Multidimensional High-Temperature Liquid Chromatography: A New Technique to Characterize the Chemical Heterogeneity of Ziegler-Natta-Based Bimodal HDPE

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ABSTRACT: High temperature two-dimensional liquid chromatography (HT 2D-LC) was recently introduced as a new technique to analyze the heterogeneities with regard to composition and molar mass present in model blends of polyolefins and various olefin copolymers. The method uses graphite as stationary phase and solvent gradients of 1-decanol → 1,2,4-trichlorobenzene as mobile phase for the compositional separation. With the aim to maximize the chromatographic resolution, the influence of the separation's temperature in the first dimension was evaluated: approaching the θ-temperature of polyethylene (PE) in 1-decanol selectively enhances the retention of higher molar mass PE standards while that of the lower molar mass ones is hardly affected. A bimodal ethylene/1-butene copolymer and its temperature rising elution fraction (TREF) fractions were separated by HT 2D-LC. For the first time, both axes of the contour plot were calibrated with regard to chemical composition and molar mass, respectively. Prefractionation of the bulk sample by TREF enhances the detectability of separated components of the 2D separation. The influence of the separation temperature, that is, working around the θ-temperature of PE in 1-decanol, can be used to enhance the chromatographic resolution of the 2D chromatography. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 1897–1906, 2013

INTRODUCTION

Developments in transition metal catalyzed olefin polymerization during the past 50 years permit to synthesize macromolecules with an improved control of chain length, stereoselectivity of monomer incorporation, and the order in which the individual monomers are linked along and across the molar mass axis. To make use of this progress, structure ↔ property relationships must be properly established. This in turn demands that adequate analytical tools have to be developed which enable to characterize the molecular heterogeneities present in olefin copolymers. Primarily, the molar mass distribution (MMD) and the chemical composition distribution (CCD), which in the case of ethylene/1-olefin copolymers is also referred to as short chain branching distribution, must be addressed.

Size exclusion chromatography (SEC) has been well known for many years and is state of the art technique to analyze the

MMD.[1] The separation is entropy controlled, mainly responding to differences in the hydrodynamic volume, which reflects the chain length/molar mass of a macromolecule. However, the size of a macromolecule in solution is also influenced by its architecture and to some extent by the chemical composition via affinity toward the used solvent. Thus, molecules having the same hydrodynamic volume but differing in their chemical composition may not be separated in SEC.[2–4] Temperature rising elution fraction (TREF), Crystallization Analysis Fractionation (CRYSTAF) and Crystallization Elution Fractionation have been developed with the aim to profile the CCD of polyolefins.[5] All are based on the crystallization of macromolecules from a hot solution in a temperature gradient. On the basis of Flory's equilibrium theory,[6] the crystallization temperature of a copolymer macromolecule is explicitly related to its content of comonomer. Mechanistically the fractionation relies on the crystallization of the longest crystallizable sequences of the polymer chains.[7]

However, as all three techniques require crystallization, they can only be applied to samples that exhibit a sufficient degree of crystallinity. TREF and CRYSTAF have been used to study the composition of blends containing various polyolefins,[8,9] the microstructure of polypropylene (PP),[10–13] and the composition distribution of copolymers of either ethylene [14–18] or propylene[19] with 1-olefins. The chemical heterogeneity, that is, the relationship between the MMD and CCD can be evaluated by coupling TREF with SEC (TREF × SEC). However, the methodical limits of TREF still apply and, being based on crystallization, TREF × SEC is a slow technique, requiring typically 1 day per sample.

High Performance Liquid Chromatography at high temperature (HT HPLC) has recently proven potential to characterize polyolefins with respect to their CCD. The key to this are the adsorption properties of graphite, which is for chromatographic applications used in the form of porous graphitic carbon (PGC) and commercially traded as Hypercarb®. Despite the large number of existing publications dealing with separations of small molecules on Hypercarb®,[23–25] the first separations of synthetic polymers on this column were published only recently.[20–22] Employing Hypercarb® in combination with a solvent gradient 1-decanol → 1,2,4-trichlorobenzene (TCB) at high temperature enabled for the first time to separate PP according to its microstructure[20] and copolymers of either ethylene or propylene with 1-olefins with regard to their co-monomer content.[21,22] This unique selectivity opened the door to use liquid chromatography to analyze the compositional heterogeneity present in nonpolar olefin copolymers. Particularly, it paves the way for a new approach to study the relationship between the distributions with regard to composition and molar mass by hyphenating the compositional separation with SEC. Technically this is realized in comprehensive two-dimensional liquid chromatography (2D-LC), where in the first stage (HPLC) the macromolecules are distinguished with regard to their chemical composition, and in the second stage (SEC) the compositionally narrow disperse fractions are fractionated according to molar mass. As a result, 2D-LC yields information on the relationship between the CCD and MMD[26]. The first reports regarding HT 2D-LC of polyolefins appeared only recently.[27–29] Being completely independent from crystallizability, high temperature two-dimensional liquid chromatography (HT 2D-LC) overcomes the methodical limitation of fractionation techniques. Furthermore, being solely based on chromatography, it may be expected that HT 2D-LC can deliver results much more rapidly than CRYSTAF or TREF.

