transition metal) on an industrial scale, they also possess a number of drawbacks. For instance, heterogeneous catalysts are typically characterized by the presence of several different active sites, each with its own rate of polymerization and chain termination, stereoselectivity, comonomer incorporation, and chain transfer reaction. As a result, these multisite catalysts yield polymers having relatively broad distributions with regard to molar mass and composition which makes them interesting for applications that require stiff, tough and yet processable material [8]. However a substantial amount of empirical optimization is necessary before polymers of desired molecular parameters can be produced. Most commercial HDPE and LLDPE resins are made with heterogeneous Z–N catalysts. Z–N catalysts used for propylene polymerization produce mostly iPP with a very small fraction of aPP which is generated by aspecific sites.

Phillips catalysts are based on Cr (IV) supported on SiO_2 (Fig. 5). In contrast to Z-N catalysts, these do not require a cocatalyst and need to be treated at high temperatures in order to become active. The MMD is controlled by the characteristics of the support. Moreover, hydrogen, the usual chain transfer agent for Z-N, metallocene, and late transition metal catalysts, is not effective for Phillips catalysts. Phillips catalysts also have significantly lower reactivity towards 1-olefin incorporation and thus are not used for the production of LLDPE. However the Phillips catalyst shows quite competitive ability with Z–N catalysts, owing to its production of HDPE with an ultrabroad MMD containing a low level of SCB and LCB. These features contribute to some unique characteristics of the produced materials for commercial applications like pipes.

Metallocenes (Fig. 6), in combination with the conventional aluminum alkyl cocatalysts used in Z-N systems, are indeed capable to polymerize ethylene, but only at a very low activity.

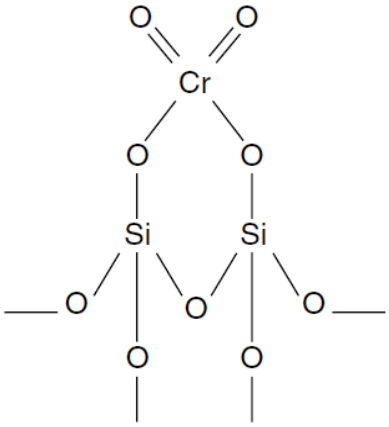


Fig. 5 Chromium (Philips) catalyst for olefin polymerization.

Fig. 6 Metallocene catalysts for olefin polymerization.

Only with the discovery and application of methyl aluminoxane (MAO) it became possible to enhance the activity, surprisingly, by a factor of 10 000 [9, 10]. Despite its significant influence on catalytic performance, the exact role of the aluminoxane component is still poorly understood. It is generally thought to act as alkylating agent that facilitates the formation of electron-deficient coordinatively unsaturated cationic alkyl species. In addition it also serves as a scavenger for impurities. Its exact structure is still controversial and it is supposed that MAO is an oligomeric compound with a degree of oligomerization varying approximately from 6 to 20. The linear structure of MAO is shown in Fig. 7.

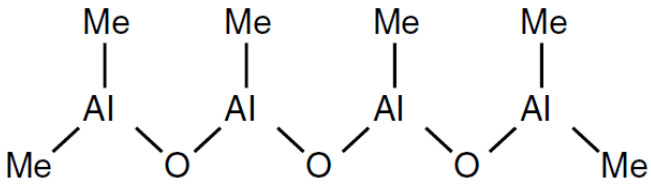


Fig. 7 Linear structure of MAO.

By tailoring the coordination environment (ligand set) of the metal center (Fig. 6), single-site catalysts are now available that can control the MMD, comonomer incorporation, and the stereochemistry of a polymer linkage in a way which is often impossible using Z-N catalysts. Using metallocene catalysts, it became for the first time possible to produce PE, PP and copolymers of ethylene or propylene with 1-olefins having a narrow MMD [2, 10-13], sPP [2, 12-14], and syndiotactic polystyrene [12, 13]. PP made with metallocene catalysts exhibits distinct advantages over conventionally produced PP, such as narrow MMD, higher stiffness and greater tensile strength [13]. Metallocene catalysts have opened new perspectives due to the possibility to copolymerize ethylene or propylene with 1-olefins, olefin macromonomers, cyclic olefins, or with sterically hindered or even functional monomers. Copolymers of ethylene with various monomers, among them 1-octene (LLDPE), norbornene and styrene, olefin based elastomers and long chain branched PE with tailored rheological properties are already produced on an industrial scale [12, 13].

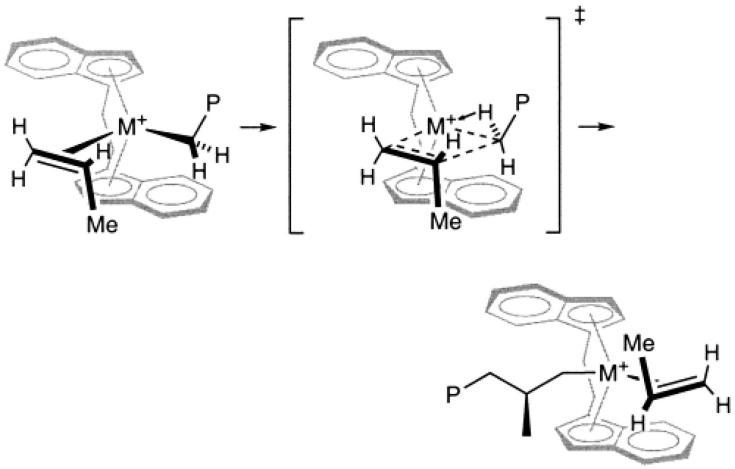


Fig. 8 Mechanism for the isospecific polymerization of propylene by ansa metallocenes [2].

Early transitional metal (Ti, Zr, V, and Cr) based Z-N and metallocene catalysts exhibit high oxophilicity, which causes them to be poisoned by most functionalized olefins. Due to this deficit, copolymers of functional olefins with ethylene are in many cases commercially still produced by free-radical polymerization. Compared to early transition metals, the lower oxophilicity and greater tolerance towards functional groups makes late transitional based catalysts potential candidates for the industrial copolymerization of ethylene with polar monomers. A major breakthrough was achieved by Brookhart who reported a set of olefin polymerization and copolymerization catalysts based on Ni(II) and Pd(II) α-diimine complexes (Fig. 9) [16-18].

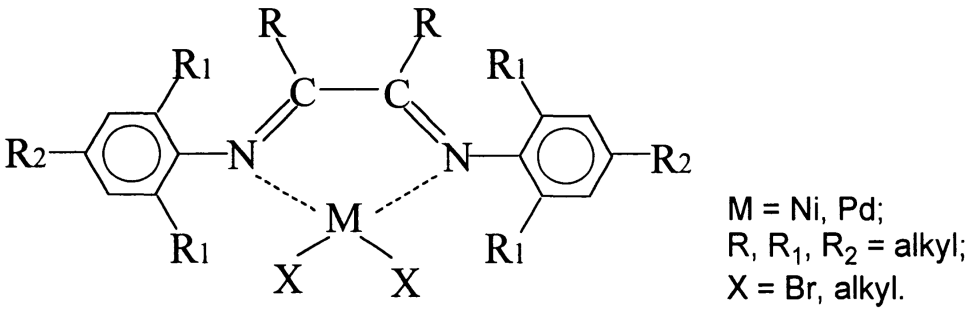


Fig. 9 Structure of Ni(II)/Pd(II) α-diimine catalysts.

These catalysts were remarkably active for the copolymerization of nonpolar olefins with polar vinyl monomers such as acrylates, methyl vinyl ketones, and silyl vinyl ethers. Methods to copolymerize ethylene with polar vinyl monomers such as methyl acrylate (MA), methyl methacrylate (MMA) and vinyl acetate (VA) to produce ethyl methyl acrylate (EMA), ethyl methyl methacrylate (EMMA) and ethyl vinyl acetate (EVA) respectively are readily available and found entrance in industrial production [15, 16].

A discussion of catalyst technology and polymerization processes is necessary in order to understand why the polymers produced by heterogeneous catalysts have their unique characteristics. The very nature of the catalyst is the reason for the CCD of the polymers produced and consequently, the necessity to characterize the molecular heterogeneities of the polymer (MMD and CCD) is directly due to the polymerization process itself. Therefore, an in

depth understanding of the polymerization process and rational catalyst design require adequate analytical tools which enable to characterize the molecular heterogeneities.

2.3. Techniques to characterize molecular heterogeneities of polyolefins

2.3.1. CCD analysis by Temperature Rising Elution Fractionation (TREF) and Crystallization Analysis Fractionation (CRYSTAF)

The two main techniques that are used to fractionate semi-crystalline polymers according to crystallinity are Temperature Rising Elution Fractionation (TREF) and Crystallization Analysis Fractionation (CRYSTAF). The fractionation mechanism of both techniques relies on differences in the crystallinity of the polymer chains from dilute solution: those with high crystallinity will precipitate at higher temperatures, while those with low crystallinity are precipitated at lower temperatures. In this section, we review the basic theory of polymer crystallization in dilute solutions to explain how solvent type, volume fraction of polymer, molar mass, and comonomer content affect chain crystallinity and equilibrium melting temperatures.

The Flory–Huggins equation for the free energy of mixing can be used to describe the thermodynamic equilibrium of a polymer solution assuming a uniform distribution of solvent and polymer segments [19-23]. The decrease in the equilibrium melting temperature of the polymer due to the presence of solvent and the number of chain segments is given by

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \left(\frac{R}{\Delta H_u}\right)\left(\frac{V_u}{V_1}\right)\left[-\frac{\ln(\nu_2)}{x} + (1-\frac{1}{x})\nu_1 - \chi_1\nu_1^2\right] \quad (1)$$

where T_m^0 is the melting temperature of the pure polymer, T_m is the equilibrium melting temperature of the polymer-diluent mixtures, ΔH_u is the heat of fusion per repeating unit, V_u and V_1 are the molar volumes of the polymer repeating unit and diluent, respectively, ν_1 and ν_2 are the volume fractions of the diluent and polymer, respectively, x is the number of segments, and χ_1 is the Flory–Huggins thermodynamic interaction parameter.

However, the crystallization step in CRYSTAF and TREF occurs in dilute solution, which makes the model more complicated as polymer segments are non-uniformly distributed through the

solution. In order to account for the non-uniformity, a general theory for dilute solutions using a chemical potential of the solvent expressed in virial form needs to be considered. Nevertheless, it has been found that increasing dilution does not significantly impact the melting temperature [24] and, therefore, eq.1 is applicable over the full compositional range.

The effect of chain length on the melting temperature of a polymer in a dilute solution can be accounted for by rearranging eq. 1 as follows

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u}\frac{V_u}{V_1}(\nu_1 - \chi_1 \nu_1^2) - \frac{R}{\Delta H_u}\left[\frac{\ln(\nu_2)}{r} + \frac{\nu_1}{r}\right] \quad (2)$$

where the number of repeating units per polymer chain (r) is used instead of x. Obviously, the second term in the right-hand side describes the impact of chain length, indicating that the equilibrium melting temperature drops with decreasing molar mass [24, 25]. However, the impact of that term becomes only significant for chains with low molar mass, i.e. for high molar masses the melting temperature is relatively independent on chain length and eq. 2 can be simplified to

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u}\frac{V_u}{V_1}(\nu_1 - \chi_1 \nu_1^2) \quad (3)$$

Eq. 3 implies that all polymers having relatively high molar mass will crystallize at the same temperature providing other factors being constant. This is in good agreement with experimental results obtained by CRYSTAF and TREF [26, 27].

In the case of copolymer solutions, the melting temperature depends also on interactions between the different monomeric units and the solvent molecules. When the crystalline phase is pure, i.e. the lattice contains only monomeric units and does not contain solvent molecules, the decrease in the melting temperature can be calculated in the same way as for the homopolymer solution. In order to take into account the interactions between both comonomers and the solvent, the net Flory–Huggins thermodynamic interaction parameter should be calculated as follows:

$$\chi_1 = \upsilon_A \chi_{1A} + \upsilon_B \chi_{1B} - \upsilon_A \nu_B \chi_{AB} \quad (4)$$

where χ_1 is the interaction parameter of a binary copolymer with pure solvent, χ_{1A} and χ_{1B} are the interaction parameters of the corresponding homopolymers with the solvent, χ_{AB} is the interaction parameter between comonomers A and B in the copolymer chain, and υ_A and ν_B are the volume fractions of comonomers A and B in the copolymer molecule, respectively.

The fraction of comonomer units in the copolymer chains is the most important factor affecting the chain's crystallinity, as comonomers act as chain defects interrupting the chain regularity and thereby lowering its crystallinity. Alamo and Mandelkern reviewed the crystallization behaviour of random copolymers of ethylene with 1-olefins using Differential Scanning Calorimetry [28]. Although the analytical conditions were far from thermodynamic equilibrium both the melting and crystallization temperature versus the comonomer content were described by a linear relationship up to 4 mol.-% of comonomer. Furthermore it turned out that the melting and crystallization temperature did not depend on the type of comonomer. The Flory theory was also utilized to explain the crystallization behaviour of these copolymers from solution [29].

TREF is based on a two step separation process: In the first cycle the sample is dissolved in a thermodynamically good solvent at elevated temperature and the solution is then loaded into a column containing a support (e.g. sea sand or glass beads). Then a cooling cycle at a slow cooling rate with no flow is started, during which the polymer is fractionated by segregation of crystals with successively decreasing crystallinity. This is followed by a second cycle, during which fresh solvent is pumped through the column while the temperature is raised. The solvent dissolves polymer fractions of increasing crystallinity (i.e. decreasing content of SCB), as the temperature is raised. These can be collected (preparative version) for further off-line follow up analysis or their concentration be monitored by an infrared detector (analytical version) to generate the CCD. Analysis of the CCD by TREF is widespread practice in the polyolefin industry. TREF has been reviewed by Wild [30], Glöckner [31], Fonseca and Harrison [32], Soares and Hamielec [33], Anantawaraskul [29] and Monrabal [34, 35].

The sample throughput in TREF is low, which means that the technique does not meet the requirements of high throughput environments. An analogous technique, CRYSTAF, was developed by Monrabal in the early 1990s [35], enabling to analyze 5 samples simultaneously and in a shorter period of time. In CRYSTAF the analysis is carried out in stirred crystallization vessels with no support. After dissolution at elevated temperature the concentration of the

polymer in solution is monitored by an infrared detector while the temperature is decreased and the polymer crystallizes. The first data points taken above any crystallization define a baseline level equal to the initial polymer concentration (Fig. 10). As the temperature is lowered the most crystalline fractions composed of linear macromolecules or macromolecules with very few SCB will crystallize first. The process will result in a steep decrease in concentration of the polymer in solution on the cumulative plot. This is followed by successive crystallization of fractions of lower crystallinity (increasing content of SCB) as the temperature continues to decrease. The last data point represents the non-crystallized (amorphous) fraction remaining in solution. The first derivative (dW/dT) of the cumulative plot (W) is commonly referred to as CCD. A linear correlation between the crystallization temperature at peak maximum of dW/dT and the average comonomer content of compositionally narrow disperse LLDPE fractions was observed for CRYSTAF [34, 35]. Therefore, the crystallization temperature of single site produced ethylene/1-olefin copolymers can be used to calibrate TREF for the compositional analysis of broadly distributed LLDPE samples in industry [26].

Monrabal et al. [36] showed that TREF, which separates samples in a crystallization and dissolution cycle, provides best resolution for combinations of iPP and PE. In contrast, CRYSTAF, which fractionates solely in a cooling cycle, is the preferred technique for separating blends of PE and EP copolymers (Fig. 10), where TREF fails.

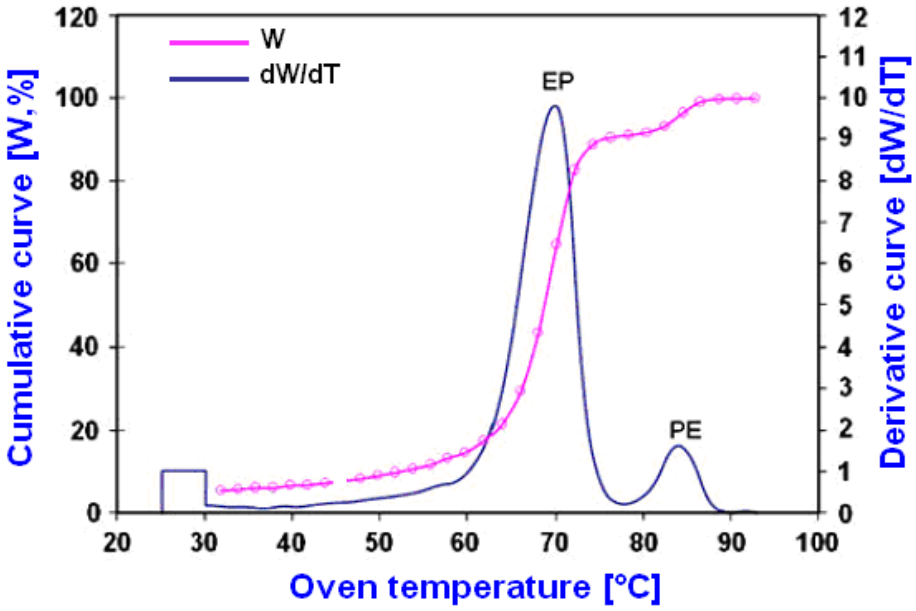


Fig. 10 CRYSTAF analysis of a blend of an EP copolymer and PE, from [36].

The effect of comonomer type on the crystallization behaviour in CRYSTAF was studied by Brüll et al. [37] for the case of single site produced propylene/1-olefin copolymers with 1-olefins ranging from 1-octene to 1-octadecene. They reported that, for their set of samples, the peak crystallization temperatures did not depend on the nature of comonomer but strongly on its content. Namely a linear correlation as it was the case for ethylene/1-octene was found. More recent work [38] investigated the effect of comonomer type using a series of single site produced ethylene/1-olefin (1-decene, 1-tetradecene, and 1-octadecene) copolymers, where authors showed independency of comonomer type.

Sarzotti et al. [39] investigated the effect of the comonomer content on CRYSTAF profiles with a series of ethylene/1-hexene copolymers having different comonomer fractions but approximately the same molar mass and thus minimizing the molar mass effect. Expectedly, the peak crystallization temperatures were significantly affected by the average comonomer content. Moreover, the crystallization profiles became broader with increasing comonomer content and it was shown that these results could be explained on a basis of Stockmayer's distribution. Pasch et al. [40] showed that CRYSTAF can be used to deformulate blends of HDPE, LDPE and PP and to retrieve quantitative information.

Cocrystallization is one of the main drawbacks in TREF and CRYSTAF. However, it is considered that TREF fits more for analyzing copolymers with complex CCD, especially if one needs more quantitative results, as the separation seems to be less affected by cocrystallization for the same cooling rate than in CRYSTAF. Obviously, TREF and CRYSTAF fail to analyze amorphous polymers or polymers with a low degree of crystallinity as was demonstrated for EVA copolymers [41-43].

A further limitation is the fact that the separation in TREF and CRYSTAF is based on crystallization, which in turn is an overall function of composition (SCB), stereoregularity, architecture and molar mass of the polymer.

Cross-fractionation with regard to chemical composition and molar mass delivers the relationship between the most relevant heterogeneities. This can be achieved by coupling TREF with a molar mass fractionation by size exclusion chromatography (SEC) yielding the bivariate MMD × CCD. TREF x SEC can be realized either on-line or off-line [42-45]. It was first introduced by Wild [42], who combined off-line a preparative fractionation by TREF with SEC analysis of the

obtained fractions. The first attempt to automate cross-fractionation of polyolefins was reported by Nakano and Goto [45] and in 2006 Ortin et al. have commercialized an automated instrument for cross-fractionation [44]. However, as the separation according to composition is achieved by TREF, it is of course only applicable to well-crystallizable samples [46-49].

2.3.2. Analysis of molar mass distribution and chemical composition distribution by liquid chromatography

2.3.2.1. General theory of liquid chromatography of polymers

The basic assumption in any chromatographic theory is that the retention is controlled by thermodynamic factors [50, 51]. In this way, mobile and stationary phases are considered as thermodynamic phases with volumes V_{mob} and $V_{stat,}$ respectively, and the retention volume V_R at isocratic conditions depends on the distribution (partition) equilibrium coefficient k of the solute between these two phases:

$$V_R = V_{mob} + kV_{stat} \tag{5}$$

k is related to the standard Gibbs free energy change (ΔG_0) and the latter can be further divided into the enthalpic and entropic contributions of the partitioning process:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -RT \ln k \tag{6}$$

$$k = \exp(\Delta S^0 / R - \Delta H^0 / RT) \tag{7}$$

Enthalpic interactions (ΔH^0) and entropic transformations (ΔS^0) of the solute molecules occur during the chromatographic retention inside the porous stationary phase (see Fig. 11). Different from low molar mass compounds, the size of a macromolecule in solution may significantly exceed the width of the monomolecular adsorption level and can be comparable or even larger than the internal pore diameter [50, 52]. When the macromolecule enters the pore it becomes confined and, therefore, cannot assume all possible conformations, which leads to a loss in

conformational entropy. At the same time, when being at the surface, the macromolecule may interact with it resulting in a change in ΔG_0. When the retention is controlled by entropic transformations, the size exclusion mode is predominant, while when the retention is ruled by enthalpic interactions, the adsorption mode is at action.

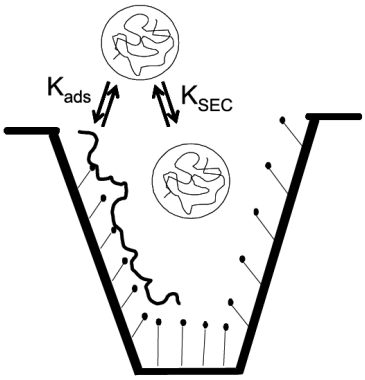


Fig. 11 Schematic representation of the behaviour of a polymer molecule in a pore [52].

2.3.2.2. Size Exclusion Chromatography (SEC)

As has been pointed out, SEC is entropy controlled and based on differences in the size of the macromolecules in solution (hydrodynamic volume) and the extent to which they are excluded from the pores of a porous column packing. The parameter, which determines the separation, i.e., the hydrodynamic volume is a function of the molar mass, the molecular architecture and the chemical composition. In ideal SEC, the separation is exclusively ruled by conformational changes of the macromolecules, while the enthalpic interactions are suppressed ($\Delta H^0 = 0$), thus

$$k = k_{SEC} = \exp(\Delta S^0 / R) \qquad (8)$$

SEC is a well-established method to determine the MMD of polyolefins [53] and requires in the case of semicrystalline polyolefins temperatures well above 100 °C. It uses a series of columns generally packed with crosslinked poly (styrene-divinylbenzene) (PS-DVB) gels with varying pore size distribution and thermodynamically good solvents suppressing enthalpic interactions, normally 1,2,4-trichlorobenzene (TCB) or ortho-dichlorobenzene (ODCB) [53].

To characterize the MMD the number average molar mass, M_n, and the weight average molar mass, M_w are widely used [51]. The first corresponds to the ordinary arithmetic average molar mass of the chains contained in the sample, whereas the second is the average molar mass of a chain in which a monomer has the highest probability to be found. The MMD is usually characterized by the dispersity, D, calculated by dividing M_w by M_n. Since per definition M_w is equal or higher than M_n, D is always > 1 and the higher D is the broader the MMD. Equations to calculate both average molar masses and D are:

$$\overline{M}_n = \frac{\sum_i N_i M_i}{N_i} \tag{9}$$

$$\overline{M}_w = \frac{\sum_i N_i M_i^2}{N_i} \tag{10}$$

$$D = \frac{\overline{M}_w}{\overline{M}_n} \geq 1 \tag{11}$$

A refractive index (RI) detector is commonly used to measure the concentration of polymers eluting from the columns (SEC/RI). More recently, infrared (IR) detectors have also been used as concentration sensitive detectors for SEC (SEC/IR). Their main advantages over the more traditionally used RI detectors are a very stable baseline and lower sensitivity towards temperature fluctuations in the IR detector cell. Additionally IR detectors can deliver information about the chemical composition of the eluting fractions. If the polymer chains are linear, there is a direct relationship between molar mass, volume in solution and elution time for a given polymer type. This is used to create a calibration curve relating elution time to molar mass. In addition, the universal calibration curve can be used to extend this relation to linear polymers of all types, provided that the relation between intrinsic viscosity and molar mass of the polymer is known (using, for instance, the Mark–Houwink equation) or measured using an on-line viscometer (SEC/RI-VISC).

Analysis by SEC becomes more complicated for polyolefins containing LCB, such as LDPE, because for these polymers the volume in solution is a function not only of molar mass but also of branching. The amount of LCB of polyolefins can be determined by comparing the behaviour

of a branched macromolecule to that of a linear one of the same chemistry [54]. Compared to a linear macromolecule, the branched one will be more compact at any given molar mass. The use of SEC/RI-VISC allows to compare the difference in intrinsic viscosity. By adding an on-line laser light-scattering (LS) detector the M_w of the chains eluting from the SEC (SEC/RI-VISC-LS) can be determined. In addition, if SEC is connected to a LS detector, the measurement of the molar mass is absolute and a calibration curve not required. However, the calculation of the molar mass requires to know the refractive index increment (dn/dc), which has to be experimentally determined. Due to the versatility of triple-detector systems such as SEC/RI-VISC-LS and the microstructural complexity of modern polyolefin resins, the use of triple-detector systems is becoming increasingly more popular [53].

SEC-FTIR of polyolefins is typically performed in two ways: either the eluent from the SEC column is sprayed onto a rotating germanium disk and subsequently analyzed offline by FTIR [55] or the SEC is coupled to a heated flow cell placed in an FTIR spectrometer [56, 57]. Hereby, profiles are obtained showing the MMD and, additionally, the content of SCB as a function of molar mass. Nowadays, besides IR spectrometers recording full spectra, IR detectors with fixed wavelengths using at least two different bandpass filters are also available for compositional analysis [58]. TCB (or ODCB or tetrachloroethylene) can be used as mobile phase for flow through FTIR detection as it is sufficiently transparent between ca. 3500-2700 cm^{-1}, which corresponds to the >C-H stretching region, i.e. the region of interest for polyolefins. Typically, at least two bands associated to methyl (CH_3) and methylene (CH_2) groups are measured and their ratio is calibrated against polymer standards (ratio method) [58, 59]. The ratio method is simple to apply and usually appropriate for samples having a medium to a high degree of SCB. This method is not applicable for very low degrees of branching (<2 CH_3/1000C) due to signal-to-noise limitations.

In sum, SEC separates macromolecules according to their size in solution. Macromolecules of the same size (hydrodynamic volume), however, may differ in their chemical composition. FTIR enables to evaluate the average chemical composition in fractions eluting from SEC but a distinction of macromolecules according to their chemical composition is not possible with FTIR.

2.3.2.3. High-Performance Liquid Chromatography (HPLC[1])

In HPLC, the distribution coefficient is a function of the entropic and enthalpic terms and therefore, the retention volume (V_R) is described by Equation 1 [51]:

$$V_R = V_{mob} + V_{pore} K_{HPLC} K_{SEC} + V_{stat,\text{int}eractive} K_{HPLC} \quad (12)$$

where V_{pore} is the pore volume and $V_{stat,\text{int}eractive}$ the volume of the "interacting part'' of the total stationary phase.

Glöckner [61] noticed that there is a fundamental difference between the behavior of low molar mass compounds and macromolecules, which is called a molar mass effect. While for the low molar mass compounds usually one molecule interacts with one active site of the stationary phase, a multiple attachment mechanism is in play for macromolecules. The reason for this is that macromolecules typically contain a large number of interacting groups (functional groups, repeat units). The polymer chain is retained as long as one interacting group is still bound to the stationary phase. *k* can be described by the probability *p* for each interacting group (repeat unit) to be adsorbed:

$$k = p/(1-p) \quad (13)$$

$$k = (k_{monomer} + 1)^n - 1 \sim V_R \quad (14)$$

where $k_{monomer}$ is the distribution coefficient of the interacting unit and *n* is the number of interactive units. Consequently, a linear increase in molar mass (number of interacting units) will lead to an exponential increase in retention volume.

[1] HPLC is the generic term comprising the subtechniques of liquid adsorption chromatography (LAC), liquid chromatography at critical conditions (LCCC) and SEC. Nevertheless, here it is used in the context of LAC due to widely used "branding" of high temperature HPLC (HT HPLC).

HPLC has been widely used to separate polymers with respect to their chemical composition. The majority of published HPLC separations of synthetic polymers has been realized at temperatures below 60 ºC [51, 61]. Dissolution and chromatographic separation of semicrystalline polyolefins, however, require temperatures of up to 130 – 160 ºC [62-64].

2.3.2.4. High Temperature HPLC (HT HPLC) of Polyolefins

The industrial production of polyolefins started in England in 1939. The first high temperature (HT-SEC) chromatograph became commercially available just in 1964. HT-HPLC methods to separate polyolefin materials according to their chemical composition, however, were not available for a long time for two reasons:

- Stationary phases which adsorb polyolefins were not known
- A dedicated HT-HPLC instrument was not on the market.

Strong retention of linear PE and iPP from dilute solutions in decalin on specific zeolites was found by Macko et al. in 2003 [46, 62-64]. Unfortunately, the adsorption was irreversible, and thus, the polymer could not be recovered. The application of chlorinated mobile phases (1,2,3-trichloropropane and 1,1,2,2-tetrachloroethane) enabled strong retention and also desorption of PE and PP samples. Under these conditions, however, PE and PP may be chlorinated and, moreover, these solvents cause corrosion of the instrumentation and thus this approach is not practicable in a chromatographic manner. The first chromatographic systems for the separation of polyolefins according to their chemical composition (HT-HPLC) were published only recently [65-67]. They were based either on the selective precipitation/dissolution (PP is soluble in ethylene glycol monobutyl ether and PE non-soluble) or on the selective adsorption/desorption of PE or PP [68-70]. Additionally to the systems that separates non functionalized polyolefins, the first chromatographic systems which can separate functionalized polyolefins according to chemical composition at high temperature were developed. It was shown that EVA [75-77], EMMA [77, 78], as well as EBA copolymers [77, 78] can be separated with regard to their chemical composition. The separations were based on a full adsorption of macromolecules from specific solvents (e.g. decalin or TCB) on bare silica as stationary phase at 140 ºC and a subsequent desorption controlled by adding cyclohexanone to the mobile phase. Crystallization is

irrelevant to the separation and, thus, cocrystallization is no longer expected to be a concern in HT-HPLC.

The first sorbent-solvent system for HT-HPLC of non-polar polyolefins was published by Macko and Pasch in 2009. They described the chromatographic separation of PE from PP as well as the separation of PP according to tacticity [70]. In detail it was shown that aPP, sPP and PE could be adsorbed on the surface of PGC from 1-decanol as mobile phase, while iPP eluted without any retention. The retained polymers were desorbed by applying a linear solvent gradient 1-decanol→TCB. It is important to note that a similar separation of the respective polymers by e.g. TREF or CRYSTAF would require much larger amounts of samples, solvents, and time. Moreover, it is not possible to selectively separate amorphous polyolefins by TREF or CRYSTAF. The chromatographic method can be essentially used to determine the degree of stereoregularity of a polymer sample. It was demonstrated that HT-HPLC enables to separate PE/PP blends [36, 39, 40, 43] or EP copolymers [38, 44]. The applications of HT-LC for the separation of polyolefins have been thoroughly reviewed by Macko et al. [71].