So far, HT 2D-LC was used to separate model blends of linear polyethylene (PE), PP, and ethylene/1-octene copolymers. A commercially important blend is bimodal HDPE, which contains a high molar mass ethylene/1-olefin copolymer and a low molar mass linear wax. Thus, the incorporation of the comonomer with regard to the molar mass axis is inverse to that of a "standard" Ziegler-Natta-based material. This is an important strategy to improve the resistance of PE towards slow crack growth and rapid crack propagation in pressure pipe applications. Such bimodal HDPE grades are synthesized in a two stage process: in the first step the reactor is fed with ethylene and hydrogen to produce an unbranched PE of low molar mass

(wax). The hydrogen is then removed and the resulting product transferred to a second reactor where a 1-olefin is added as co-monomer to produce a high molar mass comonomer.[30]

The impact of the distributions with regard to composition and molar mass on the macroscopic properties, paired with the commercial importance of bimodal HDPE, make it an extremely interesting challenge to probe the separation of these materials by HT 2D-LC. In this paper we first study the influence of the temperature on the elution of PE standards in the compositional separation. Then, we will show how this can be used to optimize the separation of a bimodal pipe grade HDPE in HT 2D-LC and compare the results from HT 2D-LC with those of TREF × SEC.

EXPERIMENTAL

Instrumentation

All experiments were realized using a prototype chromatographic system for HT 2D-LC constructed by PolymerChar (Valencia, Spain), comprising an autosampler, two separate ovens, valves and two pumps equipped with vacuum degassers (Agilent, Waldbronn, Germany). One oven is used for thermostating the SEC column and the second one, where the injector and a switching valve are housed, is used to thermostat the HPLC column. A scheme of the HT 2D-LC setup is shown in Figure 1. The hyphenation of HT HPLC and HT SEC is achieved by an electronically controlled eight-port valve EC8W (VICI Valco instruments, Houston, TX) equipped with two 200 μL loops. From the moment of injection into the HPLC column (50 μL injection loop), the eight-port valve is switched every 2 min to inject 200 μL of effluent from the HPLC into the SEC column.

For the HPLC separations in HT 2D-LC a Hypercarb® column packed with porous graphite particles of the following parameters was used: column dimension 250 × 4.6 mm^2 i.d., average particle size 5 μm, surface area 120 m^2/g and pore size 250 Å (Thermo Scientific, Dreieich, Germany). 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. For the SEC dimension a PL Rapide column H, 150 × 7.5 mm^2 (Polymer Laboratories, Church Stretton, England) was used with TCB as mobile phase at a flow rate of 2.5 mL/min. Finally, the initial chromatographic conditions were re-established. Because of the void and dwell volume of the HT 2D-LC 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.

The void volume (3.4 mL) of the HT 2D-LC system was determined by using a low molar mass polystyrene (PS) standard (M_w = 0.687 kg mol^{-1}), which was injected in 1-decanol into the HPLC column hooked up directly with the detector. The dwell volume (1.44 mL) was measured according to the procedure described by Ginzburg et al.[27,28]

For the 1D HT HPLC separations a linear solvent 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
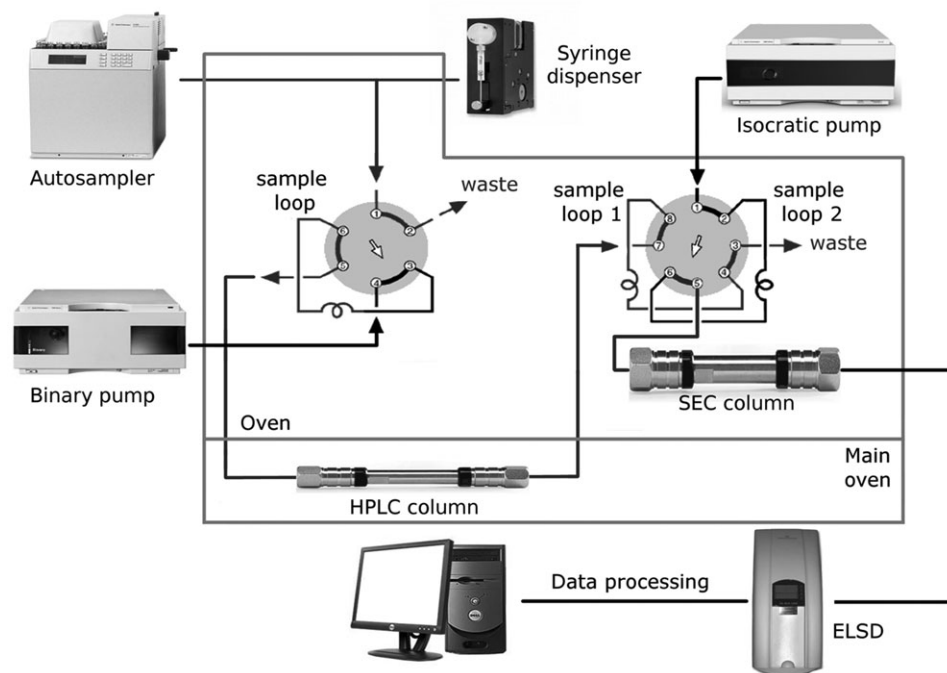
Figure 1. Setup for HT 2D-LC.

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 HT HPLC system, the gradient reaches the detector with a delay of 4.94 mL. The void volume (3.5 mL) of the HT HPLC system was determined using a low molar mass PS standard ($M_w = 0.687$ kg mol^{-1}), which was injected in 1-decanol into the HPLC column hooked up directly with the detector. The dwell volume was 1.44 mL.

In the HT HPLC and HT 2D-LC experiments, 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.

High-Temperature Chromatograph PL 220

A high-temperature chromatograph PL 220 (Polymer Laboratories, Varian, Church Stretton, England) was used to determine the averages molar masses of ethylene/1-butene samples. The temperature of the injection sample block and of the column compartment was set to 140°C. 3 PL gel Olexis columns, dimensions 300 × 7.5 mm^2 i.d., particle diameter 13 μm (Polymer Laboratories, Varian, Church Stretton, England) were used. The mobile phase flow rate was 1 mL/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 PE standards (Polymer Standard

Service GmbH, Mainz, Germany) were used for calibration of the system.

TREF × SEC

A TREF-300 (Polymer Char, Valencia, Spain) was used for cross-fractionation experiments (TREF × SEC). The instrument incorporates an oven containing a set of five stainless steel vessels with internal filters and magnetic stir bars, a syringe pump, an HPLC pump and a HT isothermal oven, where the injection valve, the multiposition switching valve and the set of SEC columns are placed. A dual band IR4 infrared detector (Polymer Char, Valencia, Spain) was used as concentration detector. A sample was first dissolved in 1,2-dichlorobenzene (ODCB) in the stainless steel vessel at a 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 to 150°C where the sample is then crystallized at 0.2°C/min. Then a discontinuous elution process is followed by increasing the temperature in 2°C-intervals. TREF fractions of 100 μL are then sequentially injected into the SEC column flushed with ODCB at flow rate 2.5 mL/min. The SEC column was calibrated with PS standards.

Solvents

1-decanol and TCB (Merck, Darmstadt, Germany) were used as the mobile phases and as components of a linear gradient 1-decanol → TCB. TCB was freshly distilled, 1-decanol was used as delivered.

Polymer Samples

Linear PE standards with weight average molar masses (M_w) in the range of 1.2–90 kg mol^{-1} and dispersities (D) of 1.12–1.37 were obtained from Polymer Standard Service (Mainz, Germany). Linear PE with an M_w of 260 kg mol^{-1} ($D = 2.9$) was obtained from PSD Polymers (Linz, Austria). A sample of linear

Table I. Molecular Characterization Data of HDPE 1 and Its TREF Fractions

Sample/ fraction	TREF elution temperature (°C)	CH$_3$/1000C (FTIR)[a]	wt. %	M_w kg mol^{-1}	D[b]
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

[a] Number of methyl groups per 1000 carbons determined by FTIR.
[b] Values of average molar masses equivalent for PE were obtained by SEC.

PE with $M_w = 1084$ kg mol^{-1} ($D = 1.17$) was donated by Prof. S. Mecking (University of Konstanz, Germany). Linear PE with $M_w = 0.74$ kg mol^{-1} ($D = 1.15$) was obtained from Macherey-Nagel (Düren, Germany).

Table I summarizes the data of the ethylene/1-butene bulk sample (HDPE 1) and its fractions (1$_1$-1$_6$) obtained by preparative TREF and Table II summarizes the data of TREF fractions of ethylene/1-butene copolymers synthesized by a Ziegler-Natta catalyst, which were used to calibrate the HPLC separation.

RESULTS AND DISCUSSION

The key for the first successful chromatographic separation of various polyolefins according to composition is the use of a carbon based stationary phase (Hypercarb®) and a solvent gradient 1-decanol → TCB, which was reported in Refs. 20–22. This sorbent-solvent system allows to separate linear PE from isotactic PP as well as to distinguish PP according to tacticity and to separate ethylene/1-alkene copolymers according to their chemical composition.[20–22] 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 strongest interaction with the carbon surface. An important question from the chromatographic per-

Table II. Analytical Data of the Ethylene/1-Butene Copolymers Used to Calibrate the Compositional Axis in HPLC

Sample code	M_w (kg mol^{-1})	M_w/M_n	CH3/1000C
2	168	3.89	5.4
3	172	3.84	6.9
4	137	3.64	8.5
5	127	3.74	12.8
6	111	3.67	14.9
7	97	3.93	16.1
8	101	3.75	17.3