PGC, now marketed under the trade name Hypercarb®, was developed by Knox et al. [72]. It consists of fully porous spherical particles having a highly flat surface. On a molecular level, PGC is made up of sheets of hexagonally arranged carbon atoms linked by the same conjugated 1.5-order bonds which are present in any large polynuclear aromatic hydrocarbon [73]. In principle there are no functional groups on the surface since the aromatic carbon atoms have fully saturated valencies within the graphitic sheets. To produce PGC, silica is employed as template which is impregnated with a mixture of phenol and hexamine and then heated to 80–160 °C to initiate polycondensation. The choice of the template material determines the size and porosity of the carbon particles that will be obtained, and, therefore, is a crucial point. The polymer is then pyrolyzed under inert atmosphere (nitrogen) at 1000 °C. In this way a highly porous amorphous carbon is produced which corresponds to carbon black. The structure of carbon is immobilized and the silica template is then dissolved using a hot aqueous potash solution and removed followed by graphitization at 2340 °C under inert atmosphere (argon). At this stage any remaining surface functions are removed, structural rearrangements are made and micropores are closed. By cooling down to 1000 °C, the replacement of argon by hydrogen can induce a reaction between hydrogen and free radicals still present at the carbon surface, thereby deactivating the surface to render it more uniform. The obtained material, PGC, has been extensively used as a

stationary phase in HPLC applications in biomedical and clinical research, pharmaceutical industry as well as in environmental and food chemistry. There are numerous publications reporting separations of oligosaccharides, pesticides, pollutants and other environmentally relevant species. Polychlorinated biphenyls and dioxins have numerous isomers, which can be well resolved by the planar surface of graphite. PGC has been an interesting stationary phase for the analysis of pharmaceutical compounds and their impurities.
In a comprehensive review of the structure, performance and HPLC retention mechanism of PGC [74], its chromatographic behaviour was summarized as showing:

- increased retention of non-polar compounds based on dispersive interactions compared with conventional silica based reversed stationary phases. Increasing the hydrophobicity of an analyte by adding $-CH_2-$ or other non-polar groups increases retention.
- a polar retention effect whereby solutes of increasing polarity showed a high affinity towards the graphite surface.
- increased selectivity towards structurally related compounds due to the flat and highly adsorptive surface of the graphite.
- unique and complex retention mechanism; the strength of interaction depends on both the molecular area of an analyte in contact with the graphite surface and upon the nature and type of functional groups at the point of interaction with the flat graphite surface.
- stability at extreme pH and temperature.

The polar retention effect makes Hypercarb® columns particularly useful for the separation of highly polar compounds and compounds containing several hydroxyl, carboxyl and amino groups, which are difficult to retain on conventional alkyl-silica phases. The effect of increased retention of non-polar compounds (based on dispersive interactions) compared with conventional alkyl-bonded silica and planarity of the surface is of particular concern when it comes to identify appropriate sorbent-solvent systems which can separate non-polar polyolefins in an interactive way.

2.3.2.5. Two-Dimensional Liquid Chromatography (2D-LC)

As discussed, polyolefins are distributed in more than one parameter of molecular heterogeneity. It is obvious that n independent parameters require n-dimensional analytical methods for accurate (independent) characterization of the different structural parameters. In practice, however, this is hardly ever possible. SEC for instance is always affected by differences of the macromolecules in their chemical composition since the hydrodynamic volume is also a function of chemical composition, and vice versa HPLC suffers from molar mass effects. Nevertheless, two- and multi-dimensional separation systems become indispensable for the separation of very complex mixtures. In chromatography, the separation efficiency of any single separation method is limited by the efficiency and selectivity of the separation mode, that is, the number of plates of the column and the phase of the selected system. The peak capacity in an isocratic separation was described by Grushka [81], as given in Equation (15):

$$n = 1 + \frac{\sqrt{N}}{4} \ln \frac{V_{pore}}{V_0} \tag{15}$$

where n is the peak capacity, N is number of plates and V_0 is the interparticle volume.

The corresponding peak capacity of an n-dimensional separation is higher due to the fact that each dimension contributes to the total peak capacity as a factor, and not as an additive term for one-dimensional methods, as described in Equation 10:

$$n_{total} = \prod n_i \sin^{(i-1)} \vartheta_i \tag{16}$$

where n_{total} represents the total peak capacity, n_i the peak capacity in dimension i, and ϑ_i is the angle between the two dimensions. The angle between dimensions is determined by the degree of independency of the used methods. For instance, when two methods are completely independent of each other and will separate two properties solely on a single parameter without affecting themselves, ϑ_i will be 90°.

In case of a two-dimensional separation system employing two mutually independent separation modes, the peak capacity is given by Equation 2 [82]:

$$n_{2D} = n_1 n_2 \sin\vartheta = \left(1 + \frac{\sqrt{N_1}}{4} \ln\frac{V_{p,1}}{V_{0,1}}\right)\left(1 + \frac{\sqrt{N_2}}{4} \ln\frac{V_{p,2}}{V_{0,2}}\right)\sin\vartheta \qquad (17)$$

Comprehensive two-dimensional liquid chromatography implemented by coupling two separations exists in three schemes: on-line; stop-and-flow; and off-line. Each approach has distinct features and drawbacks; particular approaches allow making use of one of them more advantageous than that of the other ones for some specific applications, as it was demonstrated by Fairchild et al. [83]. The resulting data is a matrix, usually represented as a contour plot, with each chromatographic separation along an axis. In the very first examples of 2D-LC separations of synthetic polymers, SEC was performed first [82] followed by HPLC in the second dimension. In these experiments, the heart-cut (off-line) approach was very frequently used; meaning, that only selected fractions were transferred into the second dimension. In recent years, the sequence of HPLC in the first dimension and SEC in the second dimension is favoured. Owing the fact the fact that state of the art SEC experiments employing new small columns with improved separation efficiencies can be performed in a very short period of time (down to several minutes) [82, 84, 85], a complete transfer of all fractions from the first dimension into the SEC column became possible (see Fig. 12).

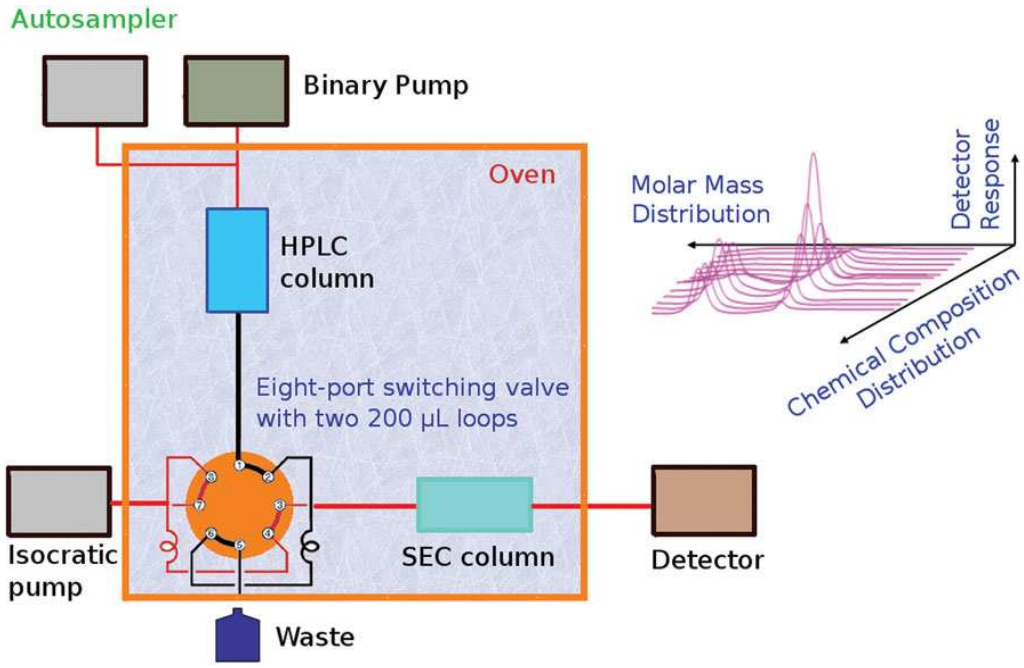


Fig. 12 Schematic configuration of HPLC × SEC setup.

The advantages and disadvantages of using either HPLC × SEC or SEC × HPLC sequences were discussed in detail by van der Horst and Schoenmakers [86, 87]. From the practical point of view, a preferred 2D-LC set-up is fractionation of a sample by HPLC and subsequent analysis of the fractions eluting from the HPLC column by SEC. Namely, HPLC was found to be less sensitive towards molar mass effects and yielded uniform fractions with respect to chemical composition. SEC is in the majority of publications used for the second dimension, which allows to use different detectors [82]. In the case of using SEC in the first dimension, each fraction is dissolved in a thermodynamically good solvent when injected into HPLC and breakthrough peaks can occur [88]. If SEC is used in the second dimension, the injected solvent from the HPLC will simply be separated from the polymer fraction. In the present treatment, we will focus exclusively on the comprehensive mode, where the entire first dimension effluent is subjected into the second dimension separation.

An eight-port valve with matching sample loops is typically used for the coupling [82]. The valve is controlled electronically and allows a complete transfer of all eluting polymer fractions from the first to the second dimension by choosing the proper flow rates in both dimensions and by adjusting the sampling time. The configuration of such a transfer valve is depicted in Fig. 13.

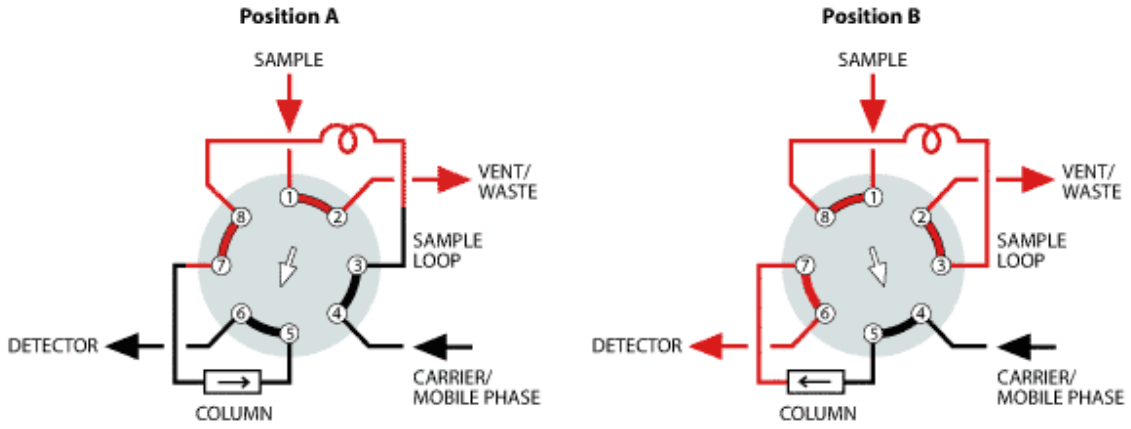


Fig. 13 Configuration of an automatic fraction transfer valve (from vici.com).

Murphy et al. [89] studied the effect of experimental variables on the separation efficiency of 2D-LC. The results showed that the shortest sampling time into the second dimension gives the best resolution and longer sampling times decrease resolution along the first dimension axis. The resolution in the second dimension was not affected by undersampling of the first dimension, but the overall result was a loss in two-dimensional resolution. To obtain the highest two-dimensional resolution, each separated peak in the first dimension should be sampled at least three times into the second dimension when the sampling is in-phase, whereas if the sampling phase is not considered, there should be at least four samples per peak.

Dilution factors are important characteristics from the point of view of analyte detectability. During the chromatographic process peaks are invariably diluted [86]. The dilution factor (*DF*) is given by Equation 13:

$$DF = \frac{V_{mob}}{V_{inj}} \frac{\sqrt{2\pi}}{\sqrt{N}} (1+k) \qquad (18)$$

At the time being, the published 2D-LC methods and available instrumentation are still limited to separation at ambient temperatures.

3. Results and Discussion

3.1. Chacterization of functionalized polyolefins by high-temperature two-dimensional liquid chromatography (HT 2D-LC)

3.1.1. HT 2D-LC of ethylene-vinylacetate (EVA) copolymers

In order to investigate the chemical heterogeneity by a conventional crystallization based technique, a model mixture containing PE, EVA copolymers with varying VA-content (Table 1) and PVAc was cross-fractionated by TREF × SEC. The 3D plot and colour coded contour plot are presented in Fig. 14.

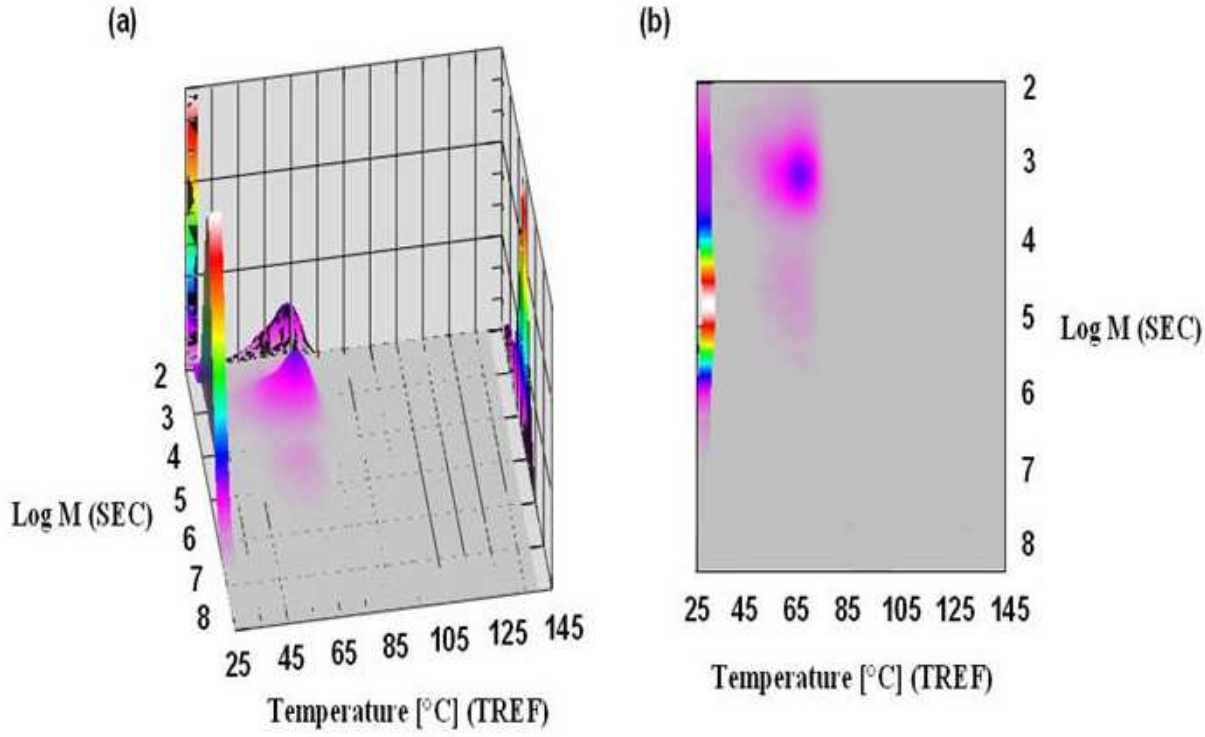


Fig. 14 a) Relief plot and b) colour coded contour plot obtained by TREF × SEC of a blend of PE (1.18 kg/mol), EVA 1 (6.5 mol. % of VA), EVA 2 (20 mol. % of VA), EVA 3 (57 mol. % of VA) and PVAc (37 kg/mol) using conditions described in the text.

The figure shows the set of SEC elugrams measured at different TREF temperatures. Taking into account the principles of TREF × SEC, the less crystalline (amorphous) portion of the blend elutes at 30 °C for which the SEC profile shows a very broad bimodal MMD. Considering the

average molar masses and the average chemical compositions of the components, it can be supposed that the soluble TREF fraction contains PVAc 37 $kg \cdot mol^{-1}$, EVA with 20 and 57 mol. % of VA and to some extent EVA with 6.5 mol. % of VA. However, no information about the chemical composition of this fraction can be obtained. The next TREF fractions with increasing elution temperature exhibit MMD in the area of lower molar masses which can be assigned to both PE (1.18 $kg \cdot mol^{-1}$) and EVA copolymers. The fractions with elution temperatures of 60 °C and 70 °C show additional peaks in the area of higher molar mass, which apparently can be assigned to EVA with 6.5 mol. % of VA. We conclude that the major part of the mixture elutes as soluble fraction and the rest elutes (cocrystallizes) in a broad zone, i.e. the cross-fractionation by TREF × SEC does not result in a selective separation of all components according to their chemical composition.

Table 1 Weight average molar mass (M_w), dispersity (D) and VA content of the polymer samples

Sample code	Sample	M_w [$kg \cdot mol^{-1}$]	D	VA [mol.%]
1	EVA	197.5	3.08	6.5
2	EVA	377.9	8.06	20.0
3	EVA	224.6	4.10	57.0

Having appropriate chromatographic systems for the compositional separation is the main requisite to realize a 2D-LC separation. As has been pointed out, EVA copolymers could be separated according to their VA-content on bare silica using TCB and cyclohexanone as components of the mobile phase. The separation is based on the full adsorption of EVA from TCB and a subsequent controlled desorption by a solvent gradient TCB→cyclohexanone [76]. The contour plot in Fig.15 shows the 2D-LC separation of the same polymer mixture as for the TREF × SEC experiment described above. The gradient separation is represented along the Y-axis whereas the elution along the X-axis corresponds to the molar mass separation.

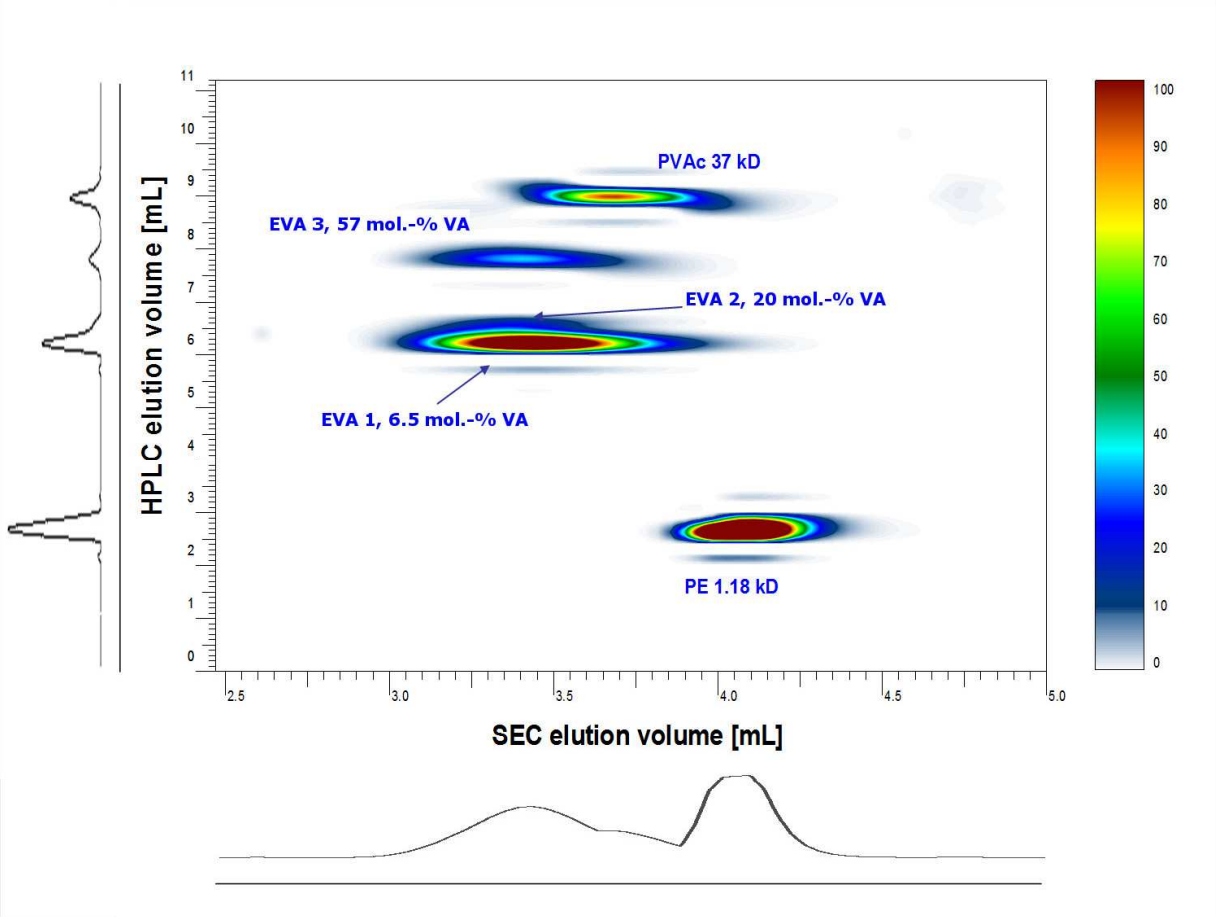


Fig. 15 Contour plot obtained by high-temperature 2D-LC of the same blend as described in Fig. 13; Columns and flow rates: HPLC: Perfectsil 300, 0.1 mL/min; SEC: PL Rapide H, 2.5 mL/min.

As can be seen, the individual samples elute in the order of their polarity. The first eluting spot can be assigned to the PE and the last one is PVAc which are the least and most polar component respectively. Between these three EVA copolymers elute. Only two of them (6.5 and 20 mol. % of VA) are not baseline separated, but the presence of two components with different chemical composition as well as with different average molar masses can be concluded. TREF × SEC by contrast did not separate the components of the mixture as clearly as 2D-LC. The small narrow part in the contour plot eluting between 5.6 and 6.0 mL, i.e., before the main spot (it looks like a narrow peak with very small intensity), is the result of the mathematical data treatment in the WinGPC software (Polymer Standards Service, Mainz, Germany). The cause for this effect will be eliminated from the software in the future.

3.1.2. Calibration of HPLC and SEC

In the majority of publications describing 2D-LC separations at room temperature, only the molar mass axis (SEC) is calibrated. Calibration of the first dimension (compositional axis) has never been reported. As HT 2D-LC has not been studied, apart from realizing this hyphenation particular stimulus lies in the calibration of both axes. Therefore, a relationship between the molar mass and the elution volume in SEC as well as a relationship between the chemical composition and the elution volume in HPLC has to be established. The SEC calibration curve is valid as long as the chromatographic system and the procedure are not changed. In a comprehensive 2D-LC set-up, two chromatographic modes (HPLC and SEC) are on-line hyphenated. This means that, instead of an ordinary injection of a polymer sample into the SEC eluent, a polymer solution in a mixed solvent is injected via an automated switching valve, which may cause a change of the hydrodynamic volume and therefore the elution volume of the sample. In order to obtain reliable results, the calibration standards for SEC should undergo the HPLC separation and then enter the SEC system via automated injection. Thus, 11 PS and 7 PE standards were injected into the 2D system and the obtained calibration curves are shown in Fig. 16 and Fig. 17.

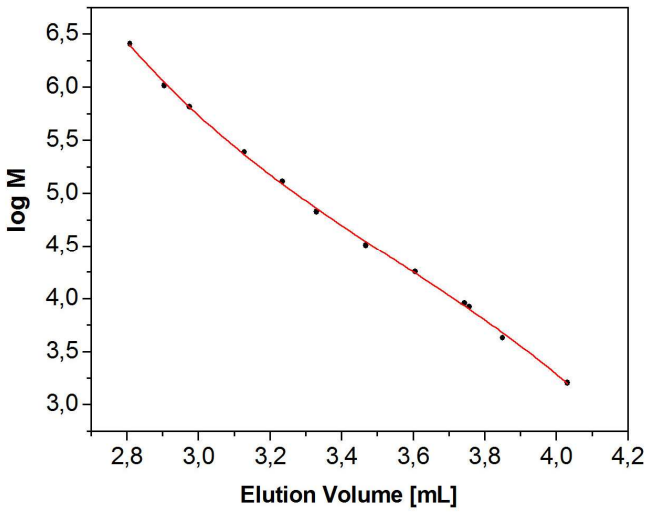


Fig. 16 Calibration curve for PL Rapide H column based on PS standards (140 °C, TCB, 2.5 mL/min) obtained in 2D-LC system (1st dimension: Perfectsil 300, TCB, 0.1 mL/min).

As can be observed in Fig. 16, the data points could be fitted with a polynomial curve quite well,

while the data points on Fig. 17 are rather scattered. It is known that the accuracy of the results strongly depends on the number of standards, the molar mass range covered by them, and the appropriate fit. One of the most important sources of error in establishing a calibration is the number of data points. Narrow disperse PS standards are readily available on the market. PE standards with a well-defined MMD are also available; however, their dispersity is generally broader (see experimental part). Therefore, the PS calibration yields a much more accurate and reliable calibration curve compared to the PE based one.

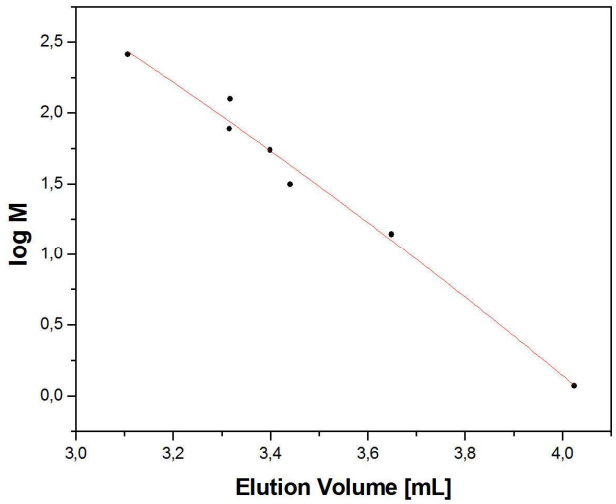


Fig. 17 PE calibration curve for PL Rapide H column (140 °C, TCB, 2.5 mL/min) obtained in 2D-LC system (1st dimension: Perfectsil 300, TCB, 0.1 mL/min).

A calibration of the HPLC requires knowledge of the delay volume of the system, i.e. when a given gradient reaches the detector. The delay volume is the sum of a void volume and a dwell volume of the corresponding system. Taking into account controversial opinions regarding the meaning of these parameters as well as the methods for their determination [49,50] we note that in the present treatment we consider the void volume as the volume of the component that is not retained by the stationary phase while the dwell volume is the volume of liquid contained in the system between the point where the gradient is formed and the injector. The dwell and the void volume of the 2D-LC system were determined modifying a procedure proposed by Bashir et al. for HPLC [90]. The void volume was measured by injecting a low molar mass PS standard (M_w = 0.687 kg/mol) into the 2D-LC system, as it is not retained by the HPLC column and elutes with the initial mobile phase composition (i.e., in TCB). The elution volume of the PS standard

corresponds then to the void volume of the chromatographic system which was determined to be 3.00 mL (Fig. 18).

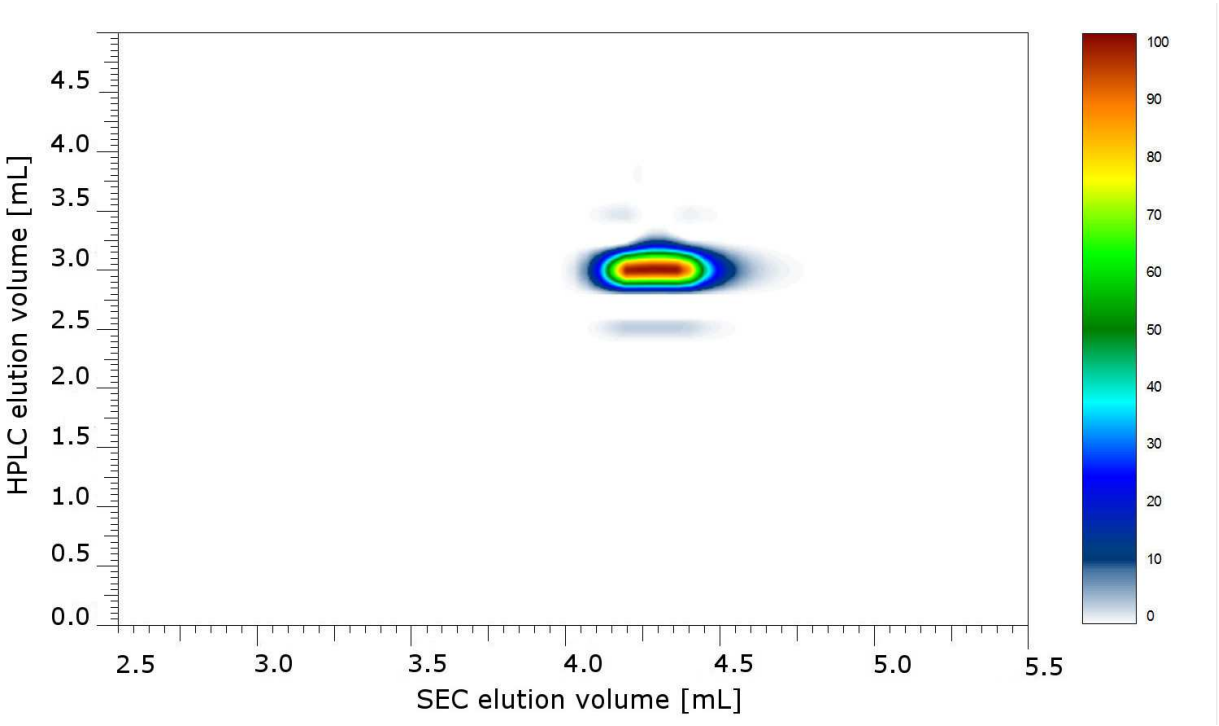


Fig. 18 2D-LC contour plot of a PS 0.687 kg/mol used to determine the void volume: Columns and flow rates: 1st dimension: Perfectsil 300, TCB, 0.1 mL/min; 2nd dimension: PL Rapide H, TCB, 2.5 mL/min.

In [90] the dwell volume was determined by subtracting the void volume from the delay volume which was measured from the onset of the UV-signal when a linear solvent gradient methanol→methanol/acetone containing 0.3 % acetone was applied. Analogously, the dwell volume was determined by subtracting the void volume from the elution volume at the onset of the ELSD signal when a linear gradient from pure TCB to a solution of PS (0.687 kg/mol) in TCB (1 mg/mL) was started. This approach gave, however, an overestimated value for the dwell volume (3.54 mL). It was considered as overestimated, because if it was used to locate the exact position of the gradient on the y-axis, some EVA copolymers would elute before the gradient, which is impossible. It is supposed that at the moment when the gradient reaches the detector the concentration of PS is not sufficient to be detected by the ELSD because the ELSD is less sensitive than a UV-detector in that case. Moreover, in 2D-LC the sample concentration after the 2nd dimension is significantly lower than after the 1st dimension solely, which means that a higher

sample concentration has to be used compared to the one-dimensional separation. Consequently, the procedure to determine the dwell volume was modified: In the first step pure TCB was pumped into the 2D system. Thereafter, the concentration of PS (0.687 kg/mol) in TCB (1 mg/mL) was abruptly changed to 100 vol. % and the data acquisition started. The contour plot resulting from the sudden change of the composition of the mobile phase is illustrated in Fig. 19.