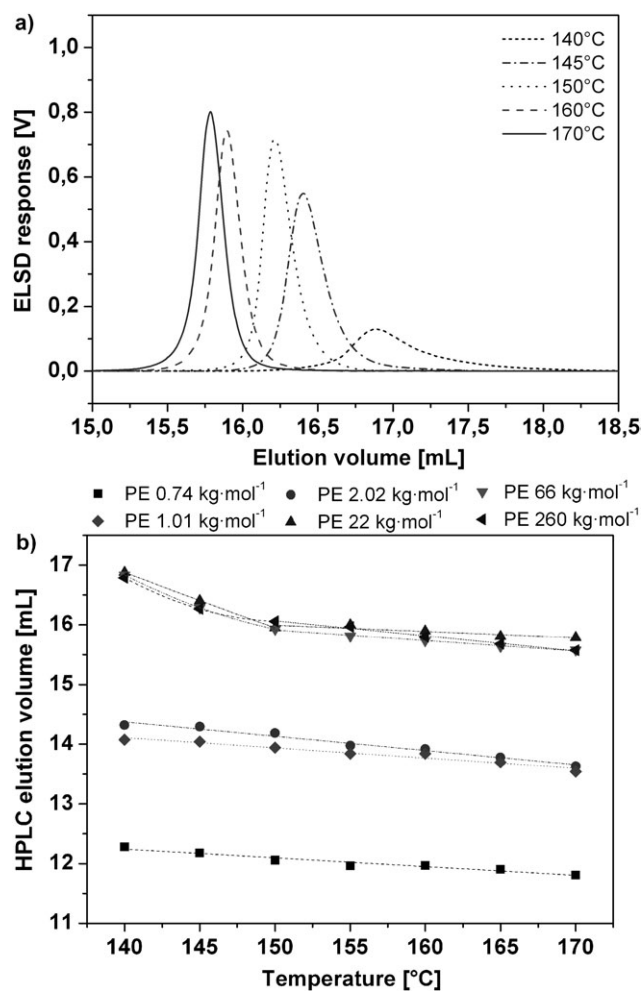[a] Values of average molar masses equivalent for PE were obtained with SEC.

Figure 2. (a) Overlay of elugrams of linear PE 22 kg/mol at 140, 145, 150, 160, and 170°C on Hypercarb®. (b) Relation between the elution volume at peak maximum and the temperature for linear PE standards. For experimental conditions see text.

spective 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. To study the effect of temperature, solutions of PE standards with varying molar mass in 1-decanol (160°C) 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^{-1} is shown in Figure 2(a). As can be observed, both the retention of the sample and the width of the peak increase when the temperature is decreased.

The correlation between the elution volume at peak maximum, M_p, and the temperature is shown in Figure 2(b). Data in Figure 2(b) are in agreement with data presented previously[20] that the retention volumes of linear PE standards in Hypercarb®/1-decanol/TCB (at 160°C) increase with the molar mass of PE.

The relationship between the temperature and the elution volume at peak maximum is linear over the whole range of
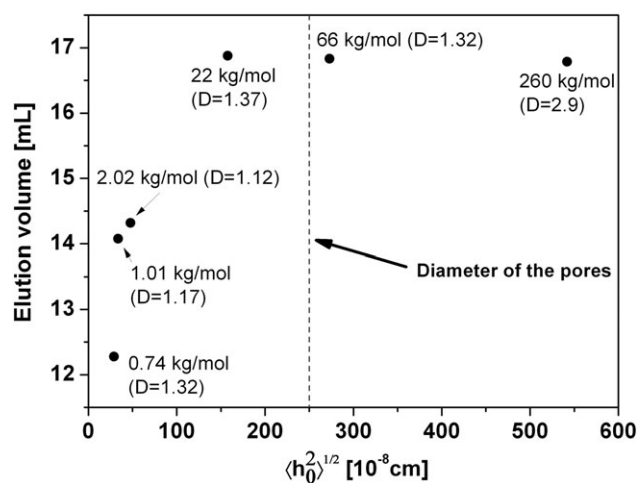
Figure 3. Relation between $\langle h_0^2 \rangle^{1/2}$ and the elution volume at peak maximum at θ-conditions.

temperatures for PE with a molar mass of 0.74, 1.01, and 2.06 kg mol^{-1}. This means that both $\triangle H_0$ and $\triangle S_0$ associated with the process of adsorption are almost invariant with temperature.[31] For PE 22, 66, and 260 kg mol^{-1} the plot is linear between 150 and 170°C, but below 150°C the slope of the curve becomes significantly steeper, that is, the interaction of those standards with the stationary phase increases. Because of 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.[32] A plausible explanation is provided when considering the state of the macromolecules in solution: according to Helmstedt et al.,[33] PE is in 1-decanol at 140°C at θ-conditions, which means that the polymer coils are in an unperturbed state. Using the reported data[33] about the molecular dimensions of PE at these conditions, a relation between the unperturbed root-mean-square end-to-end distance of linear PE ($\langle h_0^2 \rangle^{1/2}$) and the elution volume at peak maximum of PE standards can be constructed (Figure 3).