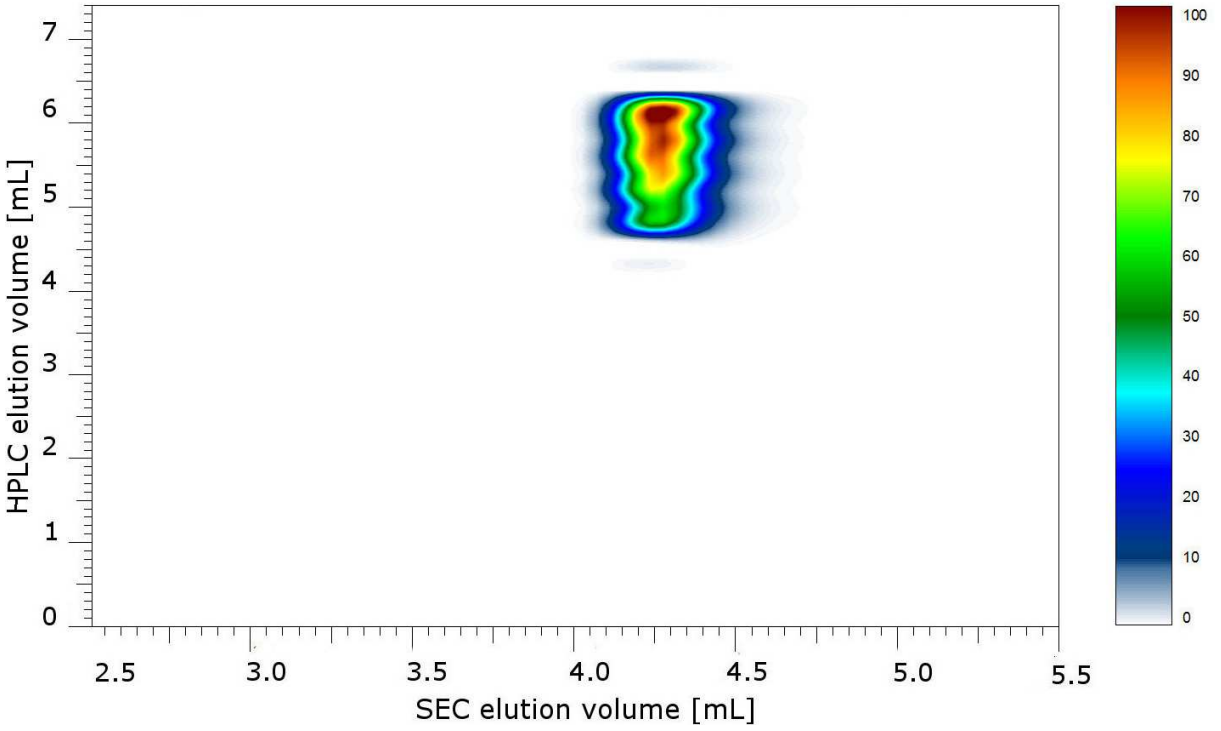


Fig. 19 2D-LC contour plot of a solution of PS 0.687 kg/mol in TCB (1 mg/mL) used for the determination of a dwell volume; Columns and flow rates like in Fig.18.

The dwell volume obtained by using this procedure was 1.44 mL and the system delay volume could be explicitly estimated using the following equation:

$$V_{system,\,2D} = V_{dwell} + V_{void,\,2D} \qquad (19)$$

As a consequence, the gradient reaches the detector with a delay of 1.44 mL. The knowledge of these chromatographic parameters allows to locate the exact position of the gradient on the y-axis of the contour plot. We previously found that the dependence between the elution volume and the average chemical composition of EVA copolymers in gradient HPLC is linear. The obtained

relationship is depicted in Fig. 20.

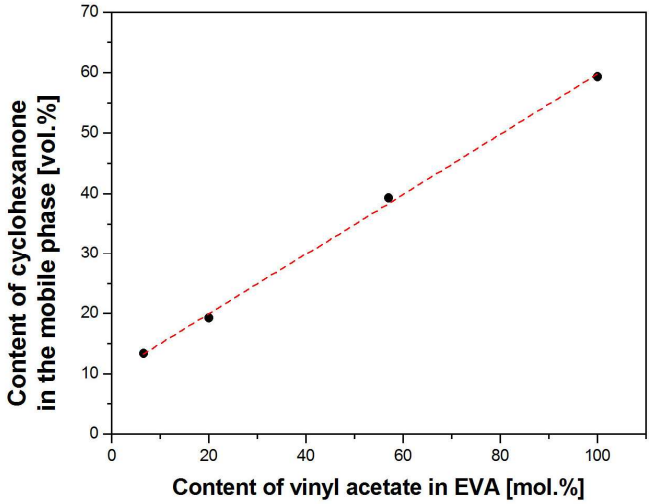


Fig. 20 Relationship between concentration of cyclohexanone in the mobile phase and the average chemical composition of EVA copolymers.

As we have determined the delay volume of the system, the content of cyclohexanone in the mobile phase can now be related to the elution volume and the dependence between the VA-content and the elution volume applied to the 2D-contour plot. Consequently, the X- and Y-axis of the contour plot were converted and thus a new contour plot is obtained (Fig. 21). Each axis in Fig. 21 represents one parameter of the analyzed polymer sample – either molar mass or the chemical composition of the analyzed polymer and as a result information which can be extracted from the contour plot is greatly enhanced.

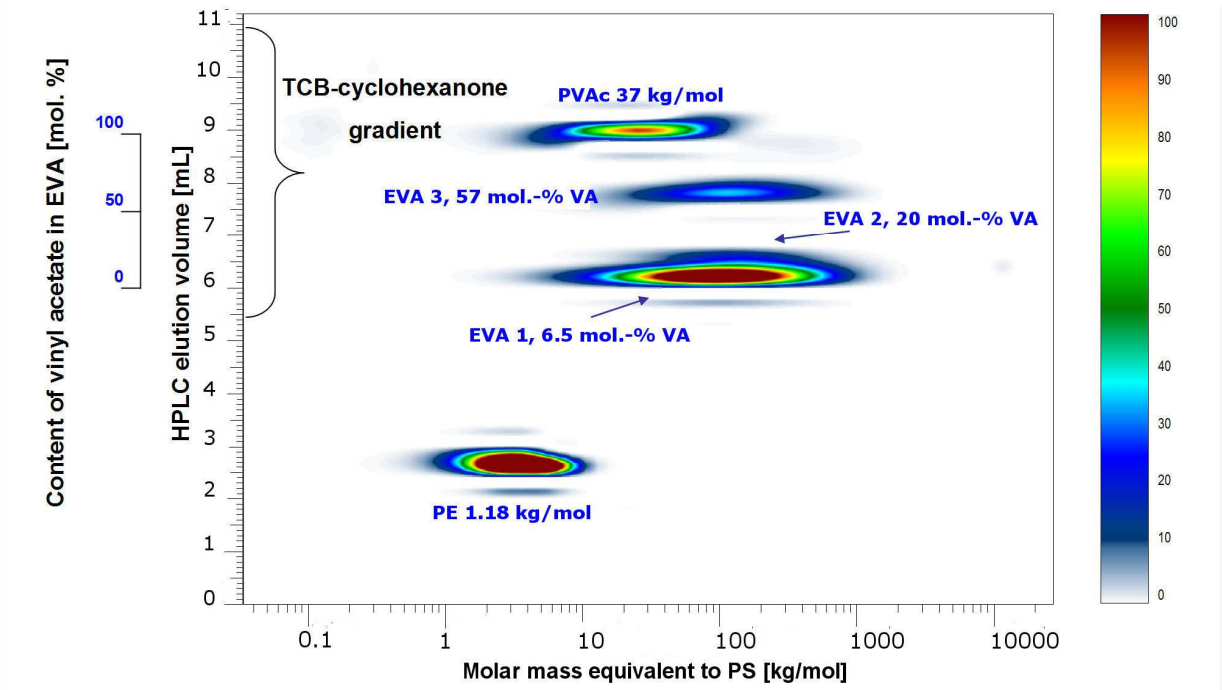


Fig. 21 Contour plot of a blend obtained from the original data (Fig. 15) with the calibrated axes.

3.1.3. Conclusions

Based on the experimental results the following conclusions can be drawn:

1) HT 2D-LC of EVA copolymers has been realized for the first time by coupling HPLC with SEC at 140 °C. This was successfully demonstrated by analyzing a blend of PE, PVAc and EVA copolymers with varying VA content. In the first step, the components were separated with regard to the content of the polar comonomer, while in the second step the obtained fractions were distinguished according to their molar mass distribution. Both distributions were obtained simultaneously in a relatively short period of time - 5 hours for a complete HT 2D-LC analysis - including sample preparation.
2) For the first time a calibration of both dimensions, HPLC and SEC, was achieved. Therefore a method to correctly determine the void and dwell volume in a 2D-LC system was developed.
3) TREF × SEC on the contrary was not able to separate the same mixture into the individual components. Although HT 2D-LC is experimentally not less demanding than TREF × SEC, a great advantage is that it can be applied to samples irrespective of their crystallinity. Thus effects of cocrystallization can be avoided which might play a role in TREF.
4) The number of applicable detectors is quite limited in HT HPLC, as a constantly changing mobile phase composition prevents one from using typical concentration detectors. The preferred detector in that case is the ELSD. Response of ELSD, at constant instrumental parameters (gas flow rate, nebulization and evaporation temperature, flow rate of effluent) is a function of the concentration of the polymer in the mobile phase. This response, however, may depend also on the nature of analyte, its molar mass and the composition of the mobile phase [76, 79, 80]. It means that the composition of the gradient and eventually also the chemical composition of the samples may influence the ELSD response to some extent. The precise quantitative evaluation of the CCD requires to calibrate the response of the ELSD, which has never been thoroughly done. On the other hand, in HT 2D-LC the analyte is detected isocratically. This means that the influence of mixed mobile phase on ELSD response is eliminated and the model that may describe this response becomes less complex. Moreover, in that case conventional SEC detectors may be employed. However, in HT 2D-LC the sample is invariably diluted twice resulting in a decrease of the detector signal. In this work the IR 4 detector (PolymerChar, Valencia, Spain)

was tested. It was found that this detector is not sufficiently sensitive to detect low concentrations of the analyte, which leads to significant loss of information. An alternative would be to use the IR 5 detector (PolymerChar, Valencia, Spain), which is known to be more sensitive than IR 4. Nevertheless, ELSD still remains the preferred detector due to its high sensitivity.

3.2. Development of HT 2D-LC of functionalized polyolefins

3.2.1. Test of experimental parameters

In 4.1 the first HT 2D-LC separation of EVA copolymers was presented, which currently is the most comprehensive mode to characterize the molecular heterogeneities present in copolymers. However, the runtime of a single HT 2D-LC experiment was about 3 hours. With the aim to increase sample throughput and thus meet the requirements of high throughput experimentation it is of great interest to decrease the time needed to realize the experiment. This in turn requires to probe the influence of flow rate on the results of the chromatographic analysis. In particular the 2nd dimension (SEC) is of interest, as this is the rate limiting step in the entire experimental protocol. The chromatograms of a blend of PE with a weight average molar mass of 1.01 kg/mol and 66 kg/mol are shown for different flow rates and injection volumes in Fig. 22 and 23 respectively.

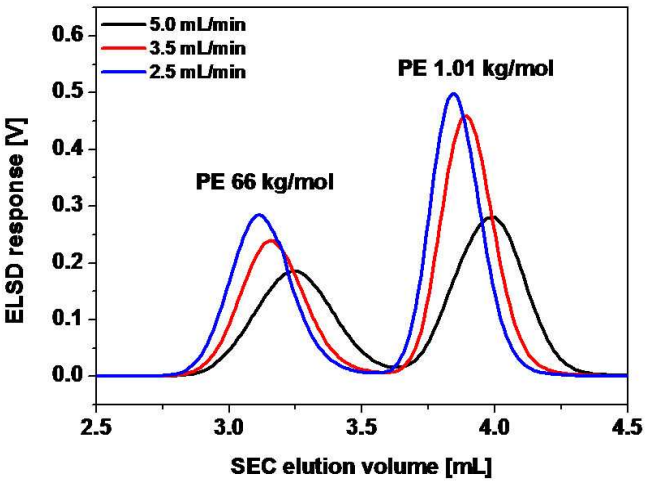


Fig. 22 Influence of the flow rate on the elution volume of PE 1.01 kg/mol and PE 66 kg/mol. Column: PL Rapide H; Temperature: 140 °C. Mobile phase: TCB; Injection volume: 200 µL.

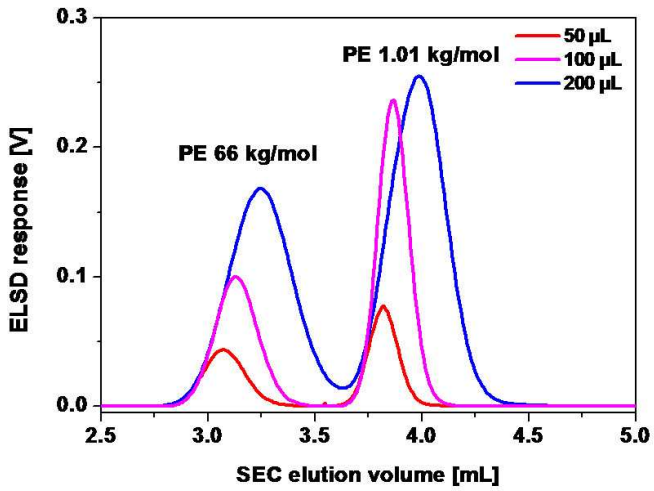


Fig. 23 Influence of the injection volume on the elution volume of PE 1.01 kg/mol and PE 66 kg/mol. Column: PL Rapide H; Temperature: 140 °C. Mobile phase: TCB; Flow rate: 2.5 mL/min.

A shift towards larger elution volumes (i.e. apparently lower molar masses) can be observed with increasing flow rate. It is known that the change in the flow rate results in a shift on the van Deemter curve [91]. According to the Einstein-Stokes relationship [92], the hydrodynamic volume of a macromolecule is inversely proportional to the diffusion coefficient which increases when the flow rate is raised. Therefore, the hydrodynamic volume of a macromolecule becomes smaller at higher flow rates and in SEC the macromolecules appear as smaller ones. Moreover, the peaks broaden, which is the result of the increased diffusion (Fig. 22). As expected the peak area increases with the larger injection volumes. Good resolution is obtained using an injection volume of 50 µL, while larger injection volumes result in a significant band broadening (Fig. 23), which is a common effect in chromatography [93]. In a comprehensive HT 2D-LC the flow rate of the first dimension is set by the injection volume into the second dimension (SEC) and by the analysis time of the second dimension. The time of the first-dimension separation determines the duration of the entire analysis. Using low volume injection loops for the second dimension implies to use slow flow rates in the first dimension.

An important question is how the composition of the mobile phase in the first dimension affects the results obtained from the second dimension. In a comprehensive 2D-LC set-up, two chromatographic modes (HPLC and SEC) are on-line hyphenated. This means that, instead of

injecting a solution of the polymer sample in the mobile phase of the SEC into the eluent, the polymer sample is introduced into the SEC column in a mixed solvent via an automated switching valve. In our case, the composition of the mixed solvent changes from pure decalin over the entire range of decalin/cyclohexanone to pure cyclohexanone. As the hydrodynamic volume of a macromolecule depends on the solvent, this could affect the SEC separation as was found in [94] for the system 1-decanol/TCB for PP homopolymers. In order to probe if there is an effect of solvent composition, two PE standards were dissolved in solvents used for the interactive HPLC separation and injected into the SEC column (Fig. 24).

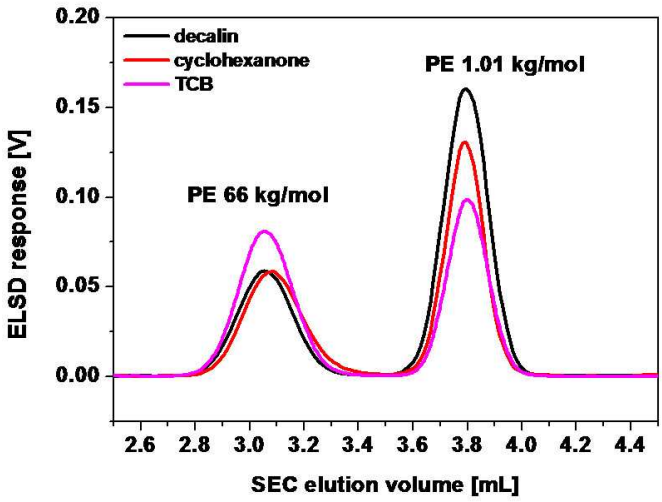


Fig. 24 Influence of the sample solvent (decalin, cyclohexanone and TCB) on the SEC elution volume of PE 1.01 kg/mol and PE 66 kg/mol. Column: PL Rapide H; Temperature: 140 °C. Mobile phase: TCB; Flow rate: 2.5 mL/min; injection volume: 50 µL.

As can be observed, the choice of solvent does not affect the molar mass separation significantly. This implicates that the change of the solvent shell (e.g. decalin→TCB) occurs easily. The influence of the injection volume on the retention of the EBA copolymer (28 wt.-% of BA) on the silica gel column is demonstrated in Fig. 25. Interestingly, the retention depends on the injection volume. This is understandable because in the used HT 2D-LC setup the gradient passes through the injection loop which forms a significant part of the system dwell volume: If a large injection loop is used, the gradient will reach the column with a corresponding delay and as a result, the polymer will elute later.

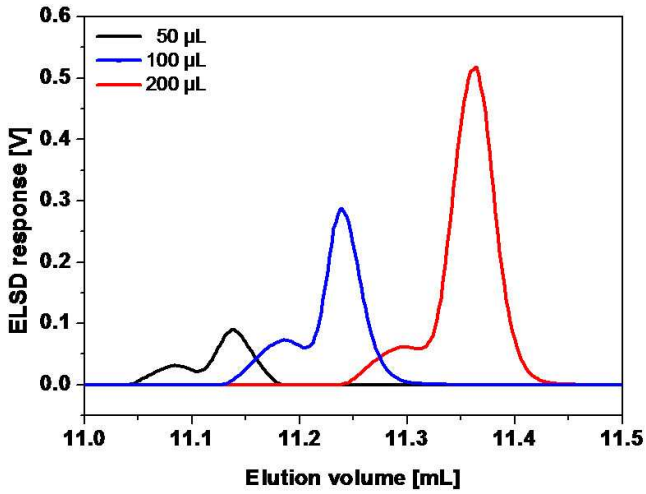


Fig. 25 Influence of injection volume on HPLC elution of EBA (28 wt.-% BA); Stationary phase: Perfectsil 300; Mobile phase: linear gradient decalin→cyclohexanone; Temperature: 140 °C, Sample solvent: Decalin; Flow rate: 0.5 ml/min.

For the isocratic SEC, the solute does not need to fully elute from the column prior to the next sampling span. This means that more than one sample can be resident in the SEC column at a given time. This opens the opportunity to speed up the complete 2D-LC analysis substantially. We have achieved this using a sampling time of 1 minute, i.e., before the SEC elution of one HPLC fraction was completely finished, the second HPLC fraction was injected into the SEC column. In order to realize it in a comprehensive way, the flow rate in HPLC was adjusted accordingly, i.e. increased from 0.1 mL/min as in 4.1 to 0.2 mL/min, while the volume of the SEC loops (200 µL) was kept constant. In this way the time required for one complete 2D-LC analysis was shortened from about 200 minutes to 100 minutes (Fig. 26). Due to the high dilution factor (~10) in 2D-LC experiments the ELSD response was very low when 50 or 100 µL loops were used and therefore 200 µL sample loops were used to inject the effluent from the HPLC column into the SEC column.

Unlike the continuous mechanism utilized in one-dimensional separations, in a comprehensive HT 2D-LC finite volumes of the 1st dimension (HPLC) are injected into the 2nd dimension (SEC). The resolution of the entire analysis may be affected by the phase of sampling, which is defined as the start of the sampling relative to an eluting peak. The sampling phase was experimentally

varied by delaying the sampling for the 2nd dimension. Fig. 26 illustrates the effect of sampling phase on the contour plot of EVA 4 (Table 2) at constant sampling time.

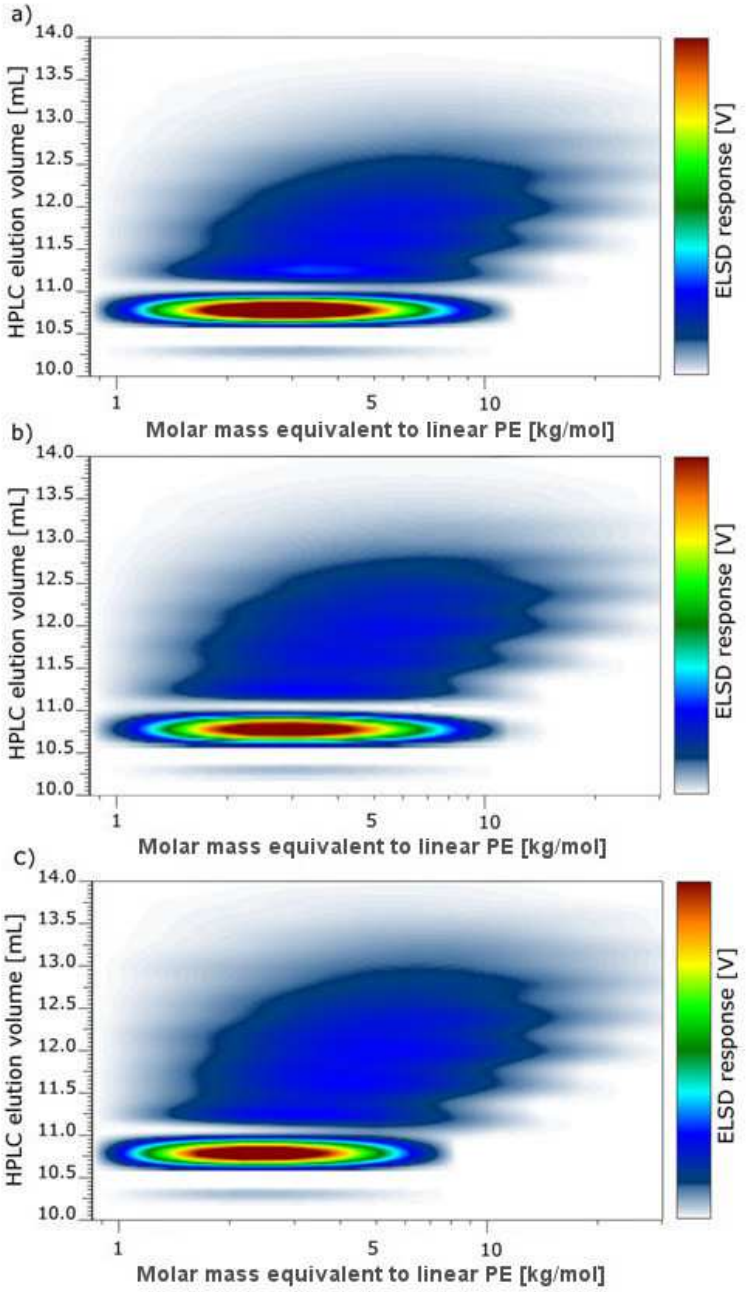


Fig. 26 Effect of sampling phase on HT 2D-LC of EVA 4: Sampling phase: a) 0 min; b) 1 min; c) 2 min; Sampling time: 1min; Columns: HPLC: Perfectsil 300; SEC: PL Rapide H; Flow rates: HPLC: 0.2 mL/min; SEC: 2.5 mL/min; HPLC injection volume: 100 µL; SEC injection loops: 200 µL.

The overall pattern of the contour plot, i.e. one main component with a peak maximum at 10.75 min elution volume on the HPLC-axis, followed by a diffuse zone is not affected by varying the sampling phase under these conditions. However, when the sampling was delayed by 2 min, 5 fractions can be singled out in the diffuse zone (Fig. 26c). In contrast, when the sampling was not delayed only 4 fractions of comparable intensity can be distinguished in this zone (Fig. 26a). The molar mass separation is not affected to a significant extent by varying the sampling phase (Fig. 27).

Table 2 Average VA content in EVA waxes and MMA content in grafted copolymers determined by NMR.

Sample code	Sample	VA or MMA-content [mol.-%]	VA or MMA-content [wt.-%]
4	EVA	14	33
5	EVA	13	32
6	EVA	13	32
7	EVA	10	25
8	PP-g-MMA	13	16
9	LLDPE-g-MMA	3	10

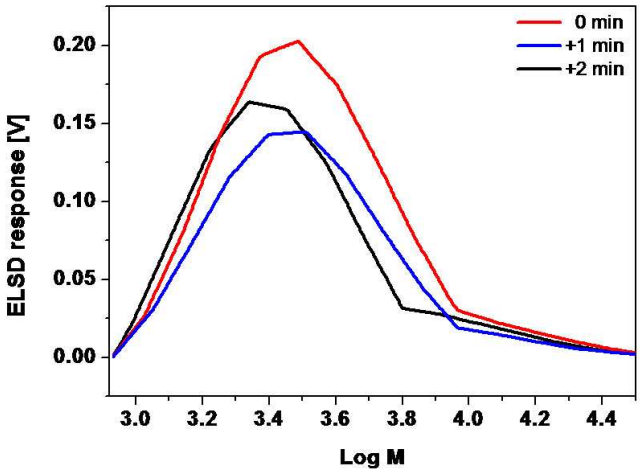


Fig. 27 Overlay of reconstructed SEC profiles from Fig. 24.

The run time of a single HT 2D-LC experiment using the conditions from Fig. 26 was only 100 minutes, while the good resolution was maintained. Such shortening of the analysis time is of paramount practical importance, in particular when responding to the demands of high throughput screening. The separation of polymers according to composition and molar mass distinguishes two of these distributions, and HT 2D-LC offers the analyst to determine the relationship between them.

3.2.2. HT 2D-LC of EVA waxes

To demonstrate the superior information obtained from HT 2D-LC over bulk analytical techniques, EVA 5-7 were analyzed by HT 2D-LC using the optimized conditions with regard to throughput as previously established. The corresponding contour plots are shown in Fig. 28 - Fig. 30.

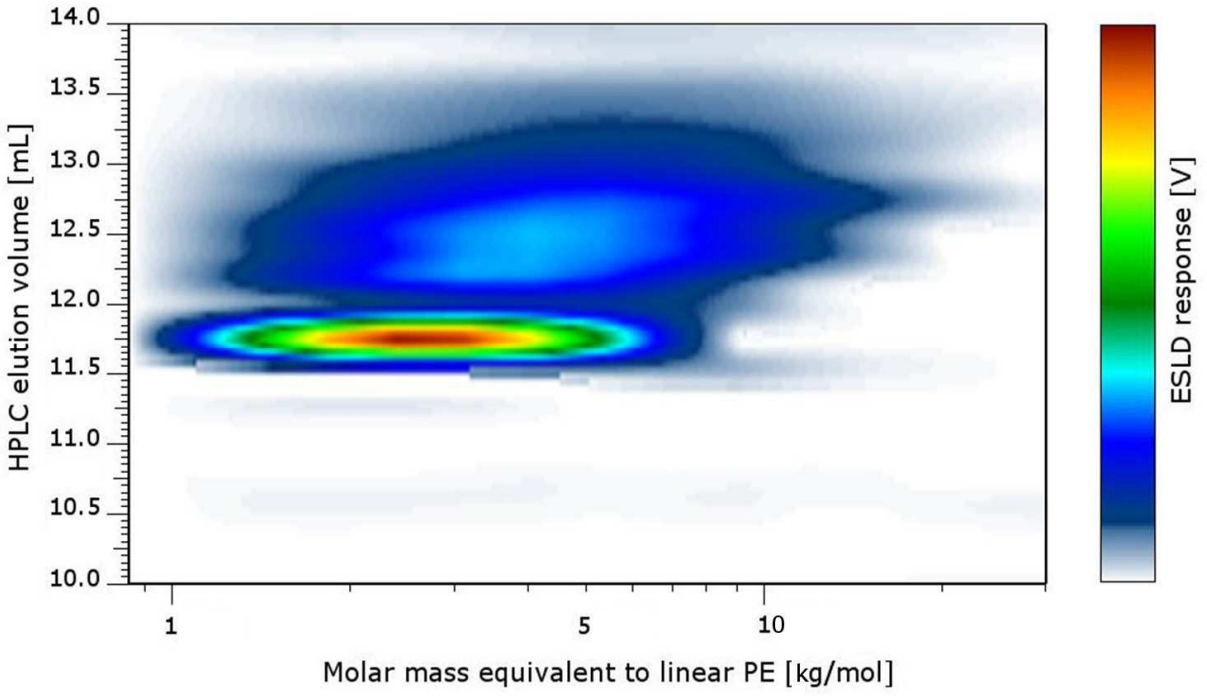


Fig. 28 HT 2D-LC contour plot corresponding to EVA 5. Experimental conditions as in Fig. 26a.

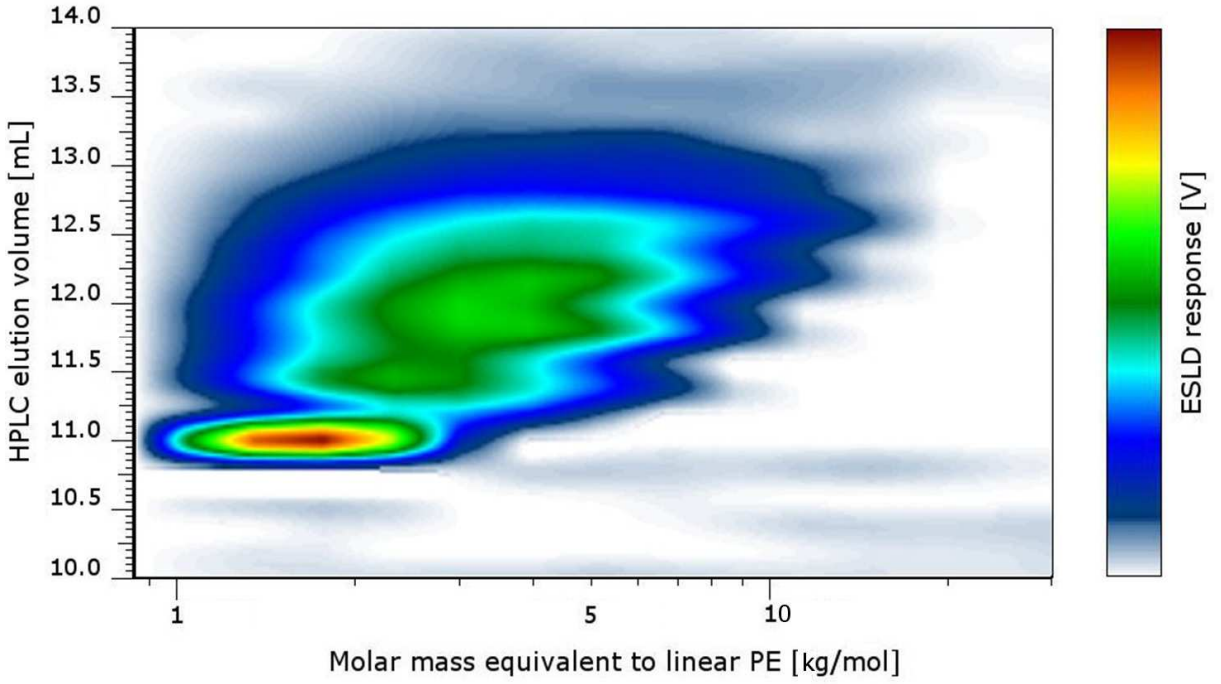


Fig. 29 HT 2D-LC contour plot corresponding to EVA 6. Experimental conditions as in Fig. 26a.