Comparing $\langle h_0^2 \rangle^{1/2}$ with the average diameter of the pores as specified by the producer it can be recognized that the PE with a molar mass of 0.74–22 kg mol^{-1} is small enough to penetrate into the pores, while those samples of higher molar mass in their maximally expanded conformation can only partially (PE 66 kg mol^{-1}) or even not (260 kg mol^{-1}) enter the pores. These speculations are true when not considering the attractive character of the graphitic surface, that is, the attractive interactions between macromolecules and the sorbent. Conversely, the surface of the graphite is extremely attractive for PE, that is, the large molecules may still enter the pore by taking up the needed conformation or uncoiling. It may therefore be speculated that the over proportionate increase of the retention volume of the higher molar mass standards when approaching θ-conditions is due to different extent of adsorption. Macromolecules are in an unperturbed state at and near θ-conditions and thus, they may access a larger surface area of the sorbent and are retained to a larger extent. The decrease in temperature may weaken the elu-

tion power of a binary solvent mixture, which in turn may lead to longer retention times of polymers. However, a linear relation was experimentally found between the elution volume and content of branching in this work (Figure 7) as well as in our previous papers for various ethylene/alkene or propene/alkene copolymers.[21,22] This indicates that the elution power of the mobile phase changed linearly during the linear gradient. The elution volume of PE changed, however, abruptly [Figure 2(b)]. In contrast to chromatographic separation mechanism of small molecules, separation of larger macromolecules is heavily affected by their conformation in solution, which is a function of polymer, temperature, mobile phase composition, etc. This is the reason, why we hypothesize that varying the temperature in our particular case leads to the change in conformations of chains that allows a better alignment of chains to the planar and very attractive porous graphite surface.

As PE 66 kg mol^{-1} was only partially recovered from the column at 135 and 130°C and not 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, that is, precipitation of PE at 130–120°C may play an additional role. Monitoring the crystallization of PE from a solution in 1-decanol in the presence of Hypercarb® packing material by solution microcalorimetry[34] showed that the crystallization of PE occurs in a broad interval ranging from 123 to 100°C, while in the absence of the PGC the crystallization takes place between 115 and 109°C.

The MMD of HDPE 1 as determined by SEC is shown in Figure 4. As can be observed, the sample has a broad MMD ranging from about 0.7 kg mol^{-1} to about 10^4 kg mol^{-1} with a shoulder in the low molar mass region.

To investigate the chemical heterogeneity of HDPE 1 by a conventional method, TREF × SEC was employed. The results are presented in Figure 5.

As can be seen, the sample elutes in a broad zone ranging from about 48–100°C indicating a broad distribution with regard to
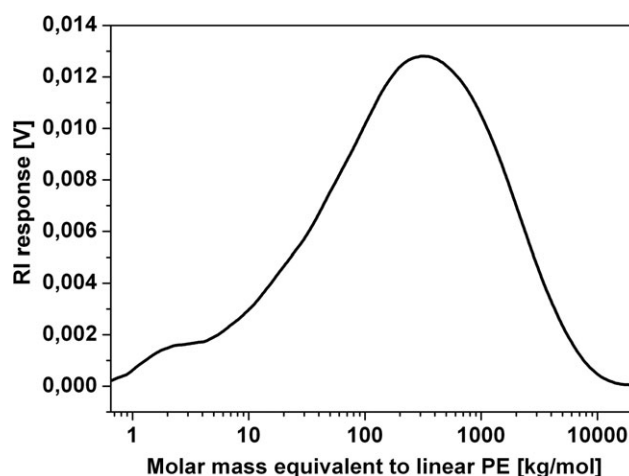

Figure 4. SEC elugram of HDPE 1. Conditions: Column PL gel Olexis; mobile phase TCB; flow rate 1 mL/min; temperature 140 °C.
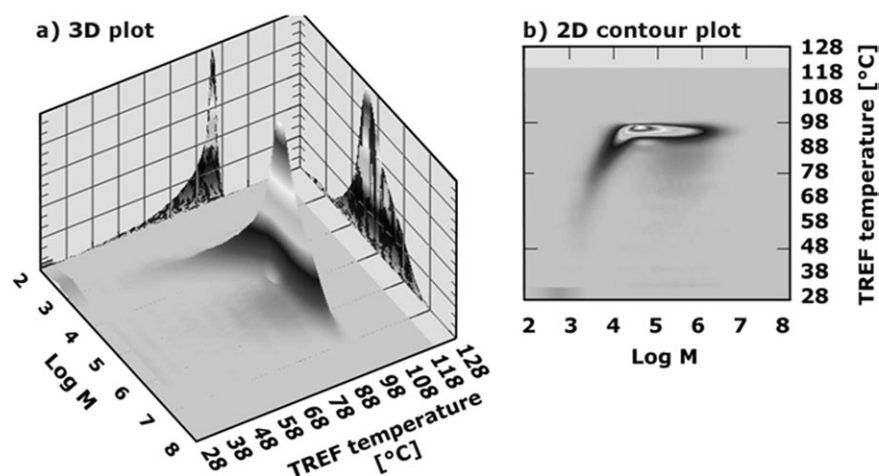
Figure 5. TREF × SEC of HDPE 1 (a) relief plot and (b) colour coded contour plot. For experimental conditions, see experimental part.

crystallinity. The sample may contain PE homopolymer with broad MMD eluting at 90–100°C.

Between 60 and 90°C a high molar mass copolymer (10^2–10^3 kg mol^{-1}) elutes in combination with a low molar mass PE (1–10 kg mol^{-1}). It can be speculated that both species are characterized by a common CH$_3$/1000C. In case of the copolymer, these are short chain branches and for the molar mass PE homopolymer, these stem from end groups of the polymer. Moreover, it contains a small amount of material 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 all components according to CCD.