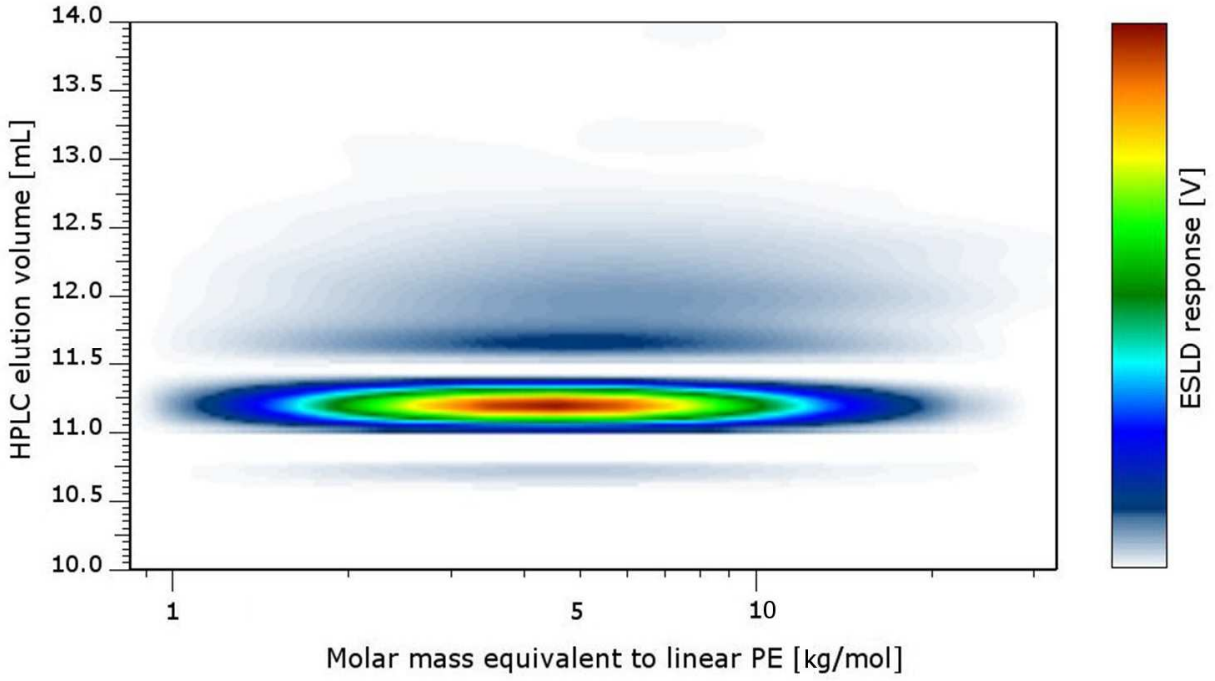


Fig. 30 HT 2D-LC contour plot corresponding to EVA 7. Experimental conditions as in Fig. 26a.

Although the average VA content of these samples varies only in the range of 10-13 mol.- % (Table 2), the shape of their contour plots differs substantially. EVA 7 has a narrow CCD with the main component eluting at a peak maximum (V_e) of 11.25 mL on the HPLC axis and a small fraction of more polar copolymer with comparable molar mass eluting later. EVA 5 and 6 are chemically broad distributed: Both contain a narrow distributed component (V_e = 11.75 mL for EVA 5 and V_e = 11.0 mL for EVA 6) and a diffuse zone of components with a higher polarity, i.e. containing a higher concentration of VA comonomer. Although having the same average chemical composition, the CCD of EVA 5 spans ca. 1.55 mL on the y-axis (Fig. 28), while that of EVA 6 spans about 2.25 mL (Fig. 29). Importantly, the elution of the chemically narrow distributed components does not ideally correlate with the average chemical composition of the respective EVAs determined by NMR: the chemically narrow distributed component in the least polar EVA 7 elutes later than the narrow chemically distributed component in more polar EVA 6. The complete understanding of this will require to quantify the diffuse zones.

Fig. 31 shows MMD reconstructed from the contour plot. Importantly, the ELSD response is related to the concentration of the analyte in the mobile phase, however, it may depend on the composition of the mobile phase and that of the eluting fractions [95]. In the present treatment the quantitative aspects of the method are not studied.

As it was shown in 3.1, the compositional axis in the HPLC separation of high molar mass EVA copolymers in HT 2D-LC can be calibrated. The main prerequisite for this is that well characterized chemically narrow distributed standards are available. In the case of HT 2D-LC of the EVA 5 - 7 the relationship between the average content of VA in the copolymer with the elution volume is not applicable, as the elution of the polymers with a low molar mass was found to depend on the latter [95]. Unfortunately, the required low molar mass standards are not readily available A possible way to overcome this problem would be to employ a preparative fractionation based on the above mentioned chromatographic system and then characterize the obtained fractions by NMR or to couple HT 2D-LC with FTIR.

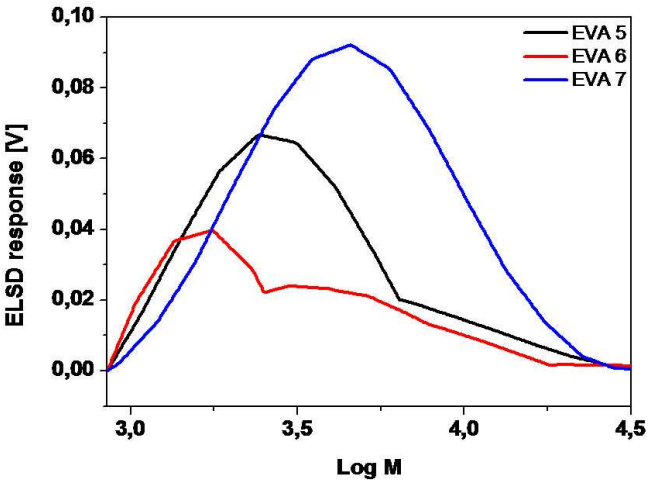


Fig. 31 Overlay of reconstructed MMD of EVA 5 - 7 from Fig. 28-30.

3.2.3. HT 2D-LC of LLDPE-g-MMA and PP-g-MMA

Albrecht et al. [96] separated random EMA copolymers containing 9–28 wt.-% MA with regard to their MA content using silica gel as stationary phase and decalin→cyclohexanone as mobile phase. The effect of chain architecture on the elution has not yet been studied. We have found that the graft copolymers PP-g-MMA (sample 8 in Table 2) and LLDPE-g-MMA (sample 9 in Table 2) do not adsorb on silica gel using the same solvent system, i.e., the samples eluted with the initial mobile phase composition without any retention. It is therefore an interesting question if the majority monomer, i.e. the olefinic one, can be used as interacting unit for a chromatographic separation. It has been found recently by Macko et al. [70,97,98] that non polar olefin copolymers can be adsorbed selectively from long chain alcohols (e.g. 1-decanol, 2-ethyl-1-hexanol) on Hypercarb® and then be desorbed by applying a gradient 1-decanol (or 2-ethyl-1-hexanol)→TCB [70, 97, 98]. Therefore, this system was tested for the separation of polyolefins grafted with functional comonomers with regard to the content of the non polar comonomer. Fig. 32 illustrates the separation of samples 8 and 9 from iPP 200 kg/mol and from PMMA with various average molar mass.

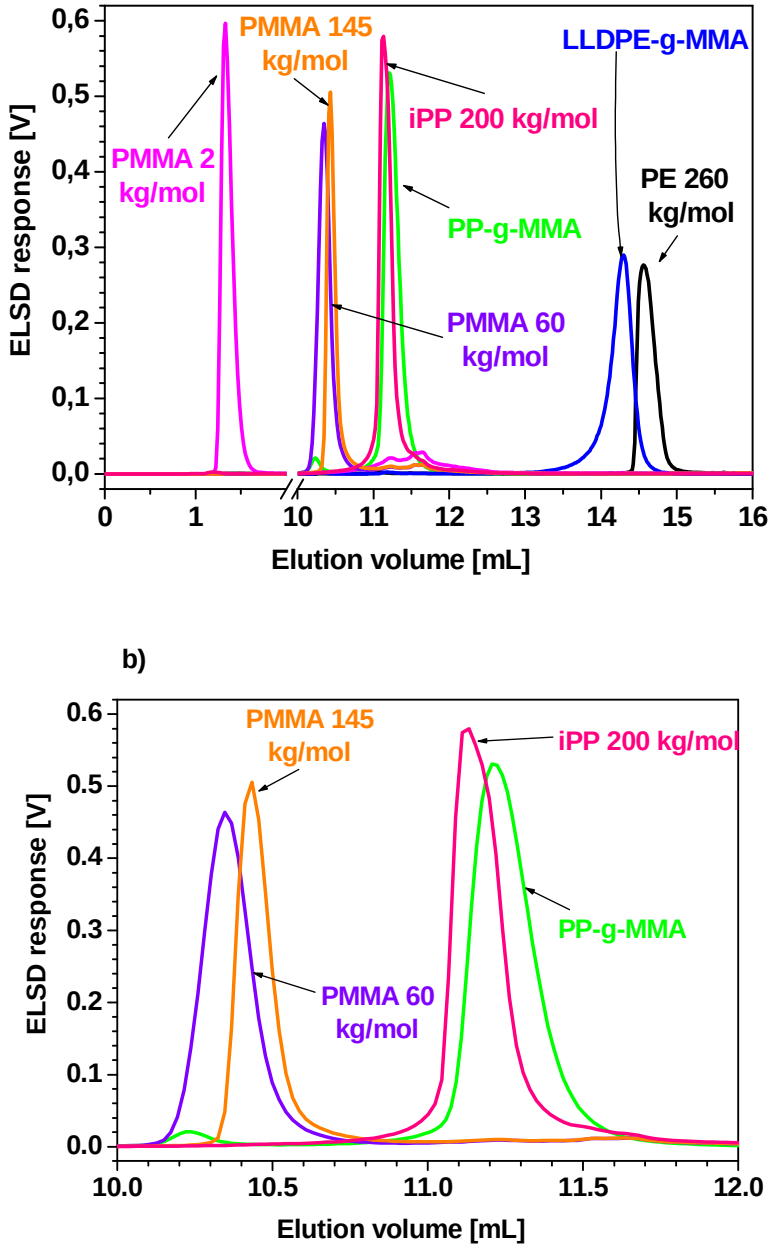


Fig. 32 a) Overlay of elugrams of PMMA 2 kg/mol, PMMA 60 kg/mol, PMMA 145 kg/mol, PP-g-MMA, iPP 200 kg/mol, LLDPE-g-MMA and PE 260 kg/mol; Stationary phase: Hypercarb®, Mobile phase: 2-ethyl-1-hexanol and linear gradient 2-ethyl-1-hexanol→TCB; Temperature: 160 °C, Sample solvent: 2-ethyl-1-hexanol and b) Enlargement of the elugram between 10 and 12 mL.

All samples, except PMMA 2 kg/mol (1.3 mL), are adsorbed on the stationary phase and elute from the column with the solvent gradient. PMMA with low molar mass (2 kg/mol) elutes before the gradient, while PMMA of high molar mass elutes only after starting the gradient elution. This is interesting, because it shows that the polar acrylate moiety leads to retention, i.e. it interacts with the stationary phase. As can be seen, sample 8 (V_e = 11.2 mL) is separated from all PMMA homopolymers and elutes close but distinctively different from the iPP (V_e = 11.1 mL). In the same way, sample 9 elutes before linear PE (V_e = 14.6 mL) with a lag of 0.3 mL. In this case both comonomers (MMA and the 1-butene) do contribute to the retention. Singling out the contributions of the individual components could be achieved by establishing a compositional calibration with regard to the olefinic comonomer using well-defined ethylene/1-butene standards of identical microstructure as the LLDPE backbone in sample 9. Indeed, as the elution of PMMA is molar mass dependent, two cases can be expected. In the first one both, MMA and LLDPE units, contribute to the retention. Second, the MMA blocks are not sufficiently long to interact with the surface and the retention is ruled by the interaction of the LLDPE-backbone with the stationary phase. However as the well-defined narrow distributed ethylene/1-butene standards are not available at the moment it cannot be decided between these two possibilities. Fig. 33 shows the 2D contour plot corresponding to the two-dimensional separation of a blend of sample 8 and iPP 60 kg/mol and Fig. 34 illustrates the two-dimensional separation of sample 9.

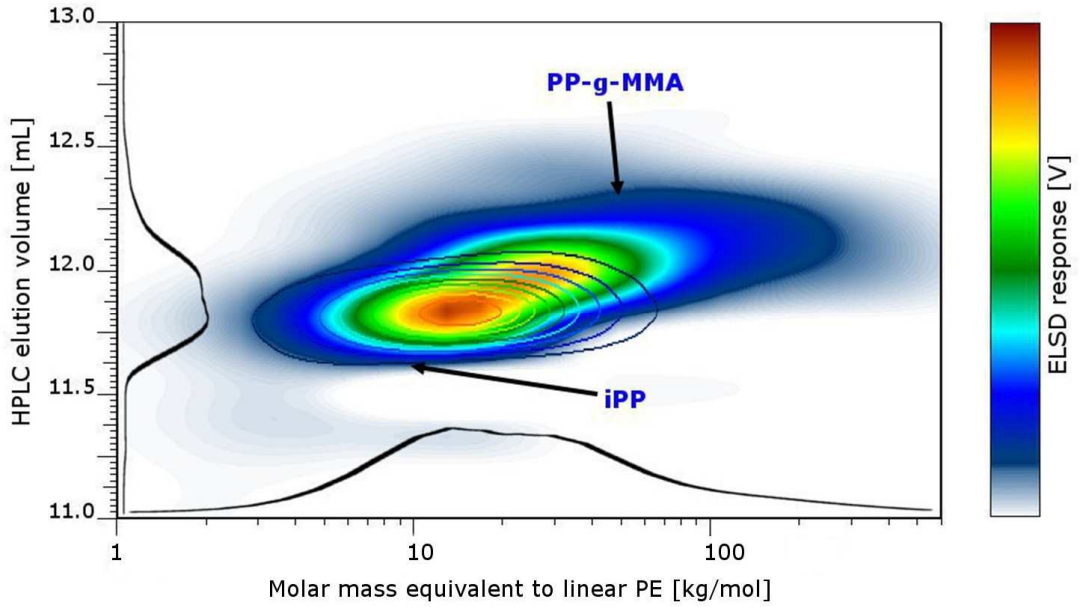


Fig. 33 Contour plot corresponding to a of a blend of iPP 60 kg/mol and PP-g-MMA (unfilled lines - iPP 60 kg/mol injected individually as a reference); columns, mobile phase and flow rates: HPLC: Hypercarb® (250 mm x 4.6 mm i.d), 4 mL 2-ethyl-1-hexanol and 10 mL linear gradient 2-ethyl-1-hexanol→TCB up to 100 vol.-% of TCB, 0.2 mL/min; SEC: PL Rapide H, TCB, 2.5 mL/min. Sampling time: 1 min. Sampling phase: 0 min. Temperature 160 °C.

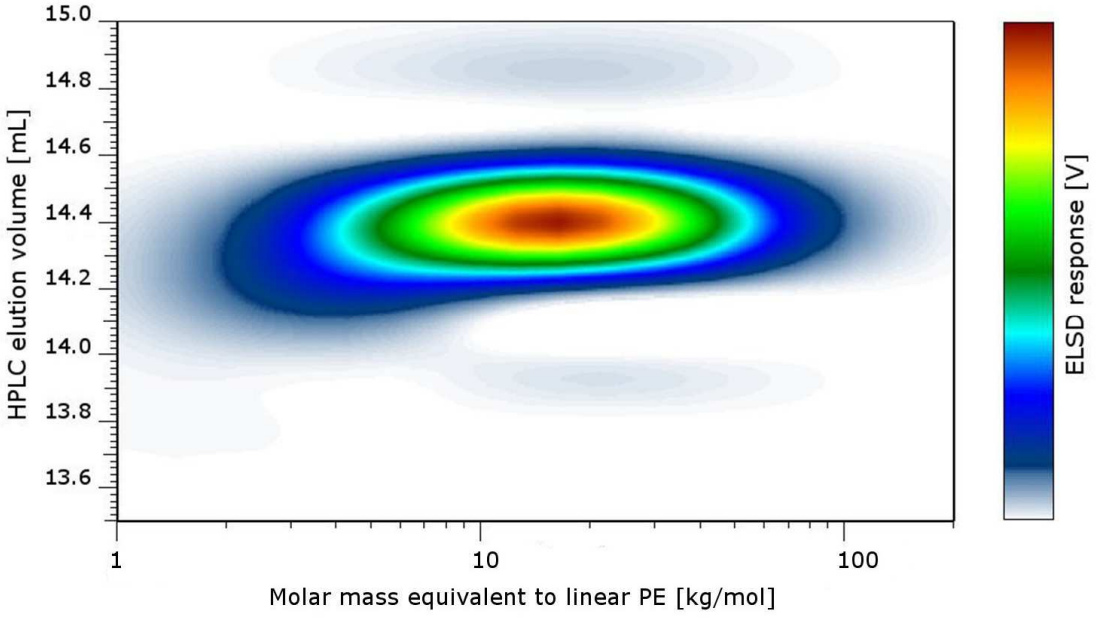


Fig. 34 Contour plot corresponding to LLDPE-g-MMA. Other conditions as in Fig. 31.

Although the components are not baseline resolved (Fig. 33), the effect of the grafted monomer on the elution can be identified by comparing with standards analyzed separately.

In order to compare HT 2D-LC with a conventional crystallization based analytical technique, a blend of PP-g-MMA and PMMA was separated by TREF x SEC. The results are depicted in Fig. 35. As can be seen, fractions of the blend crystallize between 60 °C and 100 °C. This crystalline part can be assigned to PP-g-MMA. Additionally, the contour plot indicates it contains a small amount of amorphous fraction of low molar mass and a shoulder in the area of higher molar mass showing up at 30 °C (Fig. 36). As the MMD of the amorphous PMMA 60 kg/mol is monomodal (Fig. 37), the main peak can be likely assigned to PMMA 60 kg/mol, while the shoulder is a mixture of PP-g-MMA having a low degree of crystallinity (e.g. containing atactic propylene units) and unfunctionalized atactic PP which does not crystallize at all. However, an unambiguous identification would require a chemoselective detection, e.g. by IR-spectroscopy. Thus it can be resumed that TREF × SEC does not provide a selective separation of amorphous components as the crystallizability is the function of multiple parameters, among them being comonomer content, microstructure (tacticity) and molar mass.

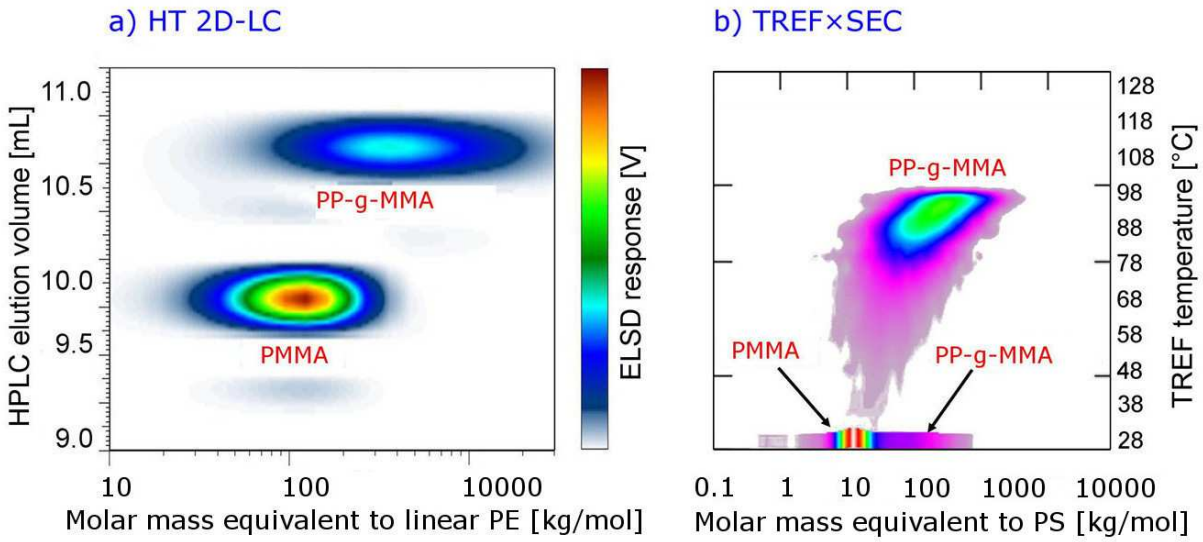


Fig. 35 Comparison of contour plots corresponding to a blend of PP-g-MMA and PMMA 60 kg/mol obtained by: (a) HT 2D-LC; (b) TREF × SEC.

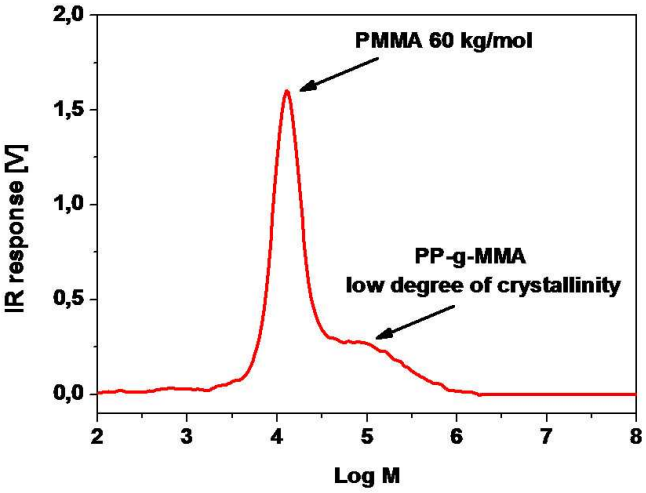


Fig. 36 Reconstructed MMD of the fraction eluting at 30 °C in TREF × SEC.

In contrast, the 2D-LC separation does not split the sample into zones with different crystallizability, but separates macromolecules according to their extent of adsorption which in the present case enables a complete deformulation into the individual components. Thus this newly developed chromatographic system opens exciting new perspectives to characterize functionalized polyolefins.

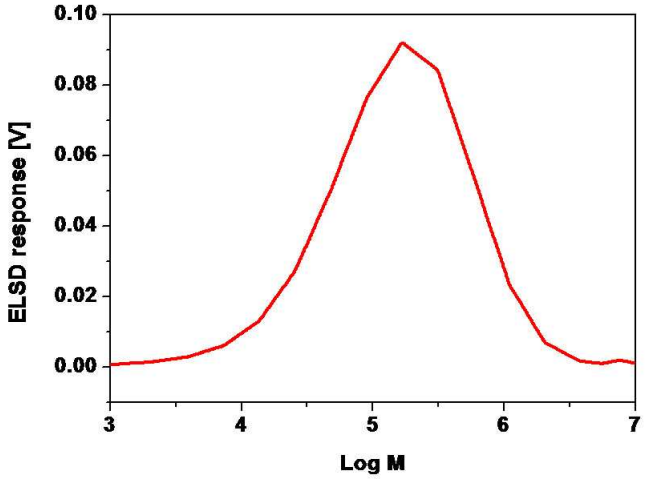


Fig. 37 Reconstructed MMD of PMMA 60 kg/mol in HT 2D-LC.

3.2.4. Conclusions

Based on the experimental results the following conclusions can be drawn:

1) The effect of experimental parameters affecting the HT 2D-LC separation of functionalized polyolefins has been tested. It was found that the increase of flow rate in SEC shifts the retention to higher elution volumes and leads to a significant band broadening. The broadening of peaks in SEC was also observed when the injection volume was increased. On the other hand, changing the sample solvent did not affect the SEC separation, but influenced the ELSD response. The results of HT 2D-LC were not much affected by varying the sampling phase.

2) By choosing suitable experimental parameters (flow rate and sampling time), the run time needed for HT 2D-LC analysis of a polymer sample was shortened from about 200 min to 100 min without any significant loss of resolution. The optimized method was applied to the characterization of industrially relevant low molar mass EVA copolymers.

3) The method failed to adsorb ethylene/1-butene copolymers and PP grafted with 10 and 16 wt.-% of MMA respectively. Using porous graphite as stationary phase and a solvent gradient 2-ethyl-1-hexanol→TCB as mobile phase it became possible to separate the grafted PP from the non grafted starting material. This effect is new and can be effectively used to separate copolymers of polar and non polar monomers based on the non polar units. These new HT 2D-LC systems and procedures may find application in the characterization of functionalized polyolefins.

3.3. Characterization of polyolefins by HT 2D-LC

3.3.1. Analysis of model blends

In 3.2 it has been shown that polyolefins grafted with functional groups can be adsorbed on Hypercarb® from 1-decanol and 2-ethyl-1-hexanol, where both the non polar polyolefin backbone and a functional group contribute to the chromatographic retention. The separation performance of the HT 2D-LC system with regard to the characterization of non polar polyolefins was tested by injecting a quaternary mixture of iPP, sPP, aPP and PE. The contour plot is shown in Fig. 38 where the compositional separation is represented along the Y-axis while the elution along the X-axis corresponds to the molar mass separation.

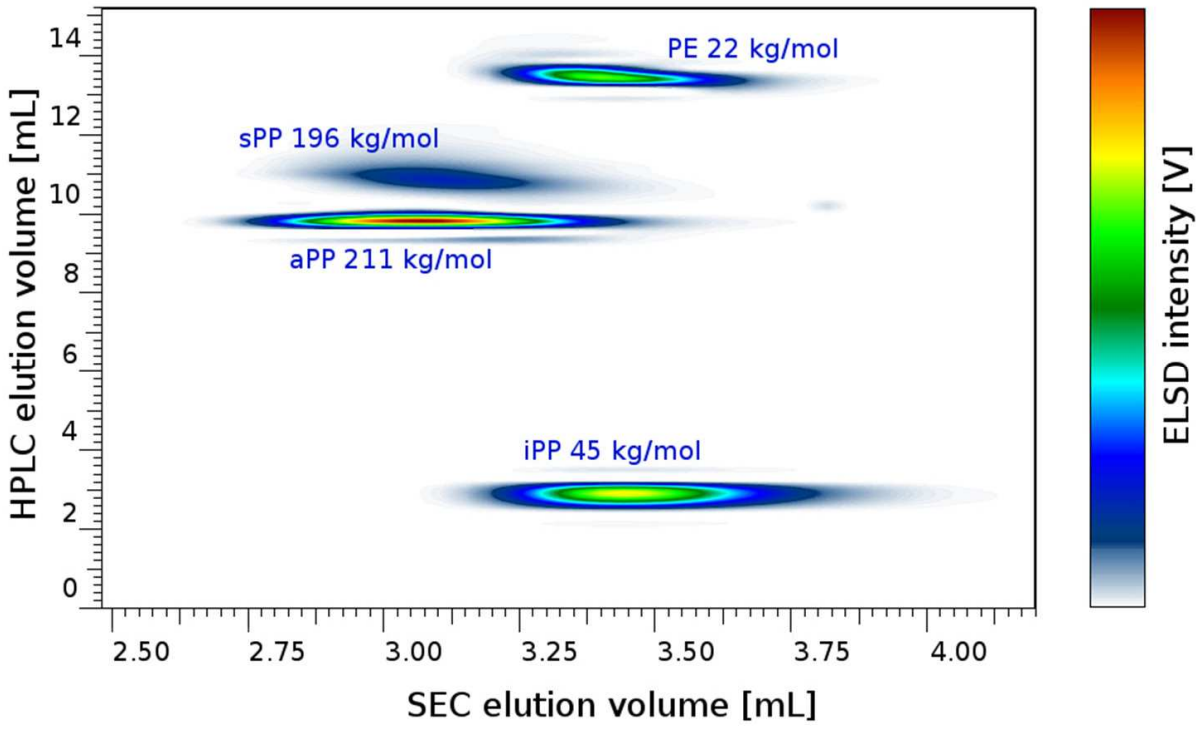


Fig. 38 Contour plot obtained by HT 2D-LC of a blend 1; Columns and flow rates: HPLC: Hypercarb®, 0.1 mL/min; SEC: PL Rapide H, 2.5 mL/min. Temperature: 160 °C.

The contour plot shows that iPP with M_w = 45 kg/mol elutes in 1-decanol while sPP, aPP and PE are fully retained on the column packing and elute only when the gradient 1-decanol→TCB was applied. All components are baseline separated which is in agreement with [70].

Table 3 Composition of blends used for HT 2D-LC and TREF × SEC measurements.

blend	Composition of blends	
	HT 2D-LC	**TREF × SEC**
1	iPP 45 kg/mol, 8.38 mg; aPP 211 kg/mol, 8.02 mg; sPP 196 kg/mol, 8.68mg; PE 22 kg/mol, 7.89 mg.	iPP 45 kg/mol, 9.5 mg; aPP 211 kg/mol, 10.00 mg; sPP 196 kg/mol, 10.85 mg; PE 22 kg/mol, 10.59 mg.
2	iPP 1.1 kg/mol, 8.12 mg; iPP 60 kg/mol, 7.6 mg; aPP 211 kg/mol, 7.20 mg; sPP 196 kg/mol, 7.96 mg; PE 1.18 kg/mol, 10.21 mg; PE 22 kg/mol, 7.22 mg.	iPP 1.1 kg/mol, 11.67 mg; iPP 60 kg/mol, 10.70 mg; aPP 211 kg/mol, 9.37 mg; sPP 196 kg/mol, 13.37 mg; PE 2 kg/mol, 10.02 mg; PE 22 kg/mol, 10.74 mg.
3	Ethylene/1-hexene copolymer, 18.6 mol. % of 1-hexene, 8.06 mg; Poly-1-hexene RB 60 kg/mol, 7.52 mg; PE 1.18 kg/mol, 8.34 mg; PE 126 kg/mol, 7.27 mg.	
4	iPP 1.1 kg/mol, 8.85mg; EP(D)M (6.3 wt.% of ENB, 60 wt. % of ethylene), 14.00mg; PE 1.18 kg/mol, 7.90 mg.	
5	iPP 1.1 kg/mol, 11.78mg; EP rubber (content of C2 10.4 wt. %, M_w = 165 kg/mol), 13.29 mg; PE 1.18 kg/mol, 11.04 mg.	iPP 1.1 kg/mol, 12.80 mg; EP rubber (content of C2 10.4 wt. %, M_w = 165 kg/mol), 12.64 mg; PE 2 kg/mol, 10.80 mg.
6	iPP 1.1 kg/mol, 7.85 mg; iPP 60 kg/mol, 10.07 mg; aPP 211 kg/mol, 8.50 mg; sPP 196 kg/mol, 15.85 mg; EP copolymer (81.3 wt. % of ethylene, M_w = 164 kg/mol, 10.63 mg; PE 2 kg/mol, 10.20 mg; PE 126 kg/mol, 4.00 mg.	

In order to study the influence of the molar mass of the components on the elution volume in HPLC, blend 2 (Table 3) was analyzed by 2D-LC. The corresponding contour plot is presented in Fig. 39. Isotactic PP 60 kg/mol is separated from the blend of aPP, sPP and PE, however, it elutes

in two peaks. The lower molar mass one elutes in 1-decanol while a fraction with higher molar mass is retained and elutes only after adding TCB to the mobile phase, i.e., after the starting the gradient elution. This effect is new because it was reported in [61] that iPP eluted solely in 1-decanol, independently of its molar mass. This effect will be described in more detail later.