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 hyphenating 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 shown in Refs. 27 and 28. Figure 6 shows the contour plot obtained from HT 2D-LC for HDPE 1 (Table I). 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.

Following a procedure, described in Refs. 27 and 28, the first dimension was calibrated with respect to composition using ethylene/1-butene copolymers of known average chemical composition (Table II). The second dimension was calibrated with respect to molar mass using linear PE standards. The compositional calibration is represented by a linear relationship between the elution volume at peak maximum, M_P, and the average content of 1-butene (Figure 7).

Similar linear relationships were found for copolymers of ethylene with various 1-olefin comonomers recently.[21] It is important to note that the extrapolation of the fitted line to 0 CH$_3$/1000C intercepts the Y-axis at the elution volume corresponding to that of unbranched PE having a molar mass less than 22 kg mol^{-1}. Mechanistically, it may be asserted that the critical sequence length needed for adsorption of the macromolecule is less than
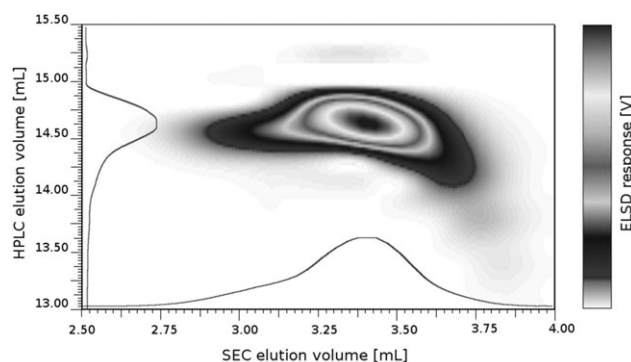

Figure 6. Contour plot including projections of the elugrams for HPLC and SEC obtained from HT 2D-LC of HDPE 1. Conditions: HPLC: Column Hypercarb® 250 × 4.6 mm^2 i.d.; mobile phase: 1-decanol → TCB; flow rate 0.1 mL/min; temperature 160°C. SEC: Column PL Rapide H; mobile phase TCB, flow rate 2.5 mL/min, temperature 160°C.
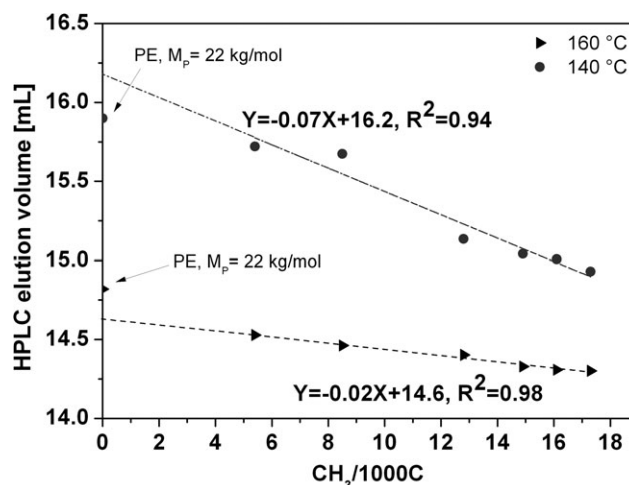

Figure 7. Compositional calibration obtained by injecting fractions of ethylene/1-butene copolymers (Table I) into the entire HT 2D-LC system at 140 and 160°C. Experimental conditions as in Figure 6.
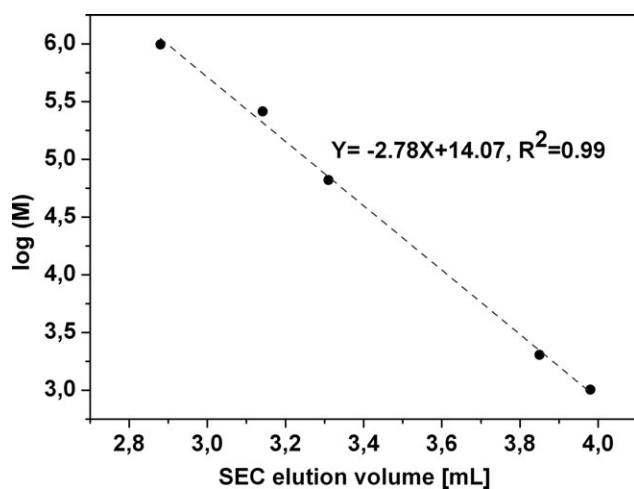
Figure 8. Molar mass calibration obtained by injecting PE standards (M_w = 1.01, 55, 66, 260, and 985 kg mol^{-1}) into the entire HT 2D-LC system. Experimental conditions as in Figure 6.

that of PE 22 kg mol^{-1}. The SEC calibration of the entire HT 2D-LC system using PE standards is displayed in Figure 8.

These relationships allow to calibrate both axes of the contour plot (Figure 9). As can be noticed, the CCD spans 1.5 mL, while the MMD ranges from 3 to 3000 kg mol^{-1}. The obtained data confirm that 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 0–20 CH$_3$/1000C of the compositional calibration. It may therefore be concluded that the interaction strength of PE with M_p < 22 kg mol^{-1} with the stationary phase is similar to that of branched copolymers and as a result co-elution of short linear macromolecules and highly branched ones may occur.