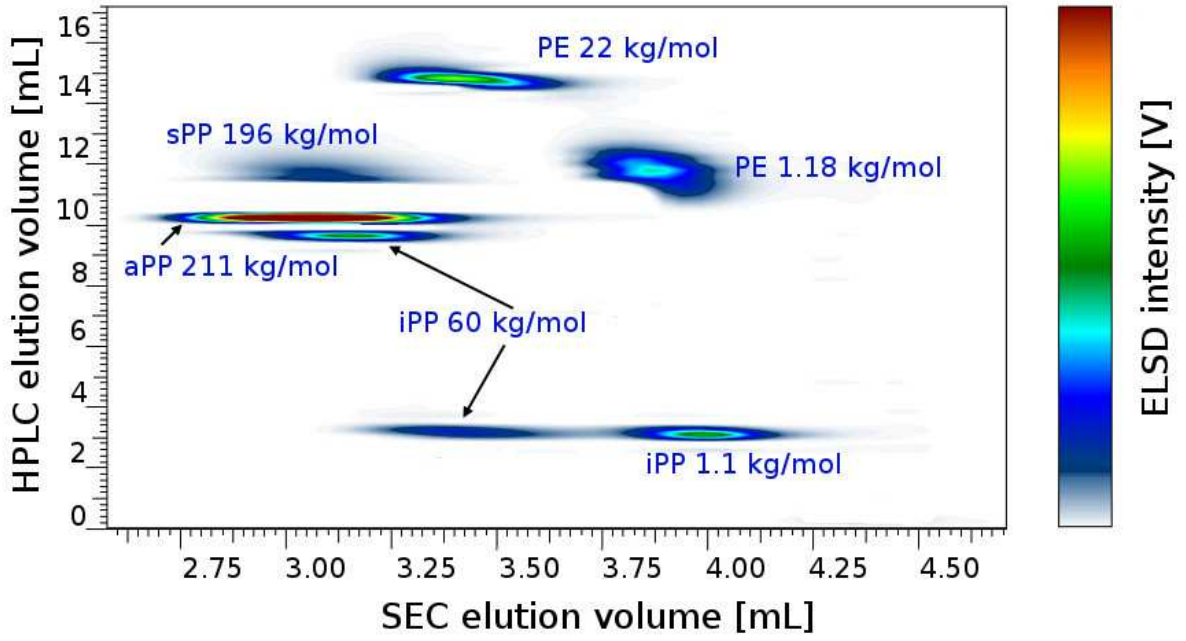


Fig. 39 Contour plot obtained by HT 2D-LC of blend 2; Exp. conditions as in Fig. 38.

Fig. 40 illustrates the separation of blend 3. As can be seen, baseline separation was achieved for all components and even the bimodal MMD of the poly-1-hexene is clearly reflected. It has been shown recently that the elution volume of ethylene/1-hexene copolymers from 1-decanol in this chromatographic system decreases with increasing comonomer content [57]. It is assumed that the backbone ethylene units adsorb on the graphitic surface and the sterically hindering alkyl branches act against the adsorption and consequently the elution volume decreases with the increasing content of 1-hexene. This behaviour is also reflected in Fig. 40. While the ethylene/1-hexene copolymer is retained and elutes only in the gradient, poly-1-hexene is not retained at all, i.e., elutes in 1-decanol. It has to be mentioned that it is of practical importance that a copolymer can be separated from both homopolymers (Fig. 40). Having such an analytical method at hand

the synthesis of the corresponding copolymer can be easier monitored and optimized and it may be helpful for the fundamental understanding of the structure↔property relationships.

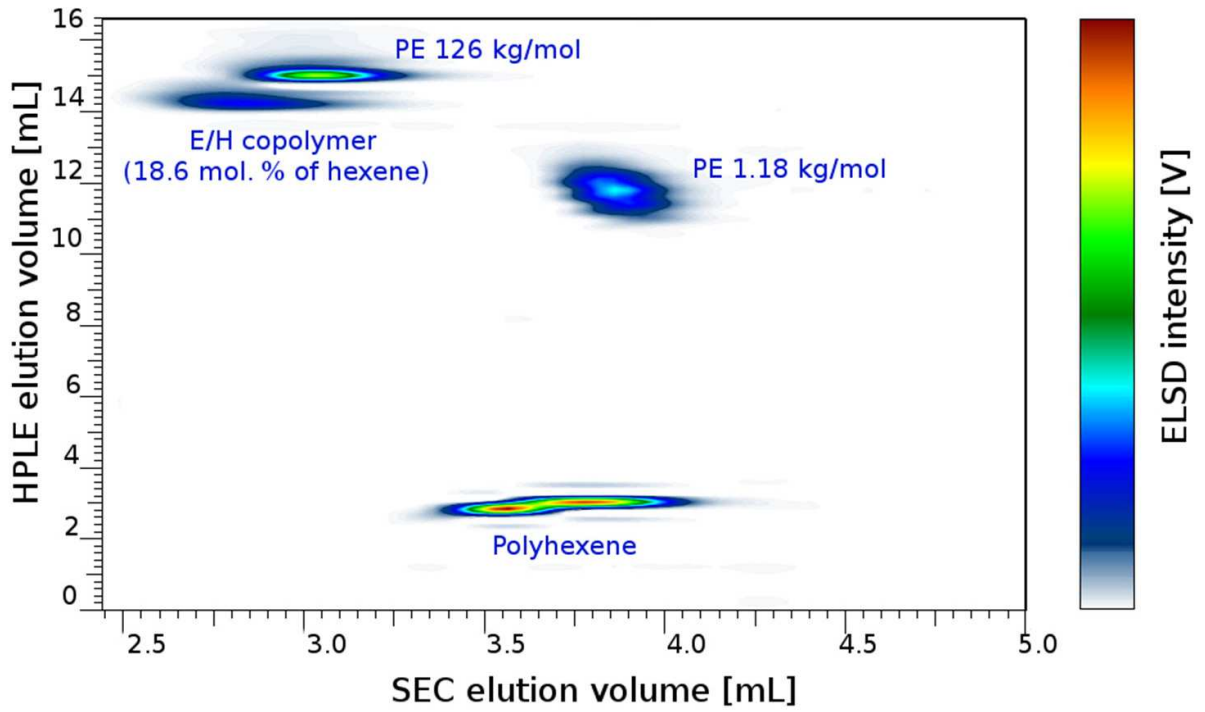


Fig. 40 Contour plot obtained by HT 2D-LC of blend 3; Exp. conditions as in Fig. 38.

The separation of blend 4 is shown in Fig. 41. As can be observed, all components are baseline resolved. EP(D)M can be perfectly distinguished from the homopolymers. It is particularly noteworthy that EP(D)M is amorphous and, thus, such a separation could not be performed by means of a conventional crystallization technique.

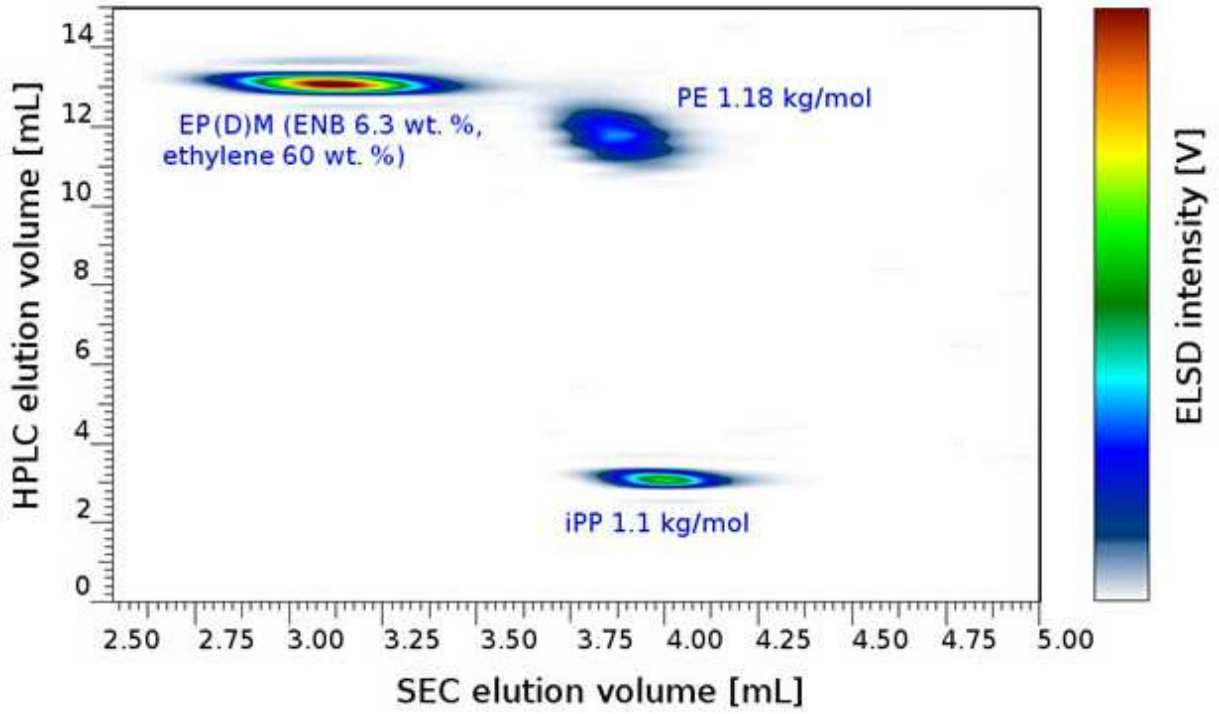


Fig. 41 Contour plot obtained by HT 2D-LC of blend 4; Exp. conditions as in Fig. 38.

The separation of another amorphous material, ethylene/propylene (EP) rubber, from a blend with PE and iPP is illustrated in Fig. 42. The rubber elutes before the low molar mass PE along the HPLC axis and exhibits a bimodal CCD. The first part contains more propylene units and, therefore, is less retained, while the stronger retained component is more PE-like. Additionally, the first part is more narrowly distributed with regard to molar mass while the more retained fraction clearly has a broader MMD.

Fig. 43 shows the HT 2D-LC separation of blend 6 containing seven components. As can be seen, the EP copolymer elutes in two spots. It is evident, that this kind of chromatographic system enables to distinguish the copolymer of interest from by-products like PP of different tacticity as well as the homopolymers and, therefore, it is extremely practical for the needs of polymer chemists.

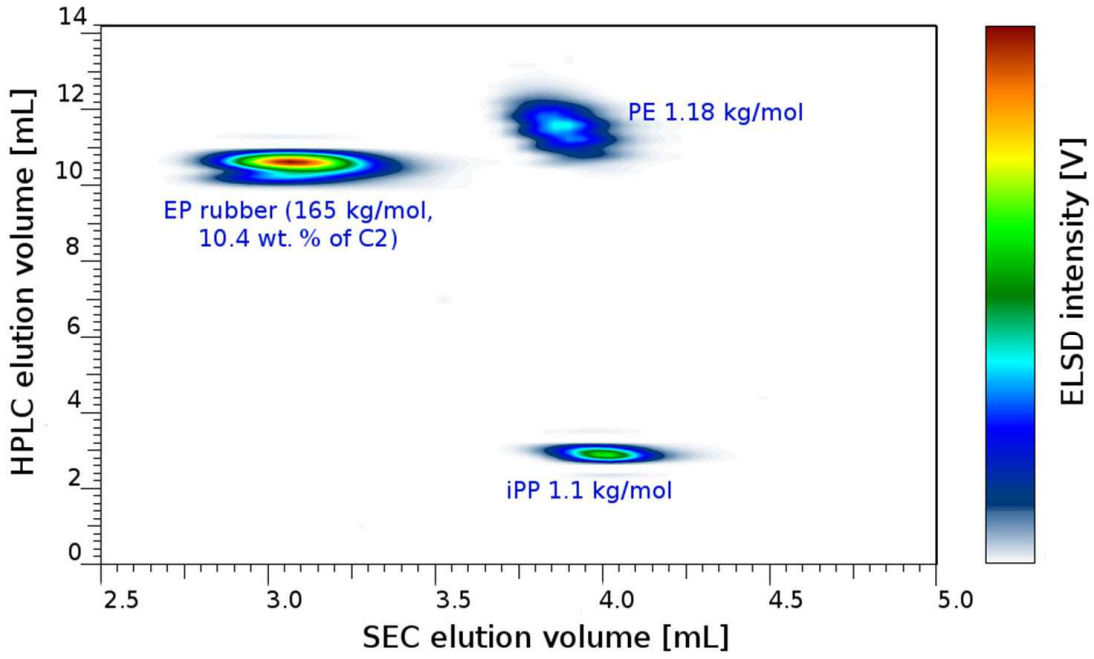


Fig. 42 Contour plot obtained by HT 2D-LC of blend 5; Exp. conditions as in Fig. 38.

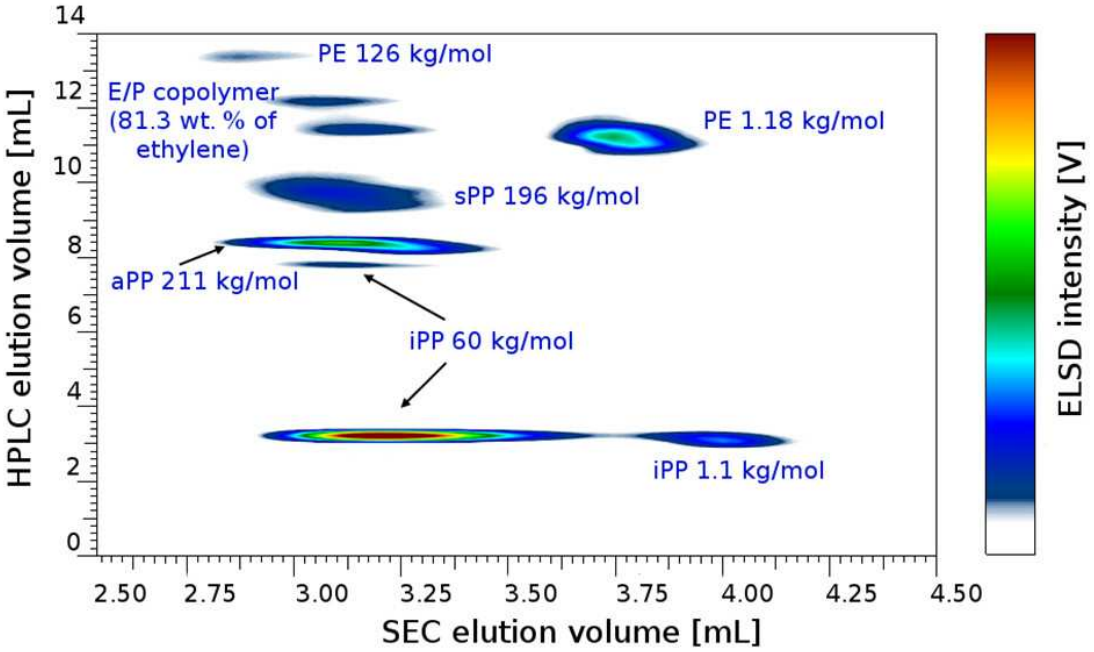


Fig. 43 Contour plot obtained by HT 2D-LC of blend 6; Exp. conditions as in Fig. 38.

3.3.2. Calibration of SEC separation in HT 2D-LC

In a comprehensive 2D-LC set-up, two chromatographic modes (HPLC and SEC) are on-line hyphenated. This means that, instead of an ordinary injection of a polymer sample into the SEC eluent, the polymer sample is introduced into the SEC column in a mixed solvent via an automated switching valve. In our case, the composition of the mixed solvent changes from pure 1-decanol over 1-decanol/TCB to pure TCB. Indeed, when the fractions of iPP are collected in the loop to be injected into the SEC column, the mobile phase in the first dimension contains only 1-decanol. On the other hand, when the loop is loaded with the fractions of PE, E/P, E/H, etc., the mobile phase in the first dimension contains both TCB and 1-decanol. Because the hydrodynamic volume of a macromolecule depends on the solvent, this may affect the calibration of the SEC. In order to study the influence of the injection solvent on the behaviour of macromolecules in SEC PE and iPP standards were individually analyzed by SEC as stand alone. The sample solvent for PE and iPP was either 1-decanol or TCB. Fig. 44 and 45 show an overlay of two SEC calibration curves constructed for iPP and PE standards of various average molar mass.

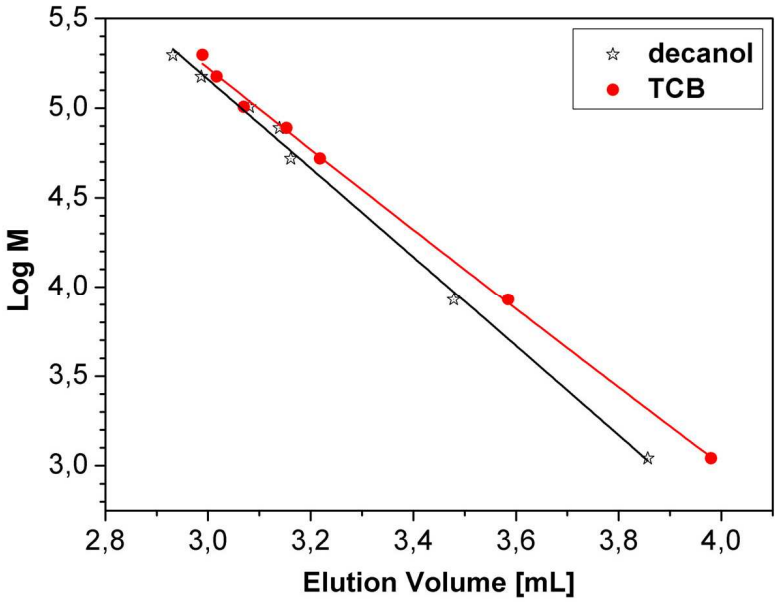


Fig. 44 Overlay of the iPP calibration curves corresponding to two different injection solvents. Stationary phase: PL Rapide H, Mobile phase: TCB, 2.5 mL/min, temperature: 160 °C.

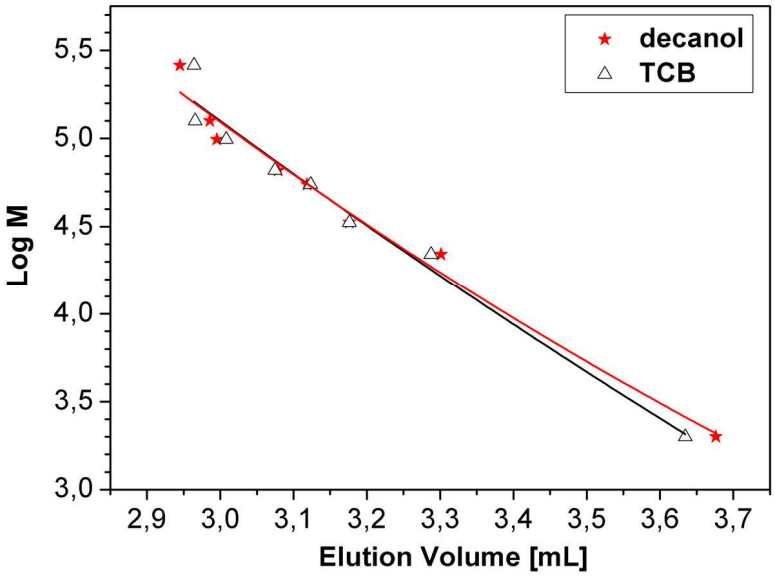


Fig. 45 Overlay of the PE calibration curves corresponding to two different injection solvents. Exp. conditions as in Fig. 43.

As can be seen, the calibration curves obtained with iPP standards corresponding to the different injection solvents are different (Fig. 44). On the other hand, the two curves obtained with PE standards overlap over almost the whole elution range except in the low molar mass region (Fig. 44). The shift between the calibration curves in Fig. 44 indicates that iPP standards have a larger hydrodynamic volume in 1-decanol than in TCB. On the other hand, the elution volumes of the PE standards (Fig. 45) do not differ substantially in 1-decanol and TCB. This may be due to the fact that either their hydrodynamic volumes in these solvents are very similar or that PE can exchange its solvation shell more rapidly (i.e., PE macromolecules are solvated with 1-decanol in the interactive column flushed with 1-decanol, however after the injection into the SEC column the macromolecules are solvated with TCB). Such a solvent independent elution enables to effectively apply a PE calibration curve over the entire gradient region.

The molar mass calibration in Fig. 45 corresponds to the SEC column alone. In order to apply this to the HT 2D-LC, the PE calibration standard should also undergo the HPLC separation and then enter the SEC system via an automated injection. Therefore nine PE standards were injected into the HT 2D-LC system at the same experimental conditions, so that each standard passes through the HPLC column before being analyzed by SEC. The obtained calibration curve is shown in Fig. 46.

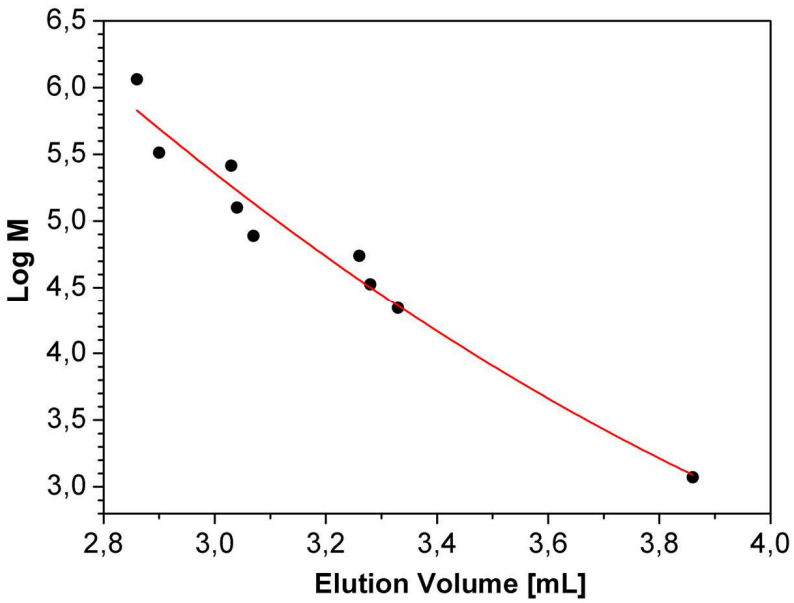


Fig. 46 Calibration curve obtained by injecting PE standards (M_w = 1.18 kg/mol, 22 kg/mol, 33.5 kg/mol, 55 kg/mol, 77.5 kg/mol, 126 kg/mol, 260 kg/mol, 325 kg/mol and 1152 kg/mol) into the entire HT 2D-LC system (elution volumes at the peak maximum); Exp. conditions as in Fig. 43.

In contrast to data shown in Fig. 44 and Fig. 45, the points in Fig. 46 are rather scattered. We notice that the scattering of points for PE standards using the identical SEC column and 2D-LC instrument was observed also in 4.1. On the other hand, a good correlation was obtained with this SEC column for PS standards in TCB with 2D-LC. The PE standards available on the market are quite broad compared to the PS ones. Moreover, the SEC column operates at a pressure recommended by the producer, but not at the recommended flow rate (2.5 ml/min in 2D-LC vs. recommended 1.5 ml/min). Increasing the flow rate, in general, decreases the chromatographic efficiency of the SEC column, i.e., the peaks broaden. The latter is a function of various parameters, including the type of polymer. This could eventually influence the determination of elution volumes for PE.

It is known that PS standards are most frequently used to calibrate SEC [51]. We found that PS standards with a molar mass < 30 kg/mol are adsorbed on Hypercarb® from 1-decanol and can be eluted in 1-decanol→TCB. PS standards of higher molar mass are insoluble in 1-decanol even at 160 °C. This means that PS standards are not suitable for the SEC calibration of the described chromatographic system.

3.3.3. Separation of isotactic polypropylene in HT 2D-LC

As mentioned in 4.3.1, it was previously observed that iPP eluted in Hypercarb®/1-decanol→TCB exclusively in 1-decanol [70] while the contour plot in Fig. 38 and 43 indicates that iPP elutes in two peaks, namely one in 1-decanol and the second one after the starting the gradient elution. In order to study the influence of the molar mass of iPP on the elution behaviour, a series of iPP, varying in their average molar mass, was separated by 2D-LC. Fig. 47 shows the results of these experiments.

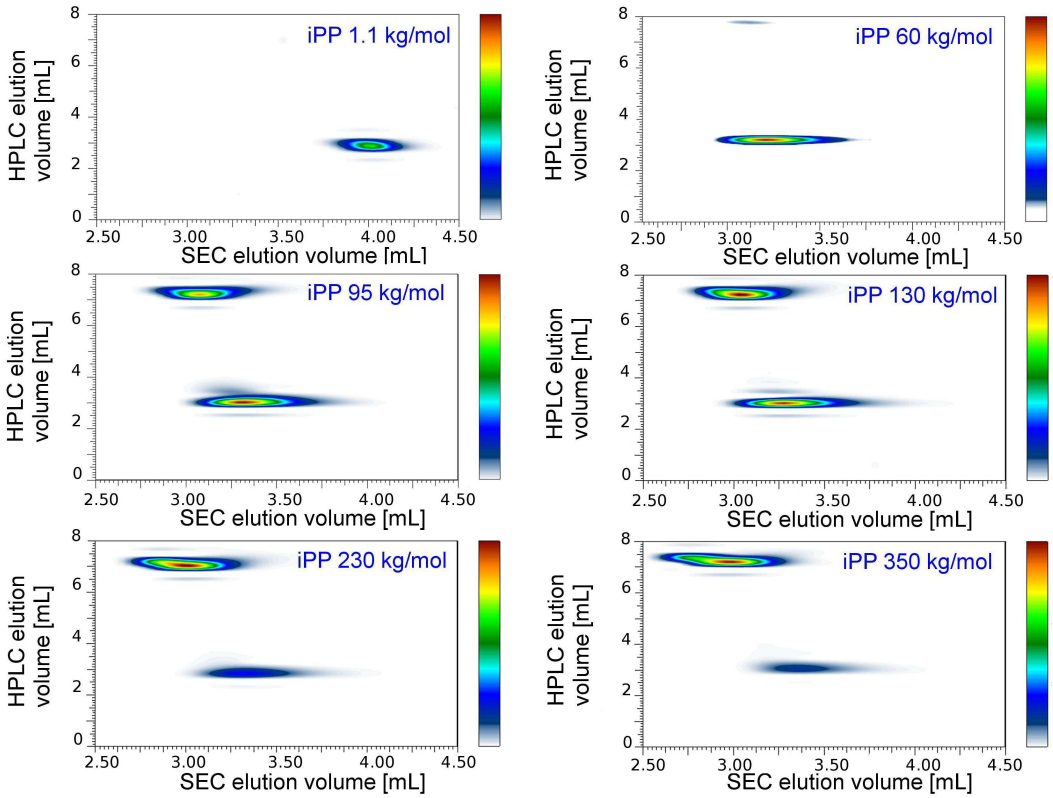


Fig. 47 Contour plots of the HT 2D-LC of iPP with different average molar masses. Exp. conditions as in Fig. 38.

All iPP standards except the one with the lowest molar mass elute in two zones meaning that they are partially retained on Hypercarb® from 1-decanol and can be desorbed by a gradient 1-decanol→TCB. The contour plots prove that the portion of iPP, which elutes in the gradient, is in all cases of larger molar mass than the part, which elutes in 1-decanol. As the analytes in HT 2D-LC are detected under isocratic conditions and, thus, the ELSD response is not affected by the

mixed mobile phase, a comparison of the contour plots proves that, the higher the molar mass of the injected iPP standard, the larger the portion which elutes in the gradient. The standard with M_w = 350 kg/mol is almost completely retained and elutes mostly in the gradient. We speculate that the 1-decanol used in this study leads to the partial adsorption of iPP, while no adsorption of the same iPP standards occurred in [70]. The solvent batch used was a different one than in the present treatment. It is hypothesized that the quality (purity) of the 1-decanol may vary from batch to batch. However, further investigation is required. Separation of polymers according to their tacticity has only been scarcely described in the literature (e.g. [70]). It is known that differences in the interaction of stereoisomeric forms of a polymer with a stationary phase may be very delicate. For example, Berek et al. [99] found that PMMA could be separated according to tacticity, if the syndiotactic (s) and isotactic (i) form were injected individually when THF as well as mixed solvents were used as mobile phase. However, if they were mixed prior to injection, a complexation of PMMA with different tacticity occurred and no separation was achieved because s- and i-PMMA form a stable complex in THF. The system Hypercarb®/1-decanol→TCB separates PP according to its tacticity, however, iPP with higher molar mass is stronger. We suppose that a small amount of polar admixtures in 1-decanol (for example, 1-nonanol or decan-diol) could increase the extent of adsorption of iPP, as it was observed. Fig. 48 illustrates the elution using 1-decanol from different producers. As can be observed 1-decanol from different producers may lead to different chromatographic behaviour.

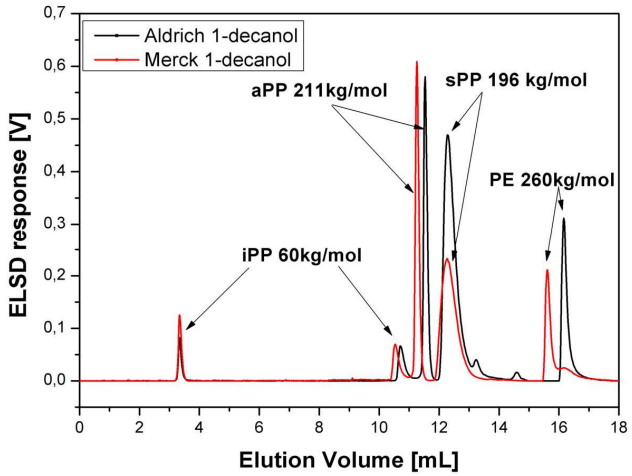


Fig. 48 Elution behaviour of a blend of iPP 60 kg/mol, sPP 196 kg/mol, aPP 211 kg/mol and PE 260 kg/mol on Hypercarb® in 1-decanol from Sigma Aldrich and Merck.

It may, therefore, be assumed that the observed change in elution behaviour is due to admixtures in the 1-decanol which are present in varying amounts. Therefore, the 1-decanol used here was analyzed by GC-MS revealing the presence of homologue linear short chain alcohols (C6 - C8) as well as branched alcohols. To mimic the effect of such alcohols on the elution behavior of PP, 1-octanol was used instead of 1-decanol. The elugrams are shown in Fig. 49.

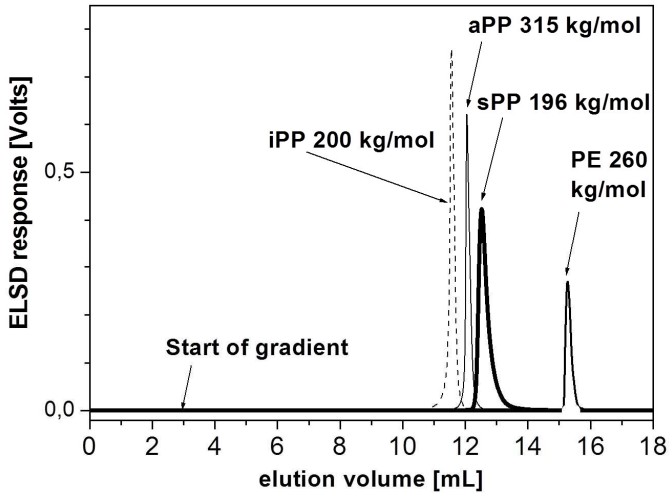


Fig. 49 Overlay of chromatograms. Column: Hypercarb®. Mobile phase: 1-octanol and a linear gradient starting from 1-octanol and ending with TCB. Temperature: 160 °C. Flow rate: 0.8 mL/min. Sample solvent: 1-decanol (PE 260 kg/mol is not soluble in 1-octanol).

Using 1-octanol instead of 1-decanol as component of the mobile phase leads to the elution of iPP exclusively in the gradient (Fig. 49). These results illustrate that relatively small changes in the polarity of the mobile phase (1-octanol contra 1-decanol) enable to substantially change the adsorption behavior of iPP.

3.3.4. HT 2D-LC vs. TREF × SEC

In order to compare the chromatographic results with a conventional technique, blends 1, 2, and 5 (Table 3) were cross-fractionated by TREF × SEC. Fig. 50 shows the contour plot of the TREF × SEC analysis of blend 1. The X-axis represents the separation in SEC mode, while the Y-axis shows the elution temperature in TREF.

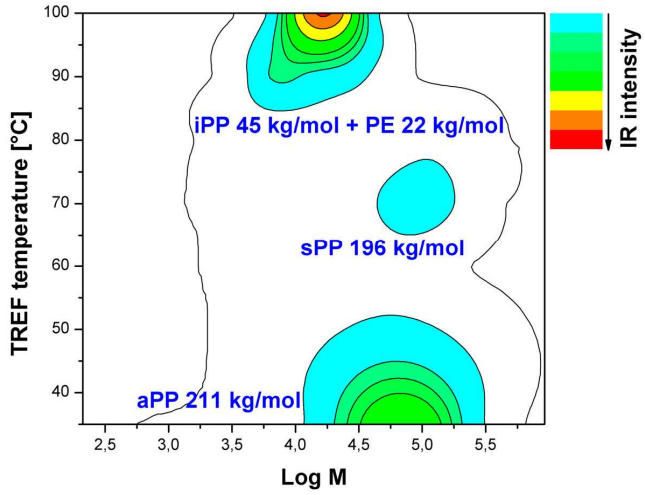


Fig. 50 Contour plot obtained by TREF × SEC of blend 1.

As can be observed, the least crystalline part elutes at 30 °C and can be assigned to aPP. The more crystalline component which elutes at about 70 °C is apparently sPP. The material eluting at about 100 °C has the highest degree of crystallinity in the mixture and can therefore be attributed to iPP and PE. However, these components are not baseline resolved and, therefore, no further information can be obtained.

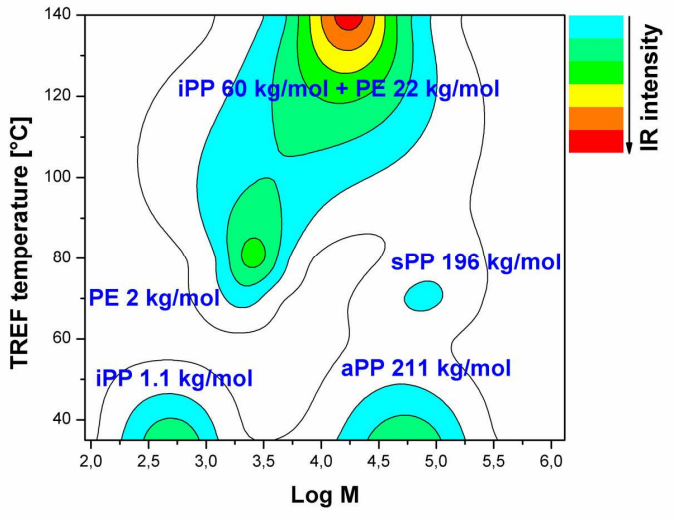


Fig. 51 Contour plot obtained by TREF × SEC of blend 2.

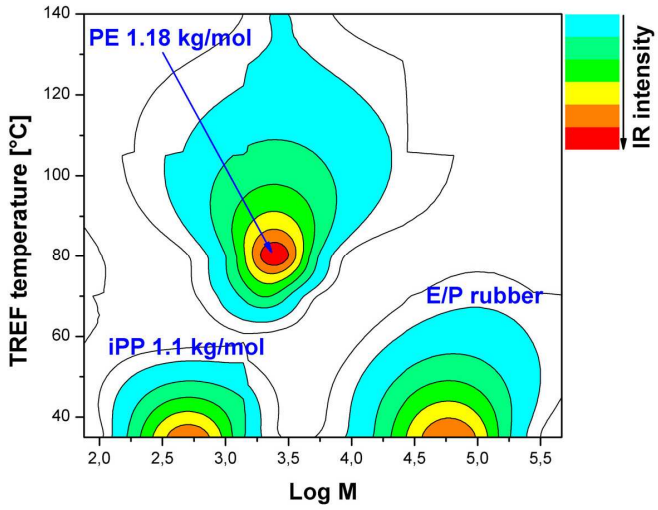


Fig. 52 Contour plot obtained by TREF × SEC of blend 5.

The result of the cross-fractionation of blend 2 is presented in Fig. 51. Considering the average molar masses and the chemical composition of the components, it can be supposed that the soluble fraction contains low molar mass iPP and aPP. The component eluting at 70 °C is sPP, while the material eluting at 80 °C is likely low molar mass PE. iPP 60 kg/mol and PE 22 kg/mol are observed to coelute in temperature range from 105 °C to 140 °C. Fig. 52 shows the TREF × SEC separation of blend 5 containing iPP 1.1 kg/mol, PE 1.18 kg/mol and EP rubber. Low molar mass iPP and the EP rubber do not crystallize and, therefore, elute at 35 °C. Low molar mass PE crystallizes at 80 °C. Considering the broadness of the elution spot assigned to PE, it can be hypothesized that it contains also a portion of the EP rubber which exhibits some degree of crystallinity. However, CRYSTAF of the rubber alone showed that it did not crystallize.

Comparing the contour plots, which were obtained via TREF × SEC, with those in Fig. 39 and 42 demonstrates that the same blends were perfectly separated into the single components by HT 2D-LC irrespective of their crystallinity.

3.3.5. Conclusions

Based on the experimental results the following conclusions can be drawn:

1) HT 2D-LC of polyolefins as well as olefin copolymers has been realized by coupling HT-HPLC with SEC at 160 °C. A Hypercarb® column packed with porous graphite particles was used as the stationary phase in the HPLC separation stage. Polystyrene divinyl-benzene based column (PL Rapide H) was used for SEC separations.

2) It could be demonstrated that the sample solvent influences the SEC separation. Namely PE standards are suitable to calibrate the SEC because their hydrodynamic volume is not affected by the injection solvent from the first dimension. By injecting PE standards into the HT 2D-LC system a comprehensive SEC calibration could be achieved.

3) Blends, containing PE, isotactic, atactic and/or syndiotactic PP, EP- and EP(D)M terpolymers and ethylene/1-hexene copolymers, were separated by HT 2D-LC and automated TREF × SEC. Comparing the newly developed method with TREF × SEC revealed that the separation by HT 2D-LC does not depend on the crystallinity of the polyolefin samples. As a result, HT 2D-LC complements TREF × SEC and gives for the first time the possibility to analyze the chemical heterogeneity of amorphous samples. Additionally HT 2D-LC saves time compared to TREF × SEC. Further investigation regarding the influence of the molar mass of polyolefins on the elution behaviour in HPLC as well as regarding the calibration of ELSD is needed.

3.4. Characterization of the chemical heterogeneity of Ziegler-Natta based pipe grade HDPE by HT 2D-LC

3.4.1. Influence of temperature and molar mass on the chromatographic behaviour of PE on Hypercarb®

The key for the first successful liquid chromatographic separation of various polyolefins according to composition is the use of PGC and a solvent gradient 1-decanol→TCB, which was reported in [70]. This sorbent-solvent system allows to separate linear PE from iPP as well as to distinguish PP according to its tacticity and to separate ethylene/1-alkene copolymers according to their chemical composition. The separations are based on selective adsorption and desorption of the macromolecules, among which linear PE is the most retained species. This in turn means that ethylene sequences show the highest interaction with the PGC surface. In that sense it is particular interesting to know the loading capacity of PGC for PE. To study this, a controlled amount of PE 260 kg/mol was sequentially loaded into a 10 cm Hypercarb® column filled with 1-decanol to evaluate the quantity of PE which will be retained by PGC. A constant flow was kept through the column. It turned out that it was possible to retain 12.5 mg of the polymer, while the pressure went up drastically (to more than 250 bars. However, the loading capacity was not yet reached, as no PE eluted from the column. Further loading of PE was not possible due to a pressure limit of the chromatographic pump. According to the data specified by the producer, the column is stuffed with 1 g of PGC having a surface area of 120 m^2/g. Therefore, more than 0.1 mg of PE 260 kg/mol can be retained per square meter of PGC.

An important question from the chromatographic point of view is the influence of temperature on the separation, because this might provide an easy handle to tune the selectivity with regard to particular molecular features. In order to study the effect of temperature, solutions of PE-standards in 1-decanol (160 °C) with varying molar mass were injected into the Hypercarb® column which was thermostated at different temperatures. The adsorbed PE standards were then desorbed by a gradient of TCB. Representatively, an overlay of elugrams of linear PE 22 kg/mol is shown in Fig. 53a. The correlation between the elution volume at peak maximum and the temperature is shown in Fig. 53b.

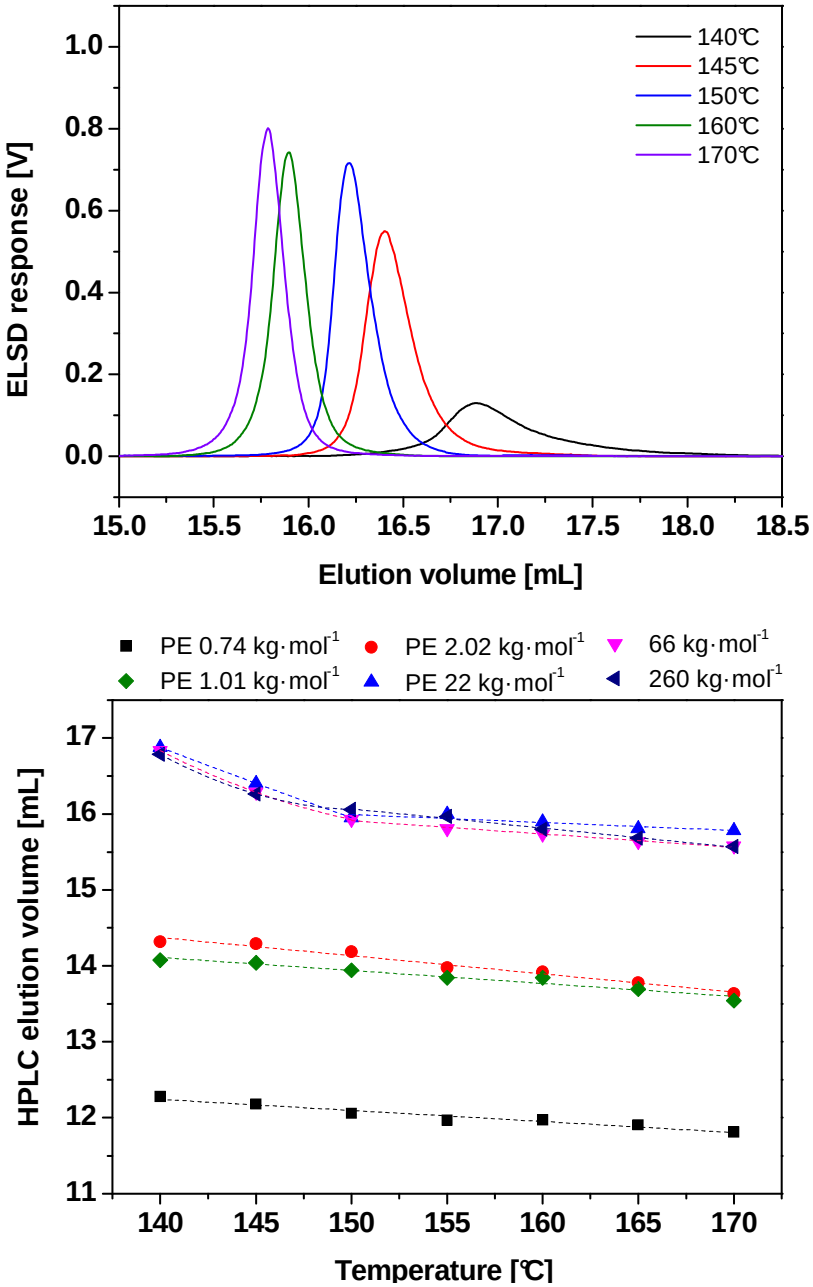


Fig. 53 Overlay of elugrams of linear PE 22 kg/mol at 140 °C, 145 °C, 150 °C, 160 °C and 170 °C on Hypercarb®. For experimental conditions see text. b) Relation between the elution volume at peak maximum and the temperature for linear PE standards. For experimental conditions see text.

As can be observed, the retention of the sample and the widths of the peaks increase when the temperature is decreased (Fig. 53 a). The relationship between the temperature and the elution

volume at peak maximum is linear over the whole range of temperatures for PE with a molar mass of 0.74 kg/mol, 1.01 kg/mol and 2.06 kg/mol. This means that both ΔH_0 and ΔS_0 associated with the process of adsorption are almost invariant with temperature [100]. For PE 22 kg/mol, 66 kg/mol and 260 kg/mol the plot is linear between 150 °C and 170 °C, but below 150 °C the slope of the curve becomes significantly steeper, i.e. the interaction of those standards with the stationary phase increases. Due to the extreme stability of the carbon stationary phase and the fact that the low molar mass samples are not affected it is highly improbable that this is the result of structural changes in the stationary phase, as this was the case for some silica gel column packings [101]. According to Helmstedt et al [102] PE is in 1-decanol at 140 °C at Θ-conditions which means that the macromolecules are unperturbed ideal statistic coils. Using the reported data about the molecular dimensions of PE at these conditions a relation between the unperturbed root-mean-square end-to-end distance of linear PE ($\sqrt{h_0^2}$) and the elution volume at peak maximum can be constructed (Fig. 54).

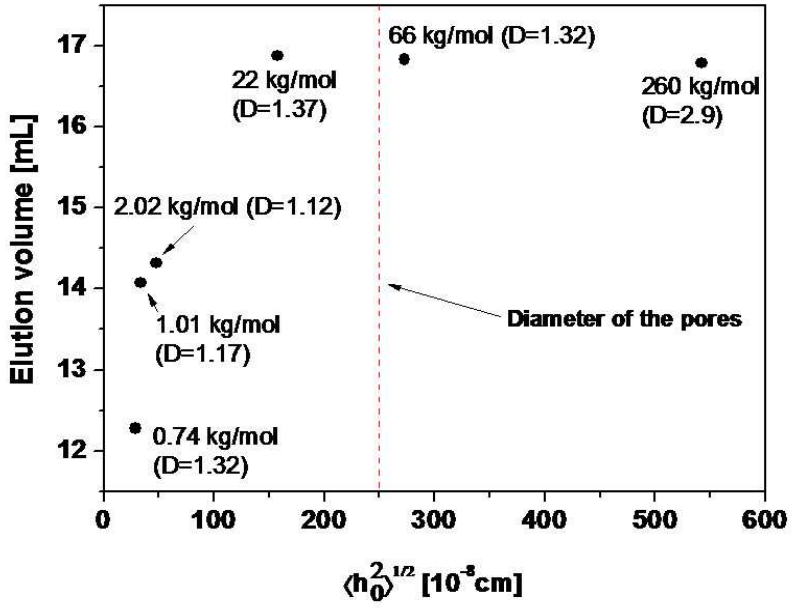


Fig. 54 Relation between $\sqrt{h_0^2}$ and the elution volume at peak maximum at Θ-conditions.

Comparing $\sqrt{h_0^2}$ with the average diameter of the pores as specified by the producer it can be recognized that the PE with molar masses of 0.74 kg/mol - 2.06 kg/mol is small enough to

penetrate into the pores, while those samples of higher molar mass in their maximally expanded conformation can only partially (PE 22 kg/mol) or even not (PE 66 kg/mol and 260 kg/mol) enter the pores. Such behaviour is supposed in SEC mode, i.e., when adsorption is minimized. On the other hand, the surface of the graphite is extremely attractive for PE in 1-decanol, i.e., the large macromolecules could uncoil and penetrate into the pores. Uncoiling and partial penetration of PE into pores, which commensurate with dimensions of macromolecules in their linear conformation, was supposed also for adsorption of PE in zeolites [103]. Increasing the temperature favors solvation of the PE macromolecule, i.e. the coil expands further, while with decreasing temperature the shrinkage is preferred. We suppose that the over proportionate increase of the retention volume of the higher molar mass standards, when approaching θ-conditions, is due to an enlarged extent of adsorption. Macromolecules are unperturbed ideal statistic coils at and close to θ-conditions [104], thus, they may access a larger surface area of the sorbent and are, thus, stronger retained [104].

As PE 66 kg/mol was only partially recovered from the column at 135 and 130 °C and not at all desorbed by a gradient of TCB at 120 °C, the corresponding data at these temperatures could not be collected. The solubility of PE in 1-decanol decreases with decreasing temperature, i.e., precipitation of PE may play an additional role at 130-120 °C.

3.4.2. Characterization of a bimodal ethylene/1-butene copolymer by SEC, TREF x SEC and HT 2D-LC

The MMD of a bimodal (pipe grade) polyethylene, HDPE 1, as determined by SEC is shown in Fig. 55. As can be observed, the sample has a broad MMD ranging from about 0.8 kg/mol to about 104 kg/mol. In order to investigate the chemical heterogeneity of HDPE 1 by a conventional technique, TREF × SEC was employed. The results are presented in Fig. 56. As can be seen, the sample elutes in a broad zone ranging from about 48 °C to 100 °C indicating a broad distribution of crystallinity. The sample may likely contain PE with broad MMD and a high molar mass copolymer eluting between 70 and 90 °C. Moreover, it contains a small amount of amorphous fraction with low molar mass showing up at 30 °C, which may be PE wax. In general, TREF × SEC does not provide a selective separation of amorphous components.

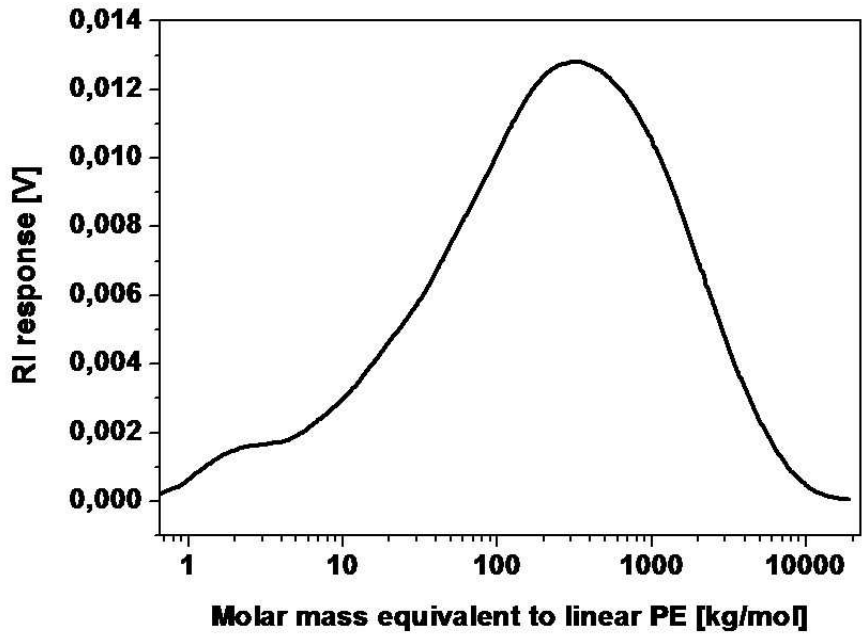


Fig. 55 MMD of HDPE 1. Conditions: Column PL gel Olexis; mobile phase TCB, flow rate 1 mL/min, T = 140 °C.

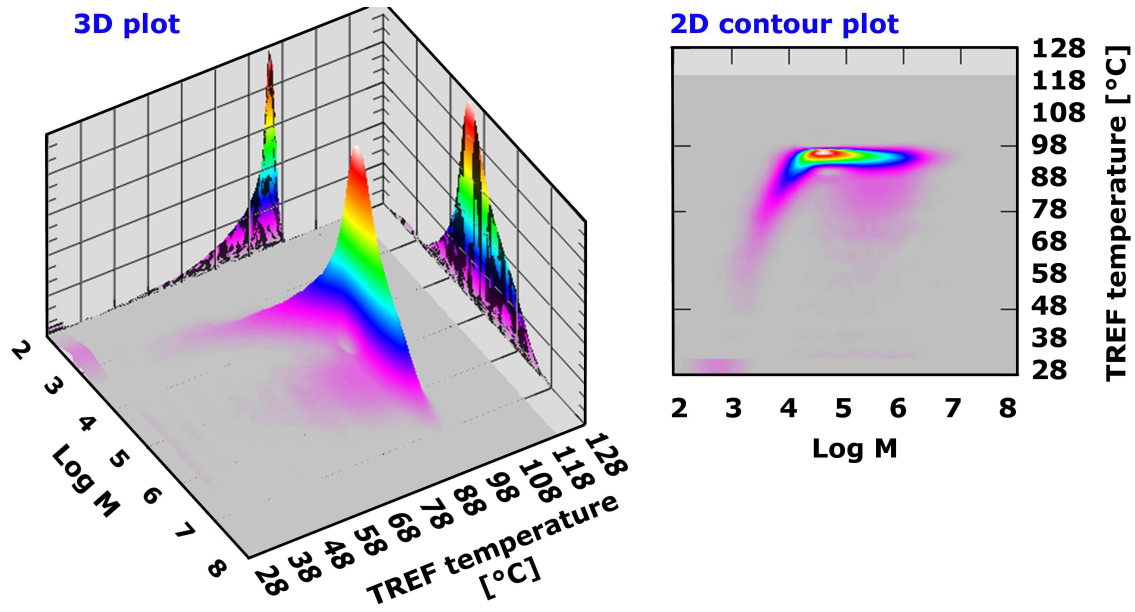


Fig. 56 (a) Relief plot and (b) colour coded contour plot of HDPE 1 obtained with TREF × SEC. For experimental conditions see experimental part.

While the separation by interactive liquid chromatography delivers information about the CCD, no information about the MMD of the eluting components can be obtained. This requires to hyphenate the separation according to chemical composition with one according to molar mass (HT 2D-LC). The technical procedure and application of HT 2D-LC were described previously. Fig. 57 shows the contour plot obtained from HT 2D-LC for HDPE 1 (Table 1). The separation according to the chemical composition is represented along the Y-axis while the elution along the X-axis corresponds to the SEC separation. As can be observed, the HT 2D-LC separation results in a "banana"-shaped spot, which reflects a broad CCD and MMD originating from the two stage synthetic route.

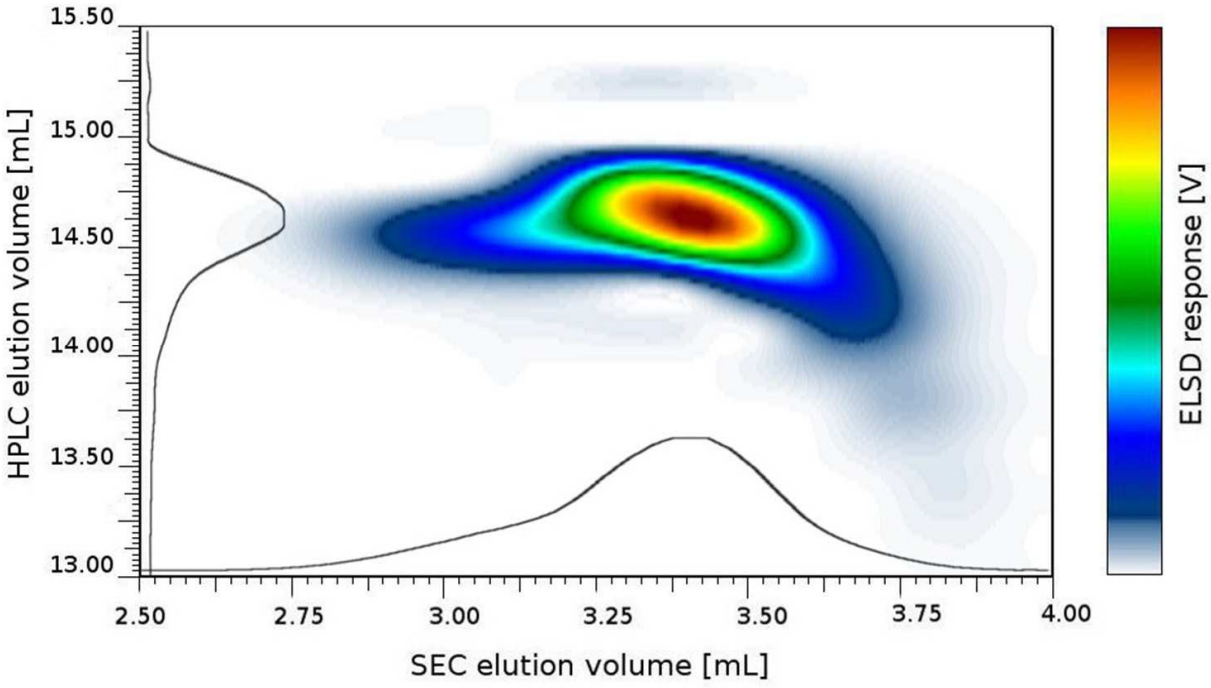


Fig. 57 Contour plot including projections of the elugram in HPLC and the MMD obtained from HT 2D-LC of HDPE 1. Conditions: HPLC: Column Hypercarb® 250×4.6 mm i.d.; mobile phase: 1-decanol→TCB; flow rate 0.1 mL/min; temperature 160 °C. SEC: Column PL Rapide H; mobile phase TCB, flow rate 2.5 mL/min, temperature 160 °C.

Following a procedure, described in 4.3, the first dimension was calibrated with respect to composition using ethylene/1-butene (EBu) copolymers with known average chemical composition (Table 4). The 2nd dimension was calibrated with respect to molar mass using PE-

standards. The compositional calibration is represented by a linear relationship between the elution volume at peak maximum and the average content of 1-butene (

Fig. **58**).

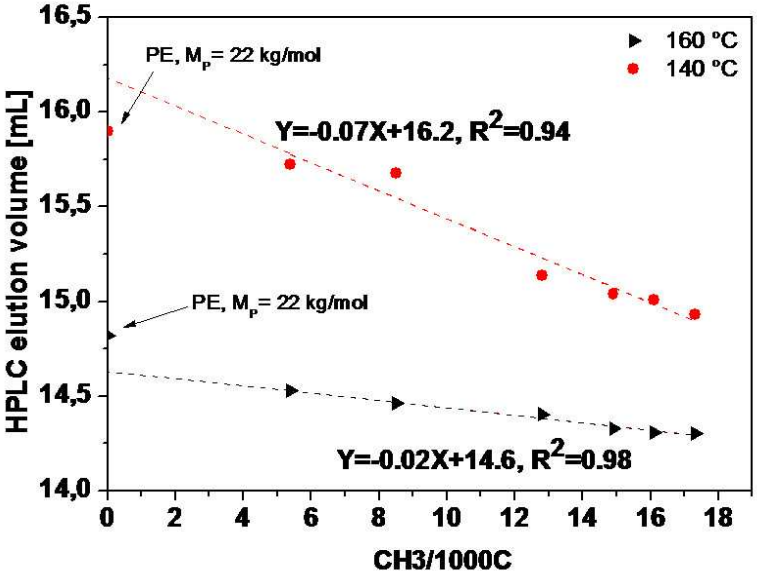


Fig. 58 Compositional calibration obtained by injecting fractions of EBu copolymers (Table 4) into the entire HT 2D-LC system at 140 °C and 160 °C. Experimental conditions as in Fig. 57. Notice: Elution volume of PE 22 kg/mol is indicated as a reference.

Table 4. Analytical data of the EBu copolymers used to calibrate the compositional axis in HPLC

Sample code	M_w [kg·mol^{-1}]	D	CH_3/1000C
EBu 1	168	3.89	5.4
Ebu 2	172	3.84	6.9
EBu 3	137	3.64	8.5
EBu 4	127	3.74	12.8
EBu 5	111	3.67	14.9
EBu 6	97	3.93	16.1
EBu 7	101	3.75	17.3

Notices: * values of average molar masses equivalent for PE were obtained by SEC.

Similar linear relationships were found for various ethylene/1-alkene copolymers recently [97]. The decrease of temperature leads to larger elution volume of the copolymers and the extrapolation of the fitted line to 0 of CH_3/1000C will intercept the y-axis at the elution volume corresponding to linear PE having a molar mass of about 22 kg·mol^{-1}, which roughly equals to 786 -[CH_2-CH_2]-units. The molar mass calibration of the entire 2D system using PE standards is displayed in Fig. 59.

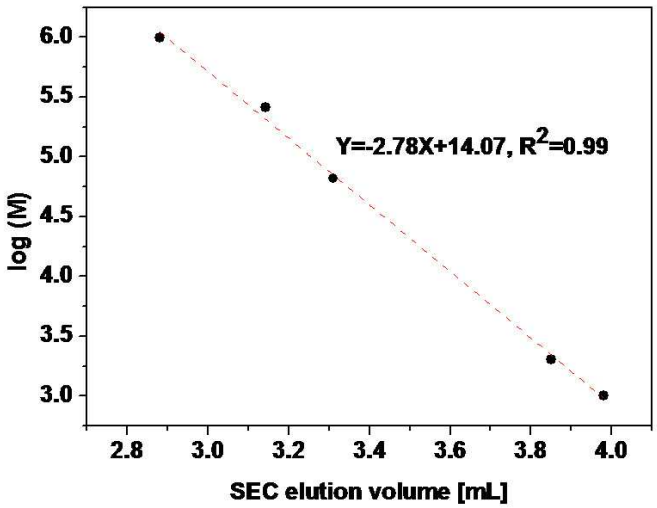


Fig. 59 Molar mass calibration obtained by injecting PE standards (M_w = 1.01, 55, 66, 260 and 985 kg/mol) into the entire HT 2D-LC system. Experimental conditions as in Fig. 57.

The relationships shown in

Fig. **58** and Fig. 59 enable to calibrate both axes of the contour plot (Fig. 60). As can be noticed, the elution volume of the CCD spans ~1.5 mL, while the MMD ranges from ~1 kg/mol to 3000 kg/mol. The obtained data confirm that the HDPE 1 contains a high molar mass copolymer and a homopolymer with broad MMD. It has to be noticed, that the elution volume of PE with $M_p <$ 22 kg·mol^{-1} falls into the area from 0 to 20 CH3/1000C of the compositional calibration. It may therefore be concluded that the interaction strength of PE with M_p < 22 kg/mol with the stationary phase is similar to that of branched copolymers and as a result co-elution of short linear macromolecules and branched ones may occur.

As has been shown, HT 2D-LC can be performed in a much shorter period of time by overlaid injections without significant loos of resolution in SEC. Therefore, the same approach can be

applied for the characterization of HDPE 1. Moreover, it has been recently found that adsorption of polyolefins on Hypercarb® increases from specific branched alcohols like 2-ethyl-hexanol [105]. The stronger retention of polyolefins on Hypercarb® from such alcohols is likely due to the lower affinity of those alcohol molecules to the planar PGC surface (via their ethylene sequences), which in turn, facilitates anchoring of polyolefins on the surface. Fig. 61 shows the result of such an HT 2D-LC experiment.