The contour plots obtained from TREF (Figure 5) and HT 2D-LC (Figure 9) respectively for the analyzed sample look similar, but are not identical. Namely, TREF is based on crystallization, while crystallization plays no role in the HT 2D-LC analysis. For example, a small spot is visible at a TREF-elution temperature of 28°C in the TREF contour plot (Figure 5), while such a spot is missing in the contour plot from HT 2D-LC (Figure 9), because HPLC does not distinguish between amorphous and crystalline materials.

HDPE is mostly semicrystalline, and, thus, can be separated by TREF. TREF, however, fails to separate components, which are amorphous or of low crystallinity and this is one reason for the difference between the contour plots from TREF and HT 2D-LC. An additional reason may be differences in the response of the detectors used. When suitable experimental parameters are applied, HT 2D-LC requires much less time per analysis than TREF.

To obtain more insight into the heterogeneity, HDPE 1 was fractionated by preparative TREF. As TREF fractionates primarily according to crystallinity (short chain branches), the fraction crystallizing at 80°C is expected to contain a mixture of low molar mass PE homopolymer and high molar mass copolymer; both characterized by the same CH$_3$/1000C. This is in agreement with SEC data (Table I). The next fractions have a lower

number of short chain branches; the last two fractions seem to represent mostly crystalline PE homopolymer in combination with a small amount of the copolymer (2.7–2.9 CH$_3$/1000C). For a high molar mass homopolymer 0–1 CH$_3$/1000C are expected. 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 are shown in Figure 10 and the results are summarized in Table III.

Table III 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 I.

The first TREF fractions (the least crystalline ones) contains low molar mass PE and a portion of copolymer [Figure 10(a)]. The second and third fraction contain PE and compositionally broad distributed copolymer [Figure 10(b and c)] in different ratios. These components obviously differ in their molar masses and can be well separated by adsorption/desorption and by SEC [Figure 10(a–c)]. In the fourth fraction [Figure 10(d)], co-elution of unbranched PE and a copolymer can be observed. No values for M_p can be determined for fraction 1_4 due to overlapping of the peaks. The fifth and sixth fraction [Figure 10(e and f)] contain PE homopolymer of increasing molar mass and copolymers with less branching. These components overlap on the molar mass axis due to similar MMDs.

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 copolymer and wax (Table III). The assignment of PE with molar mass of 1–5 kg mol^{-1} in the HPLC dimension in Figure 10(a–c) was done according to Ref. 28. Within this molar mass range, the PE standards elute in HT HPLC at smaller elution volumes than PE with M_w > 20 kg mol^{-1}. Therefore, an unambiguous compositional calibration (Figure 7) must take into account the effect of the molar mass on the elution. Comparing the elution temperatures of the TREF fractions with their HT 2D-LC contour plots reveals that the degree of crystallinity (i.e., higher temperature in TREF) increases with the decreasing number of branches.

Figure 11 displays a cumulative overlay of the contour plots of all TREF fractions obtained by HT 2D-LC.
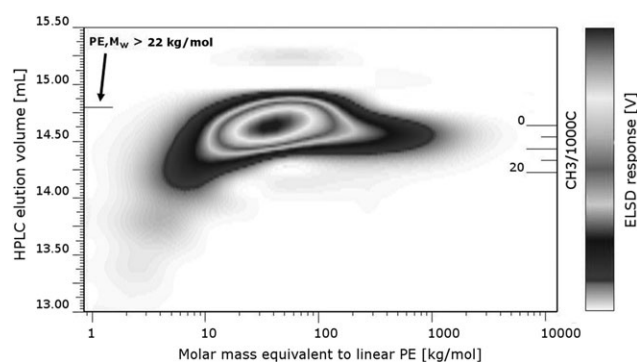