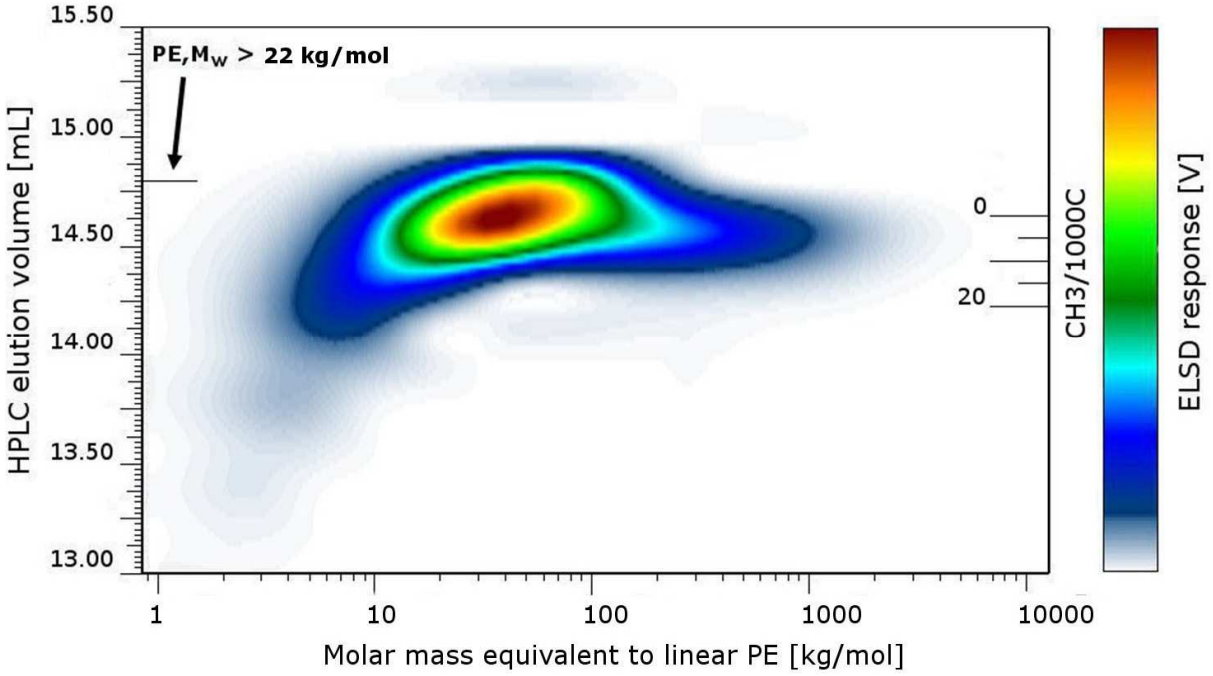


Fig. 60 Contour plot of HDPE 1 obtained from HT 2D-LC. Experimental conditions as in Fig. 57.

In order to obtain more insight into the microstructure, the HDPE sample was fractionated by prep TREF. Since TREF fractionates according to crystallinity, the first fraction collected at 80 °C is expected to contain semicrystalline as well as less crystalline components, while the next fractions are expected to be increasingly crystalline (Table 5). By studying the weight portion of the individual TREF fractions, it can be noticed that the crystalline part constitutes the most of the sample. The obtained fractions were then analyzed by HT 2D-LC. The corresponding contour plots from HT 2D-LC are shown in Fig. 62 and the results are summarized in Table 6.

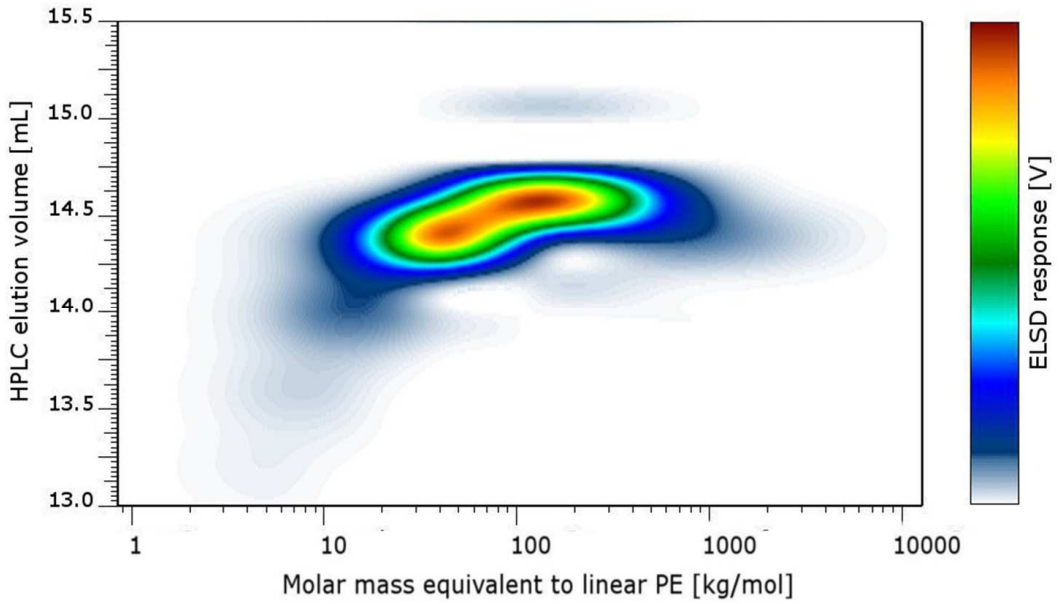
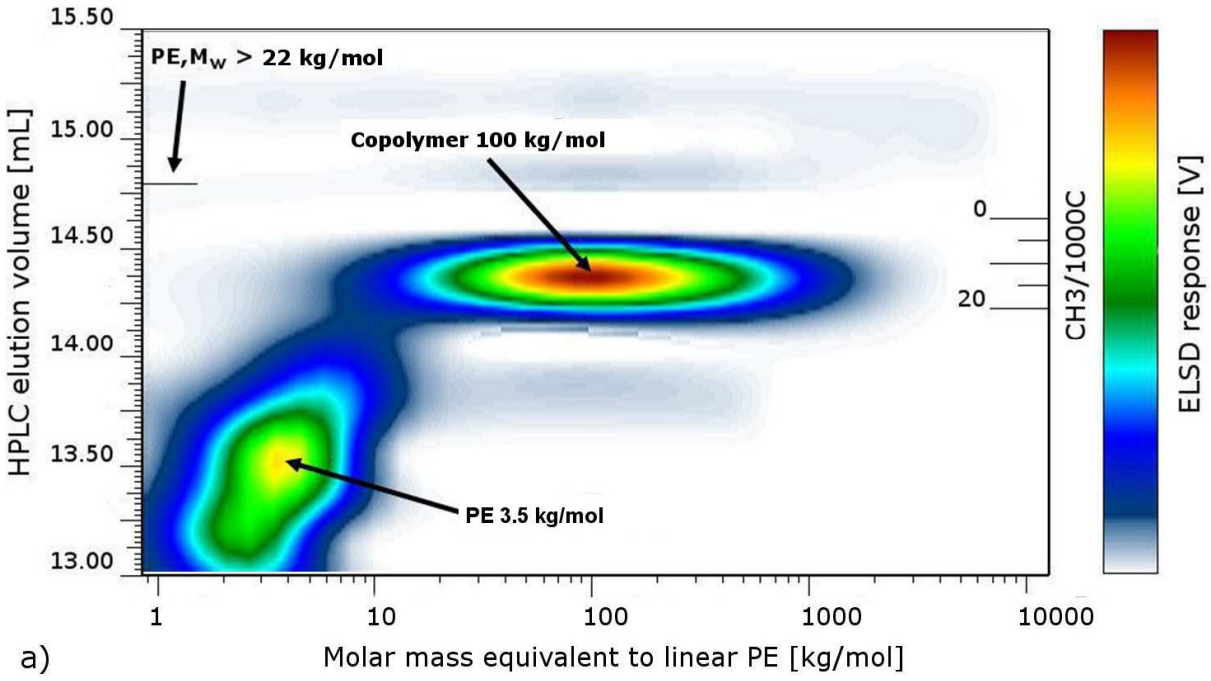


Fig. 61 Contour plot of HDPE 1 obtained from HT 2D-LC; columns, mobile phase and flow rates: HPLC: Hypercarb® (250 mm x 4.6 mm i.d), 4 mL 2-ethyl-1-hexanol and 10 mL linear gradient 2-ethyl-1-hexanol→TCB up to 100 vol.-% of TCB, 0.2 mL/min; SEC: PL Rapide H, TCB, 2.5 mL/min. Sampling time: 1 min. Sampling phase: 0 min. Temperature 160 °C.

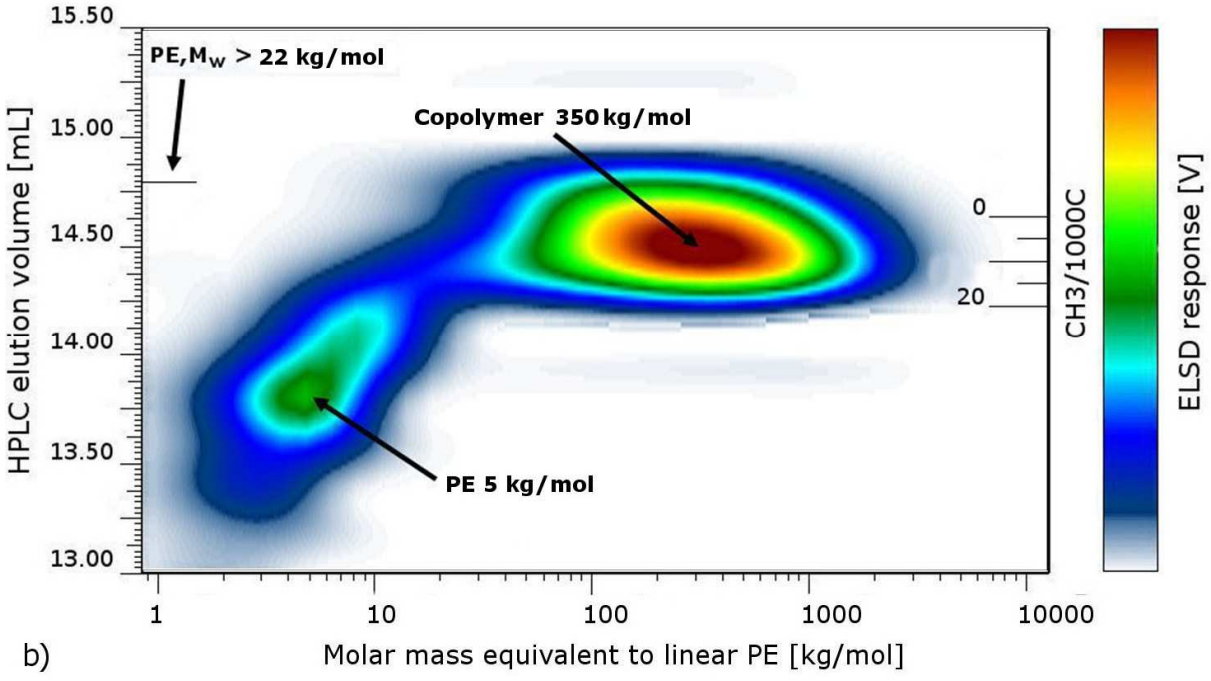
Table 5. Molecular characterization data of HDPE 1 and its TREF fractions.

Sample/Fraction	**TREF elution temperature**	**CH_3/1000C**	**[wt.-%]**	**M_w [kg/mol]**	**D**
HDPE 1	-	7	100	255	39.7
1_1	up to 80	14	11.6	278	69.5
1_2	80-85	10.2	8.7	233	47.1
1_3	85-90	6.2	16.6	243	33.3
1_4	90-92	4.7	9.7	278	22.3
1_5	92-95	2.7	23.0	199	13.4
1_6	95-100	2.9	30.4	306	17.4

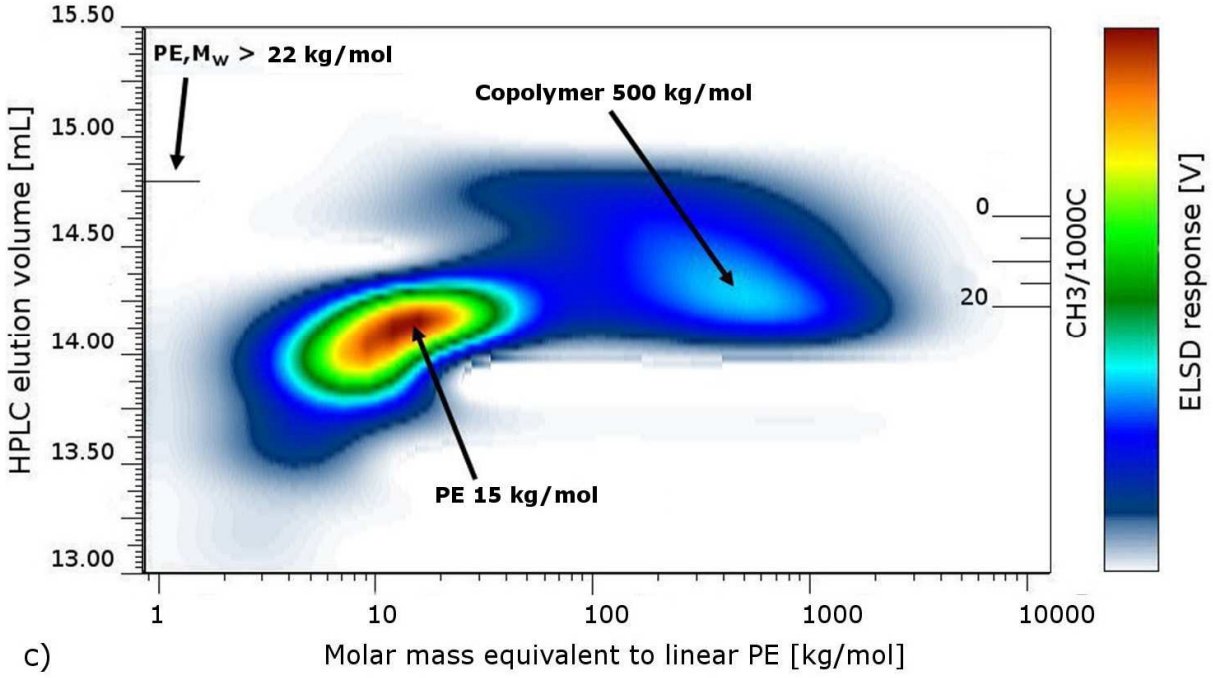
Notices: *number of methyl groups per 1000 carbons determined by FTIR, **values of average molar masses equivalent for PE were obtained by SEC.


PE,M_W > 22 kg/mol
Copolymer 100 kg/mol
PE 3.5 kg/mol
HPLC elution volume [mL]
15.50
15.00
14.50
14.00
13.50
13.00
1
10
100
1000
10000
Molar mass equivalent to linear PE [kg/mol]
0
20
CH3/1000C
ELSD response [V]

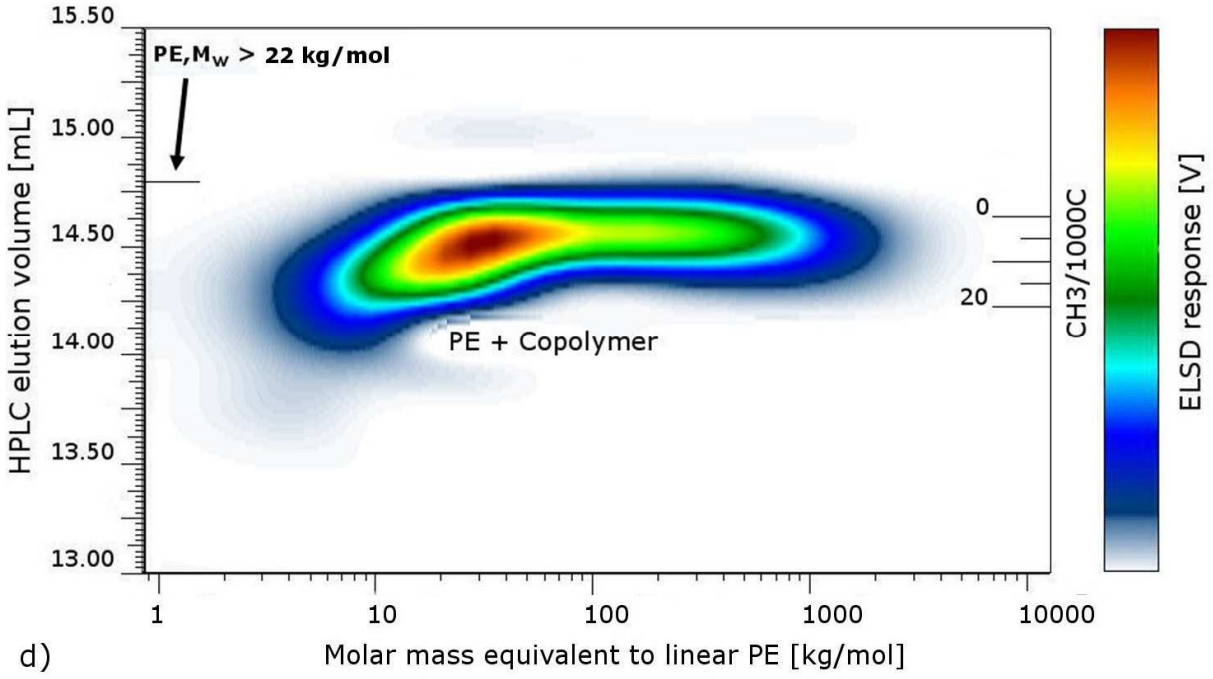
a)


PE,M_W > 22 kg/mol
Copolymer 350 kg/mol
PE 5 kg/mol
HPLC elution volume [mL]
15.50
15.00
14.50
14.00
13.50
13.00
1
10
100
1000
10000
Molar mass equivalent to linear PE [kg/mol]
0
20
CH3/1000C
ELSD response [V]

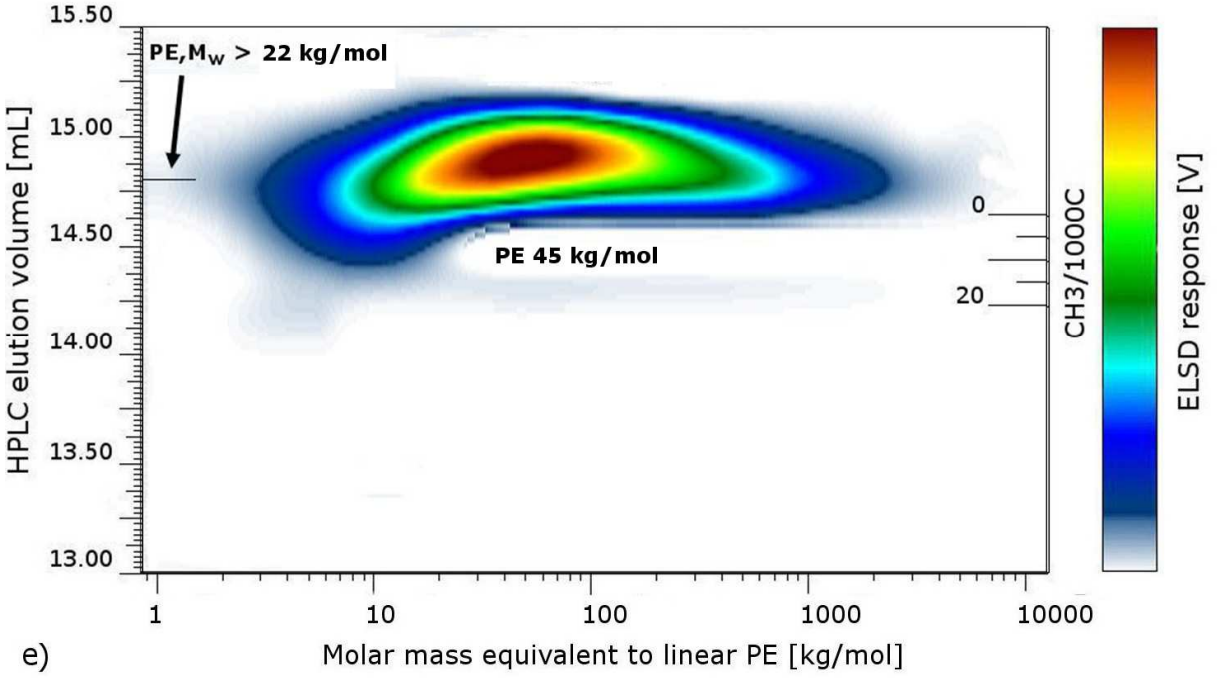
b)


PE,Mw > 22 kg/mol
Copolymer 500 kg/mol
PE 15 kg/mol
HPLC elution volume [mL]
15.50
15.00
14.50
14.00
13.50
13.00
1
10
100
1000
10000
Molar mass equivalent to linear PE [kg/mol]
0
20
CH3/1000C
ELSD response [V]

c)


PE,Mw > 22 kg/mol
PE + Copolymer
HPLC elution volume [mL]
15.50
15.00
14.50
14.00
13.50
13.00
1
10
100
1000
10000
Molar mass equivalent to linear PE [kg/mol]
0
20
CH3/1000C
ELSD response [V]

d)



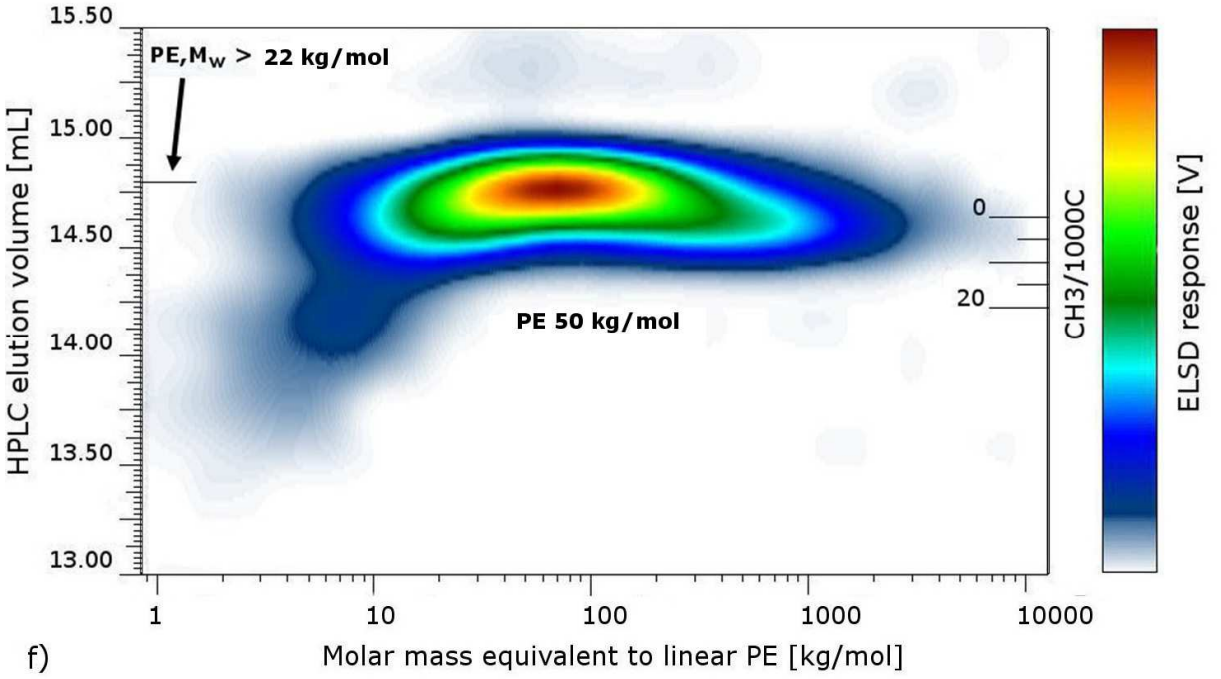


Fig. 62 a) – f) Contour plot of fractions 1_1 - 1_6 respectively obtained from HT 2D-LC, Experimental conditions as in Fig. 57.

Table 6 summarizes the data obtained from the projections of the contour plot on the molar mass and compositional axis for the individual fractions and compares them to those from the molecular characterization as reported in Table 5.

Table 6. Peak maximum molar mass, M_p, and CH_3/1000C at peak maximum obtained from the projection of the contour plot on the molar mass and compositional axis in HT 2D-LC respectively and the corresponding values from FTIR.

Sample/ fraction	**M_p (PE) [kg/mol] (HT 2D-LC)**	**M_p (copolymer) [kg/mol] (HT 2D-LC)**	**Span width CH_3/1000C (HT 2D-LC)**	**Peak maximum of CH_3/1000C (HT 2D-LC)**	**CH_3/1000C (FTIR)**
HDPE 1	not identified	not identified	0 to 15	5	7
1_1	3.5	100	5 to 20	11	14
1_2	5	300	0 to 20	7	10.2
1_3	15	500	0 to 20	15	6.2
1_4	30	N/D	0 to 12	4	4.7
1_5	45	-	0 to 5	-	2.7
1_6	50	-	0 to 10	-	2.9

The first fraction (Fig. 62a) contains low molar mass PE and a portion of copolymer. The second (Fig. 62b) and third fraction (Fig. 62c) contain PE and compositionally broad distributed copolymer. In the fourth fraction (Fig. 62d) coelution of unbranched PE and a copolymer can be observed. The fifth and sixth fraction (Fig. 62e,f) contain PE of increasing molar mass. No values for M_p can be determined for fraction 1_4 due to overlapping of the peaks. Expectedly, the compositional data obtained from HT 2D-LC deviate from those obtained by off line infrared spectroscopy of the TREF fractions, as the latter represent averages from the copolymers and wax

(Table 6). The PE standards within the molar mass range 1 - 5 kg/mol elute in HPLC (Fig. 62a – c) at smaller elution volumes than PE with M_w > 20 kg/mol. It means that PE-wax may co-elute with a part of ethylene-butene copolymers in HPLC.

Comparing the elution temperatures of TREF fractions with the 2D-LC contour plots reveals that the degree of crystallinity (i.e., higher elution temperature in TREF) increases with the decreasing number of branches. Secondly, the degree of crystallinity depends on the molar mass, i.e. the higher the molar mass the higher crystallinity. Fig. 63 displays a cumulative overlay of the contour plots from HT 2D-LC of all TREF fractions.

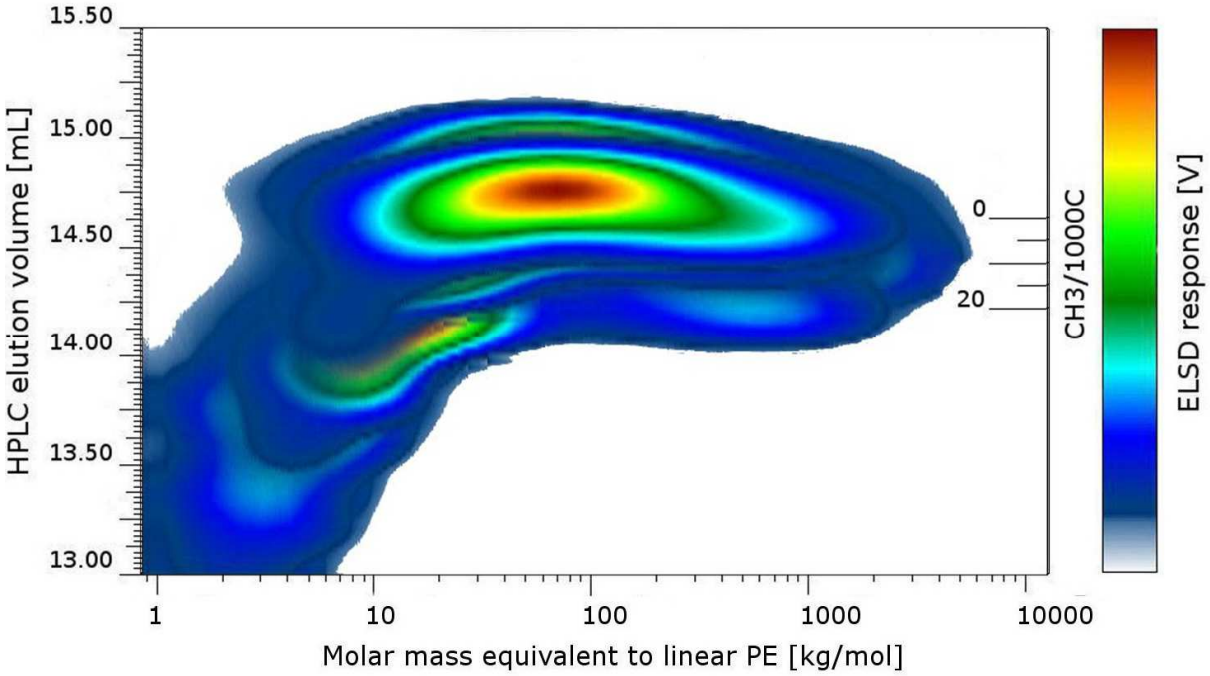


Fig. 63 Overlay of contour plots of TREF fractions 1_1 - 1_6 obtained from HT 2D-LC (respective weight portions of the TREF fractions are not accounted for).

The cumulation of the equally weighed contour plots from 2D-LC of the TREF fractions leads to a broader distribution with regard to both composition and molar mass than the 2D-LC analysis of the mother sample and the overlay in Fig. 63 clearly visualizes the presence of material in compositional and molar mass regions, where no fractions are detectable in case of the analysis of HDPE 1. Namely, overlaying the contour plots of TREF fractions shows an MMD from about 2 kg·mol^{-1} to 3000 kg·mol^{-1}, while the MMD obtained in the analysis of the bulk sample ranges from 7 kg·mol^{-1} to 1000 kg·mol^{-1}. This is due to the fact that all TREF fractions were injected

into the 2D-LC at identical concentration, while in the mother sample these are present in different concentrations (Table 5). As a consequence, the overlay of the contour plots in Fig. 62 can not coincide with the contour plot of the mother sample in Fig. 57. Thus a TREF analysis prior to HT 2D-LC enhances the information obtainable from the chromatographic separation.

As it has been shown, that lowering the temperature favours the interaction of PE with the porous graphitic carbon and that the retention increases more for large molecules (Fig. 53). This could be utilized to improve the separation in HT 2D-LC. The contour plot of the mother sample at 140 °C is shown in Fig. 54. Moreover, a calibration of the compositional axis was carried out at 140 °C (Fig. 63). The relationship between the elution volume and the degree of branching is steeper at 140 °C than at 160 °C, which means that the interaction of the macromolecules is stronger at θ-conditions. However, at the same time the dispersion of the eluting peak increases which results in a more pronounced co-elution of short linear macromolecules and longer branched copolymers in the first dimension.

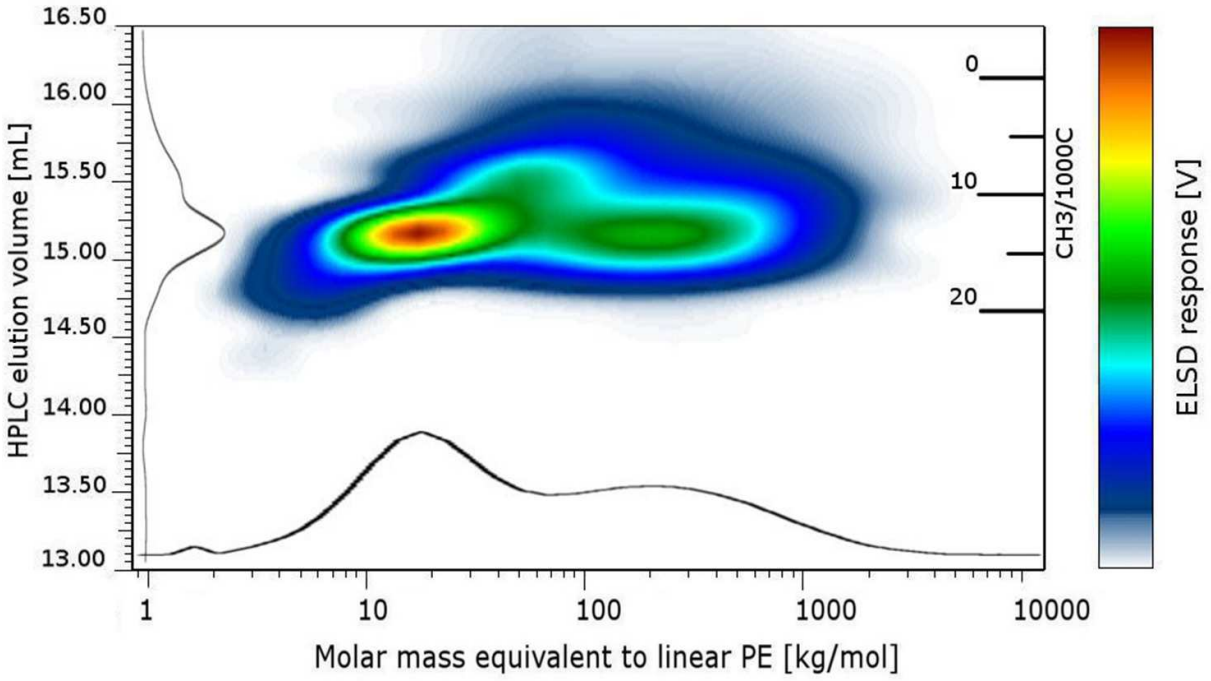


Fig. 64 Contour plot including projections of CCD and MMD obtained with HT 2D-LC of HDPE 1. Temperature in HPLC: 140 °C. Temperature in SEC: 160 °C. Further experimental conditions as in Fig. 56.

Lowering the temperature to 140 °C leads to a contour plot with a bimodal cumulative CCD and a cumulative MMD, which are shown on the x- and y-axes in Fig. 64. Fig. 65 overlays the elugrams as reconstructed for the SEC (Fig. 65a) and HPLC (Fig. 65b) dimension from the 2D-LC contour plots at 140 and 160 ° C.

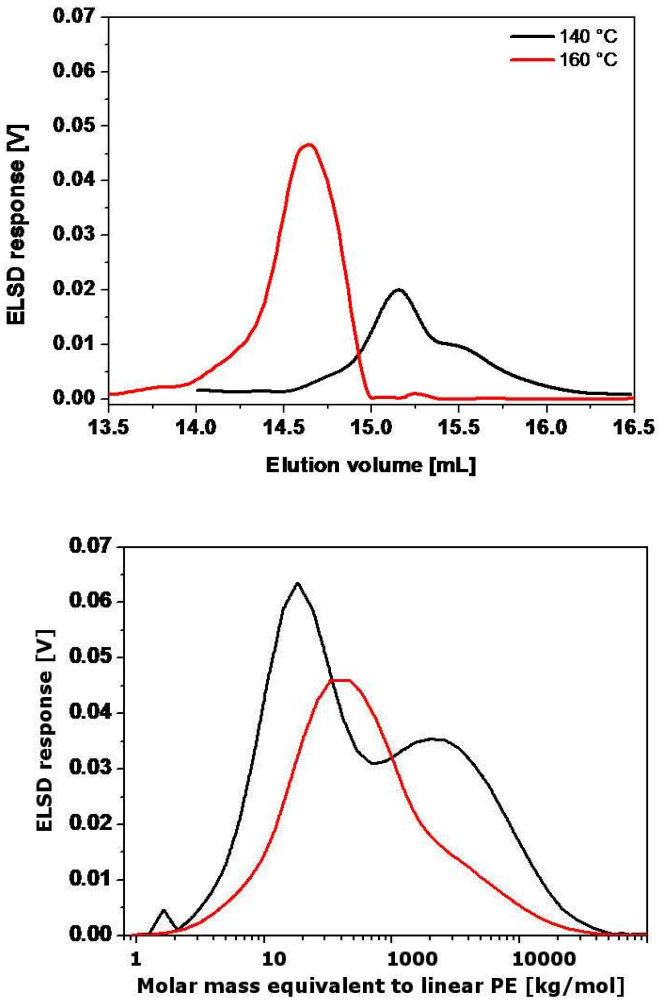


Fig. 65 Overlay of reconstructed curves of HDPE 1 from Fig. 56 and Fig. 63: a) HPLC; b) SEC.

It can be seen that the lowering the temperature in HPLC leads to a clearly recognizable bimodal MMD (Fig. 64b). This can be explained by the fact that lowering the temperature in HPLC leads to a better selectivity and means that the fractions loaded into the SEC column are chemically more homogeneous. As a result, the hydrodynamic volume becomes less affected by CCD and the resolution in SEC is increased. These results show that temperature in 2D-LC has to be

carefully chosen to achieve optimum separation. If a series of samples of the same type should be compared, the experimental parameters in 2D-LC should be kept constant.

3.4.3. HT 2D-LC of polymer samples with different stress cracking resistance

Environmental stress cracking resistance (ESCR) is an important criterion for practical applications of polyolefins because it is a principal failure mechanism for products made of polyolefins like for example, PE pipes. ESCR is frequently estimated using the full notch creep test (FNCT). Such tests are cost intensive and extremely time-consuming. Therefore, an interesting approach would be to estimate ESCR from molecular characterization data, which can be obtained in much faster way. The Ziegler-Natta based pipe grade HDPE 1 has superior ESCR properties, i.e., 300 hours according to FNCT. The contour plot of HDPE 1 was presented in Fig. 56. For comparison, a chromium based pipe grade, HDPE 2, was analyzed by HT 2D-LC and the corresponding contour plot is shown in Fig. 66. In contrast to HDPE 1, HDPE 2 has average ESCR properties. i.e. only 30 hours as determined per FNCT.

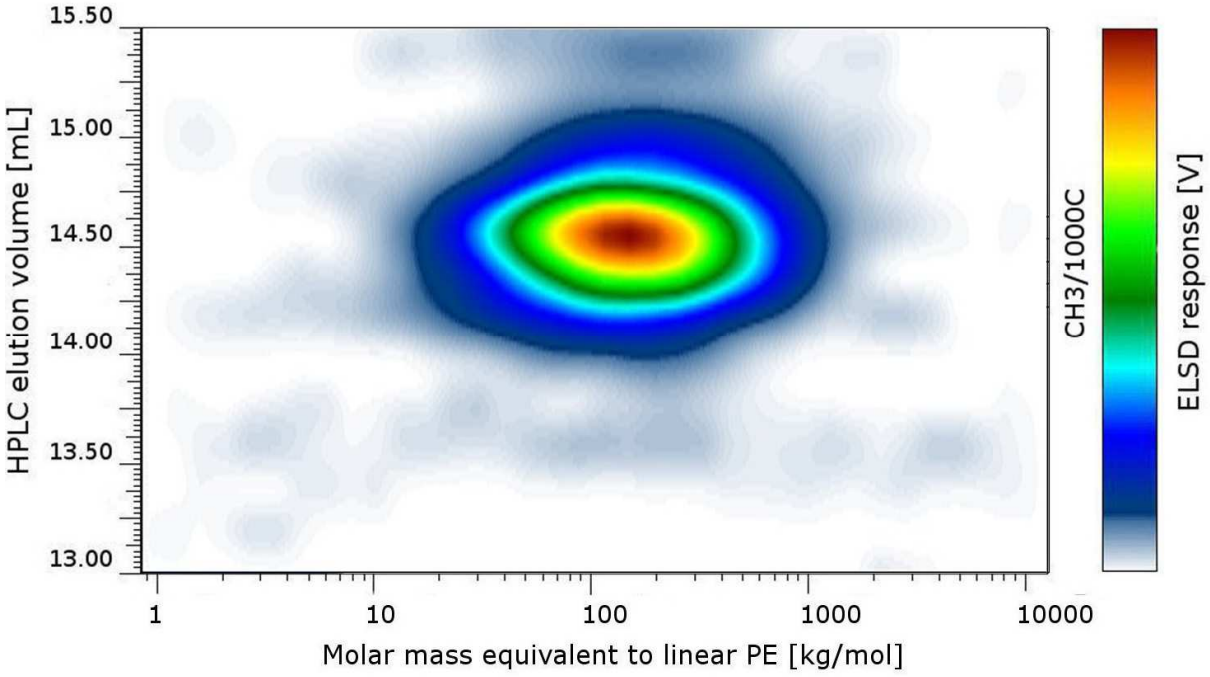


Fig. 66 Contour plot of HDPE 2 obtained from HT 2D-LC. Experimental conditions as in Fig. 56.

As has been pointed out, the one-dimensional separation technique is not capable to completely unravel the chemical heterogeneity. Indeed, although the average chemical composition and molar mass of the respective samples are similar, their chemical heterogeneities are much different (see Fig. 56 contra Fig. 65). As has been found, HDPE 1 contains a low molar mass PE (homopolymer) and a high molar mass copolymer, i.e. a multimodal CCD and MMD. This is called often inverse comonomer incorporation. The material has superior ESCR. In contrast to HDPE 1, HDPE 2 has only average ESCR and contains a high molar mass copolymer (Fig. 65). This example illustrates that the developed method may potentially provide a key to understand structure↔property relationships of a polyolefin material, as it can qualitatively differentiate between two PE materials having different ESCR with regard to their chemical heterogeneity.

3.4.4. Conclusions

Based on the experimental results the following conclusions can be drawn:

1) The effect of temperature on the separation of linear PE-standards using a Hypercarb® column as stationary phase and a gradient 1-decanol→TCB as mobile phase was studied. The elution volume at peak maximum abruptly increases when approaching θ- temperature for high molar mass PE-standards while that of low molar mass ones increases linearly. Simultaneously the broadness of the peaks of high molar mass PE-standards increases.
2) A bimodal pipe grade HDPE was separated using HT 2D-LC for the first time. The separations according to comonomer content and according to molar mass were calibrated using compositionally narrow distributed ethylene/1-butene samples and linear PE standards respectively. A prefractionation of the bulk sample using TREF prior to 2D-LC analysis and subsequent analysis of the individual TREF fractions by HT 2D-LC further increases the information obtained from the two dimensional analysis.

4. Experimental part

4.1. Instrumentation

4.1.1. High-temperature HPLC and HT 2D-LC

All experiments were realized using a prototype chromatographic system for high-temperature two-dimensional liquid chromatography constructed by PolymerChar (Valencia, Spain), comprising an autosampler, two separate ovens, valves and two pumps equipped with vacuum degassers (Agilent, Waldbronn, Germany) (Fig. 67). One oven was used for thermostating the SEC column, while the second one, where the injector and a switching valve were housed, was used to thermostat the HPLC column. A scheme of the HT 2D-LC setup is shown in Fig. 67. The hyphenation of HT-HPLC and HT-SEC was achieved by an electronically controlled eight-port valve EC8W (VICI Valco instruments, Houston, Texas, USA) equipped with two 200 μL loops. From the moment of injection into the HPLC column (50 μL injection loop), the 8-port valve was switched every 2 min in order to inject 200 μL of effluent from the HPLC into the SEC column.

Table 7. Specification of the used chromatographic columns.

Column	Column packing	Column dimensions [mm]	Particle size	Supplier
Nucleosil 500	Silica gel	250 × 4.6	5	MZ Analysentechnik, Mainz, Germany
Perfecsil 300	Silica gel	250 × 4.6	5	MZ Analysentechnik, Mainz, Germany
Hypercarb®	PGC	250 × 4.6	5	Thermo Scientific, Dreieich, Germany
Hypercarb®	PGC	100× 4.6	5	Thermo Scientific, Dreieich, Germany
PL Rapide H	PS-DVB	150 × 7.5	6	Polymer Laboratories, Church Stretton, England
PL Olexis gel	PS-DVB	300×7.5	13	Polymer Laboratories, Church Stretton, England

First dimension HPLC separations were carried out on a silica gel Nucleosil 500, a silica gel Perfecsil 300 and Hypercarb® columns (Table 7). A column PL Rapide H packed with PS-DVB was used in the second dimension (SEC) (Table 7). A linear gradient 1-decanol→TCB was applied in the first dimension at a flow rate of 0.1 ml/min. Starting with 100 % of 1-decanol for 40 min, the volume fraction of TCB was linearly increased to 100 % within 100 min and then held constant for 40 min. Finally, the initial chromatographic conditions were re-established. Because of the void and dwell volume of the system, the gradient reaches the detector with a delay of 4.84 mL. TCB was used as the mobile phase in the second dimension (SEC) at a flow rate of 2.5 mL/min.

For the one-dimensional HPLC separations a linear gradient 1-decanol→TCB was used at a flow rate of 0.5 mL/min. Starting with 100 % of 1-decanol for 10 min, the volume fraction of TCB was linearly increased to 100 % within 20 min and then held constant for 10 min. Finally, the initial chromatographic conditions were re-established. Because of the void and dwell volume of the system, the gradient reaches the detector with a delay of 4.94 mL.

In the HT-HPLC and HT 2D-LC an evaporative light scattering detector (ELSD, model PL-ELS 1000, Polymer Laboratories, Church Stretton, England) was used for detection. The following parameters were set on the ELSD: Air flow rate 1.5 L/min, nebulizer temperature 160 °C, evaporation temperature 260 °C. Ovens, the autosampler and all transfer lines were thermostated at 160 °C. The 2D-LC system was handled with software provided by Polymer Char (Valencia, Spain). WinGPC-Software v.7.0 (Polymer Standards Service, Mainz, Germany) was used for data acquisition and evaluation.

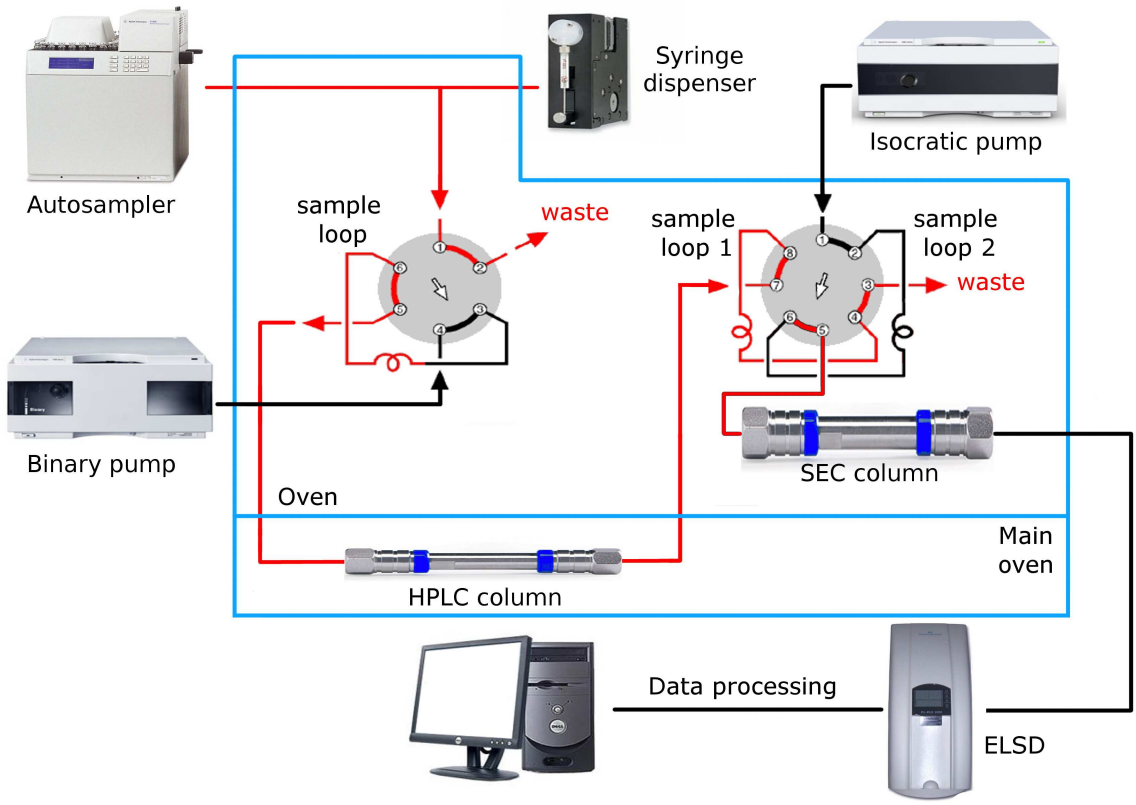


Fig. 67 Setup for HT 2D-LC.

4.1.2. HT SEC

A high-temperature chromatograph PL GPC 220 (Polymer Laboratories, Varian Inc, Church Stretton, England) was used for determining averages of molar masses. The temperature of the injection sample block and of the column compartment was set to 140 °C. The column was PL gel Olexis (Table 7). The mobile phase flow rate was 1mL/min. The samples were dissolved for 2 h in TCB at a concentration of 1 mg/mL and a temperature of 150 °C. 200 µL of the polymer solution were injected. Narrowly distributed polyethylene standards (Polymer Standard Service GmbH, Mainz, Germany) were used for calibration of the system.

4.1.3. TREF × SEC

A TREF-300 (Polymer Char, Valencia, Spain) was used for cross-fractionation experiments

(TREF × SEC). The instrument incorporates an oven used for sample preparation, high precision TREF column oven equipped with a set of 5 stainless steel vessels with internal filters and magnetic stir bars, syringe pump, HPLC pump and a high temperature isothermal oven, where the injection valve, multiposition switching valve and the set of GPC column are placed. A dual band IR4 infrared detector (Polymer Char, Valencia, Spain) was used as the concentration detector. A sample was first dissolved in 1,2-dichlorobenzene (ODCB) in the stainless steel vessel at concentration of 2 mg/mL. Once the sample is dissolved, 300 µL are taken from the vessel through its filter and loaded into the TREF column heated up to 150 °C where the sample is then crystallized at 0.2 ºC/min. Then a discontinuous elution process is followed by increasing the temperature in 2 °C-steps. TREF fractions with volume 100 µl are then alternatively injected one after other into the SEC column flushed with ODCB at flow rate 2.5 mL/min. The SEC column was calibrated with PS standards.

4.1.4. ^{1}H and ^{13}C NMR Spectroscopy

The ^{1}H- and ^{13}C -NMR measurements were carried out using a Varian (Sao Palo, US) Mercury-VX 400 spectrometer (9.4 T) equipped with a 5-mm 4nuc probe. The ^{1}H NMR spectra were acquired at a Larmor frequency of 400.11 MHz using a 10° excitation pulse, 32 k data points (corresponding with an acquisition time of 2.3 s at a spectral width of 6.4 kHz), a relaxation delay of 2 s, and a total of 256 scans. Fourier transformation was done after zero filling the data to 32 k time domain points and exponential filtering of 0.3 Hz.

The ^{13}C NMR spectra were recorded at a Larmor frequency of 100.6 MHz using a 90° excitation pulse with 1H decoupling during the acquisition time (inverse-gated decoupling for quantitative evaluation). The acquisition of the spectra was set by 64 k data points (corresponding with an acquisition time of 1.3 s at a spectral width of 25 kHz), a relaxation delay of 15 s, and a total of 1000-3000 scans. Fourier transformation was done after zero filling the data to 64 k time domain points and exponential filtering of 1.0 Hz.

All ^{1}H - and spectra ^{13}C -NMR spectra were calibrated to the resonance lines of benzene [δ (1H) = 7.16 ppm] and of the CH_2-units of PE [δ □(13C) = 29.98 ppm], respectively.

4.2. Solvents

Decalin, 1-decanol, 2-ethyl-1-hexanol, 1,2,4-trichlorobenzene (TCB) and cyclohexanone (Merck, Darmstadt, Germany) were used as the components forming mobile phases. TCB was freshly distilled, the other solvents were used as delivered.

4.3. Polymer Samples

The EVA copolymers were obtained from Exxon-Mobil Chemical (Meerhout, Belgium) and Bayer (Leverkusen, Germany). The compositional data given by the producers and the molar mass data of the copolymers are summarized in Table 1.

EVA waxes were obtained from BASF (Ludwigshafen, Germany). Samples of PP and ethylene-butene copolymers (LLDPE) grafted with MMA, i.e., PP-g-MMA and LLDPE-g-MMA (1.6 mol.-% of 1-butene (or 6.1 wt.-%)) were donated by BYK Kometra GmbH (Schkopau, Germany). The contents of MMA and the ethyl branches in LLDPE-g-MMA were determined by NMR spectroscopy. EBA copolymer with 28 wt.-% of BA and M_w = 114 kg/mol (D = 5.4) was obtained from Arkema (Paris, France).

PE standards with M_p in the range of 1.18 – 126 kg/mol (D = 1.12-1.59), PVAc with M_w = 45.5 kg/mol (PD = 2.43), PS with M_p in the range of 1.62 – 2570 kg/mol (PD = 1.02 – 1.07) and PMMA with M_p in the range of 2-145 kg/mol were obtained from Polymer Standard Service (Mainz, Germany). Linear PE with M_w = 260 kg/mol was obtained from PSD Polymers (Linz, Austria). A sample of sPP with M_w = 196 kg/mol was purchased from Sigma-Aldrich (Munich, Germany). A sample of aPP with M_w = 211 kg/mol was provided by Dr. I. Mingozzi (LyondellBasell, Ferrara, Italy). iPP standards with M_p in the range of 60 – 350 kg/mol were purchased from American Polymer Standards Corp. (Mentor, OH, USA). iPP with M_w = 45 kg/mol was synthesized at the University of Stellenbosch.

Ethylene/1-butene mother sample (HDPE 1) with a density of 0.948 g/cm3 and melt flow index (MFI, 190/21.6) of 9.5 dg/min and its fractions (1_1-1_6) obtained by preparative TREF. The sample HDPE1 was synthesised using a Ziegler-Natta catalyst at LyondellBasell (Frankfurt am Main, Germany). The ESCR of the material was 300 hours according to a full notch creep test

(FNCT, ISO 16770, 80°C, 4 MPa). Table 5 summarizes the data of TREF fractions of ethylene/1-butene copolymers, which were used to calibrate the HPLC separation.

Ethylene/1-hexene (HDPE 2) with a density of 0.945 g/cm3 and MFI (190/21.6) of 6 dg/min was synthesized with a chromium based catalyst at LyondellBasell. The ESCR of the material (FNCT, ISO 16770, 80°C, 4 MPa) was 30 hours.

5. Summary and Conclusions

Developments in polyolefin catalysis during the last 50 years made it possible to synthesize polymer structures with an improved control of regio- and stereoselectivity, branching (their number and length) and the order in which monomers are incorporated into a polymer chain. To take full advantage of this control, it is essential that the structure↔property relationships are properly established. Constructing these relationships as well as understanding catalyst and process performance requires adequate analytical tools which enable a complete characterization of the molecular heterogeneity (MMD, CCD, tacticity, SCB, LCB) of polymers.

In the past 30 years many analytical techniques have been developed to characterize the molecular heterogeneity of polyolefins: SEC has been used to determine the MMD and the crystallization based techniques TREF and CRYSTAF to determine the CCD. Most importantly, hyphenated TREF x SEC has been used to determine the bivariate CCD x MMD. However, three key deficits associated with any crystallization-based techniques are the notoriously long run time, the narrow working range with regard to comonomer content and cocrystallization.

As an alternative liquid chromatography at high temperatures (HT-HPLC) could be used for the compositional separation and - hyphenated to SEC to yield HT 2D-LC – overcome these issues and analyze the CCD x MMD. The aim of this work was therefore to develop HT 2D-LC protocols for the characterization of functionalized polyolefins as well as non-functionalized polyolefins. The results of the present thesis can be summarized as follows:

I. A dedicated instrument was constructed in a bilateral collaboration with PolymerChar (Valencia, Spain) and corresponding software to operate the instrument was developed and elaborated. The proof of concept was made by the HT 2D-LC of a blend of PE, PVAc and EVA copolymers with varying VA content: In this protocol the components were in the 1st dimension separated with regard to their VA-content using bare silica gel as stationary phase and TCB→cyclohexanone as mobile phase. In the 2nd step the obtained fractions were distinguished according to their molar mass (SEC). For the first time a calibration of both dimensions, namely HPLC and SEC, was achieved. Therefore a method to correctly determine the void and dwell volume of the HT 2D-LC system was developed. TREF × SEC on the contrary was not able to

separate the same mixture into the individual components due to cocrystallization and the limitations with regard to crystallinity of the analyte.

II. The effect of experimental parameters affecting the HT 2D-LC separation has been tested. It was found that increasing the flow rate in SEC shifts the retention to higher elution volumes and leads to a significant band broadening. A broadening of peaks in SEC was also observed with the increasing injection volume. On the other hand, change of the sample solvent did not affect SEC separation, but influenced the ELSD response. The HT 2D-LC separation was not much affected by varying the sampling phase. By choosing suitable experimental parameters (flow rates and sampling time), the run time needed for a complete HT 2D-LC analysis was brought down from about 200 min to 100 min without any significant loss of resolution. The optimized method was applied to industrially relevant low molar mass EVA copolymers. The method failed to adsorb ethylene/1-butene copolymers and PP grafted with 10 and 16 wt.-% of MMA respectively. Using Hypercarb® as stationary phase and a solvent gradient 2-ethyl-1-hexanol→TCB as mobile phase it became possible to separate the grafted PP from the non grafted starting material. This effect is new and can be effectively used to separate copolymers of polar and non polar monomers based on the non polar units. These new HT 2D-LC protocols may find application in the characterization of functionalized polyolefins, where silica based stationary phases fail.

III. HT 2D-LC of non polar polyolefins as well as olefin copolymers has been realized by coupling HT HPLC with SEC at 160 °C using Hypercarb® as the stationary phase for the HT HPLC stage. It could be demonstrated that the sample solvent from the HT HPLC dimension influences the SEC separation. Namely PE standards are suitable to calibrate the SEC dimension because their hydrodynamic volume is not affected by the injection solvent from the first dimension. Thus a molar mass calibration of the comprehensive HT 2D-LC could be achieved. Polyolefin blends, containing PE, isotactic, atactic and/or syndiotactic PP, ethylene/propylene, ethylene/1-hexene copolymers or ethylene/propylene/diene rubber, were separated by HT 2D-LC and the results compared to those from TREF × SEC.

IV. The effect of temperature on the compositional separation of linear PE-standards using Hypercarb® as stationary phase and 1-decanol→TCB as mobile phase was studied. The elution volume at peak maximum abruptly increases when approaching θ-temperature for high molar mass PE-standards while that of low molar mass ones increases linearly. Simultaneously the

broadness of the peaks of high molar mass PE-standards increases. A bimodal pipe grade HDPE was separated using HT 2D-LC for the first time. The separation according to comonomer content and according to molar mass were calibrated using compositionally narrow distributed ethylene/1-butene samples and linear PE standards respectively. Pre-fractionating the bulk sample using TREF prior to HT 2D-LC analysis and subsequent analysis of the individual TREF fractions by HT 2D-LC further increases the information obtained from the two dimensional analysis.

The work has resulted in a number of scientific publications in peer-reviewed journals:

1. Ginzburg, A., Macko, T., Dolle, V., Brüll, R.; *High-temperature two-dimensional liquid chromatography of ethylene-vinyl acetate copolymers*, J. Chromatography A, 1217, 6867-6874, 2010.

2. Ginzburg, A., Macko, T., Dolle, V., Brüll, R.; *Characterization of polyolefins by comprehensive high-temperature two-dimensional liquid chromatography (HT 2D-LC)*, European Polymer J., 47, 319-329, 2011.

3. Ginzburg, A., Macko, T., Dolle, V., Brüll, R.; *High-temperature multidimensional liquid chromatography: a new technique to characterize the chemical heterogeneity of Ziegler-Natta based pipe grade HDPE*, J. Polym. Sci. Part A : Polymer Chemistry., submitted.

4. Macko, T., Ginzburg, A., Remerie, K., Brüll, R.; *Separation of high impact polypropylene using interactive liquid chromatography*, Macromol. Chem. Phys., 213, 937–944, 2012.

5. Chitta, R., Ginzburg, A., van Doremaele, G., Macko, T., Brüll, R.; *Separating ethylene-propylene diene terpolymers according to the content of diene by HT-HPLC and HT 2D-LC*, Polymer, 52, 5953-5960, 2011.

6. Ginzburg, A., Macko, T., Brüll R.; *Characterization of functionalized polyolefins by high-temperature two-dimmensional liquid chromatography*; American Laboratory 2011, 43, 11-13

7. Ginzburg, A., Macko, T., Malz, F., Troetsch-Schaller, Strittmatter, J., Brüll, R., *Characterization of functional polyolefins by high-temperature two-dimensional liquid chromatography*, J. Chromatogr., submitted.

8. Brüll, R., Macko, T., Ginzburg, A., Dolle, V., Wang, Y.; *High-temperature liquid adsorption chromatography and HT-2D-liquid chromatography of polyolefin*s; Macromol. Rapid Commun. 31, 2010, 53-54.

6. Acknowledgements

This research forms part of the research programme of the Dutch Polymer Institute (DPI), project Nr. 642/643. DPI financial support is highly acknowledged. The author thanks to Dipl. Ing. Alberto Ortin, Juan Sancho-Tello, Ms. Nuria Mayo and Dr. Benjamin Monrabal (PolymerChar, Valencia, Spain) for measuring TREF×SEC and a technical help. The author appreciates very much their continuous effort to improve both the HT 2D-LC instrument and the corresponding software.

7. List of Abbreviations

CCD	Chemical Composition Distribution
MMD	Molar Mass Distribution
HT 2D-LC	High-Temperature Two-Dimensional Liquid Chromatography
PE	Polyethylene
PP	Polypropylene
iPP	Isotactic Polypropylene
sPP	Syndiotactic Polypropylene
aPP	Atactic Polypropylene
HDPE	High Density Polyethylene
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
LCB	Long Chain Branching
SCB	Short Chain Branching
Z-N	Ziegler-Natta
MAO	Methylalumoxane
MA	Methyl Acrylate
MMA	Methyl Methacrylate
VA	Vinyl Acetate
EMA	Ethylene Methacrylate
EMMA	Ethylene Methyl Methacrylate
EVA	Ethylene Vinyl Acetate
PVAc	Polyvinyl Acetate
PMMA	Polymethyl Methacrylate
PS-DVB	Polystyrene-divinylbenzene
HPLC	High Performance liquid Chromatography
SEC	Size Exclusion Chromatography
TREF	Temperature Rising Elution Fractionation
CRYSTAF	Crystallization Analysis Fractionation
TCB	1,2,4-trichlorobenzene

ODCB	o-dichlorobenzene
RI	Refractive Index Detector
IR	Infrared Detector
Visc	Viscometer Detector
dn/dc	Refractive index increment
LS	Light-scattering
FTIR	Fourier Transform Infrared Spectroscopy
ELSD	Evaporative light scattering detector
n	Peak capacity
N	Plate number
DF	Dilution factor
T^0_m	Melting temperature of the pure polymer
T_m	Equilibrium melting temperature of the polymer in solution
ΔH_u	Heat of fusion per repeating unit
V_u	Molar volumes of the polymer repeating unit
V_1	Molar volumes of the diluent
ν_1	Volume fractions of the diluent
ν_2	Volume fractions of the polymer
X	The number of segments
χ_1	Flory–Huggins thermodynamic interaction parameter
r	The number of repeating units per polymer chain
χ_{1A}	Interaction parameters of the homopolymer A with the solvent
χ_{1B}	Interaction parameters of the homopolymer B with the solvent
χ_{AB}	Interaction parameter between comonomers A and B in the copolymer
υ_A, ν_B	Volume fractions of comonomers A and B in the copolymer molecule
V_{mob}	Mobile phase
V_{stat}	Stationary phase
V_R	Retention volume
k	Distribution (partition) equilibrium coefficient
ΔG_0	Standard Gibbs free energy change

ΔH^0	Standard enthalpy change
ΔS^0	Standard entropy change
k_{SEC}	SEC distribution coefficient
M_n	Number average molar mass
M_w	Weight average molar mass
D	Polydispersity index
V_{pore}	Pore volume
$V_{stat,\text{int}eractive}$	Volume of the "interactive part'' of the total stationary phase
$k_{monomer}$	Monomer retentionn coefficient
n	The number of interactive units
PGC	Porous graphitic carbon
V_0	Interparticle volume
n_{total}	Total peak capacity
I	The number of dimensions
ϑ_i	Angle between dimensions

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Eidesstattliche Erklärung

Ich erkläre hiermit an Eides Statt, dass ich meine Dissertation selbständig und nur mit den angegebenen Hilfsmitteln angefertigt und noch keinen Promotionsversuch unternommen habe.

Darmstadt, den. 2 November 2012,
Anton Ginzburg