Figure 9. Contour plot obtained from HT 2D-LC of HDPE 1. Conditions as in Figure 6.
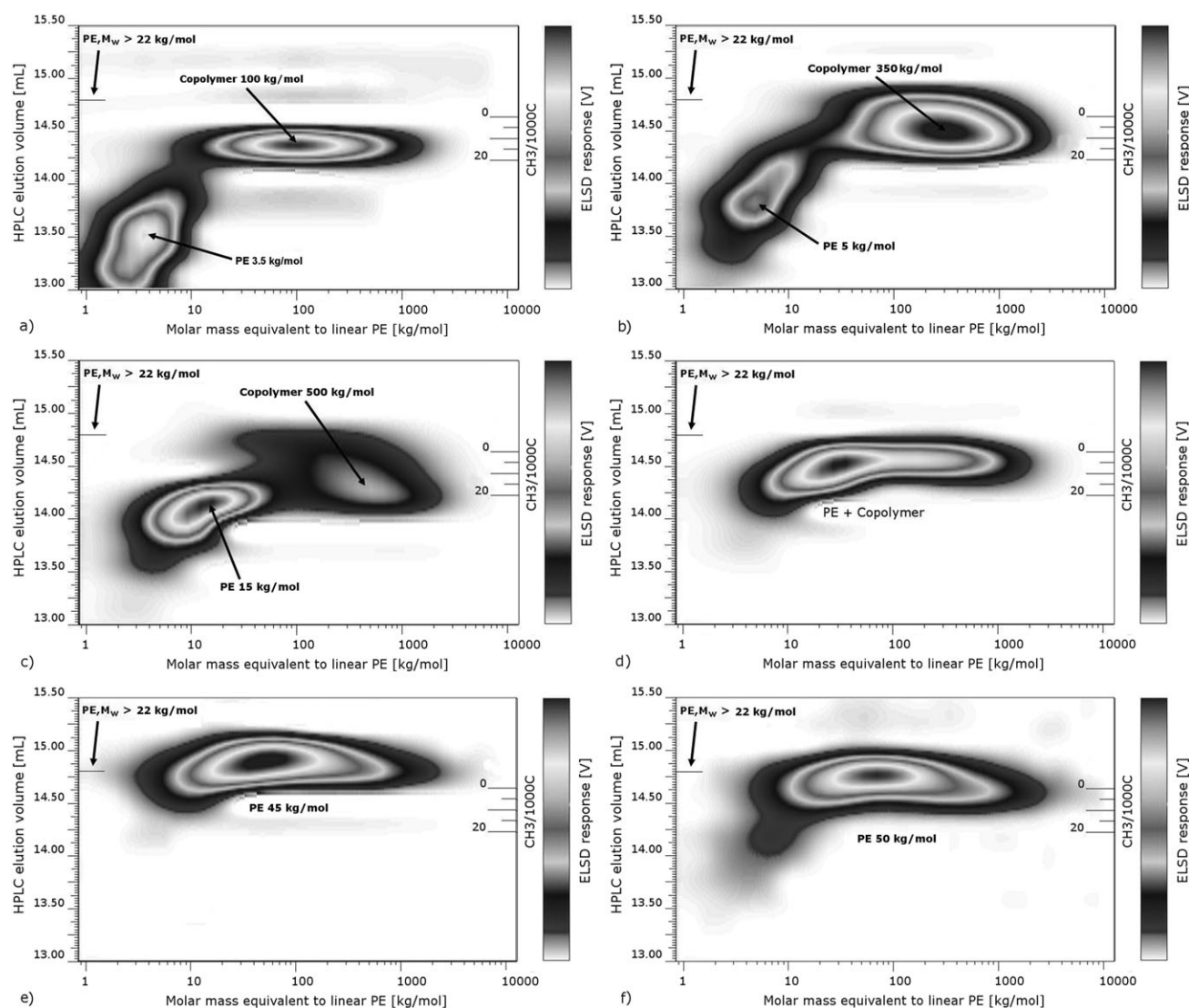
Figure 10. (a–f) Contour plot of TREF fractions 1_1-1_6, respectively, obtained from HT 2D-LC, Experimental conditions as in Figure 6.

The accumulation of the equally weighted contour plots from the HT 2D-LC analysis of the TREF fractions leads to broader distributions with regard to composition and molar mass than the HT 2D-LC analysis of the mother sample. Figure 11 clearly visualizes the presence of materials in compositional and molar mass regions where no fractions are detectable in the case of HT 2D-LC of the bulk sample HDPE 1 (Figure 9). Overlaying the contour plots of TREF fractions yields an MMD ranging from 2 kg mol^{-1} to 6000 kg mol^{-1}, while the MMD obtained in the analysis of the bulk sample ranges from 7 to 1000 kg mol^{-1}. This is due to the

Table III. 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 Values from FTIR

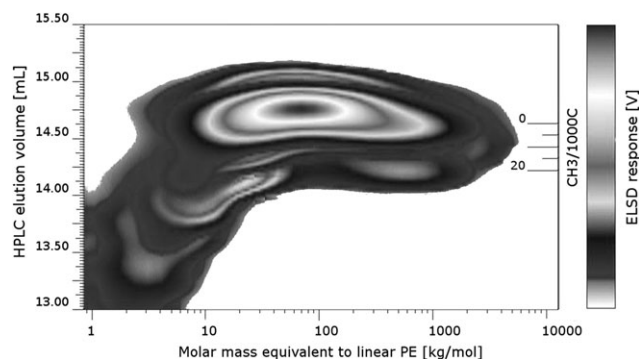| Sample/fraction	M_p (PE) (kg/mol) (HT 2D-LC)	M_p (copolymer) (kg mol^{-1}) (HT 2D-LC)	Span width CH$_3$/1000C (HT 2D-LC)	Peak maximum of CH$_3$/1000C (HT 2D-LC)	CH$_3$/1000C (FTIR)
1	Not identified	Not identified	0–15	5	7
1_1	3.5	100	5–20	11	14
1_2	5	300	0–20	7	10.2
1_3	15	500	0–20	15	6.2
1_4	30	N/D	0–12	4	4.7
1_5	45	–	0–5	–	2.7

Figure 11. Overlay of the 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).

fact that all TREF fractions were injected into the HT 2D-LC at identical concentration, while in the mother sample these are present in different concentrations (Table I). As a consequence, the overlay of the contour plots in Figure 11 can not coincide with the contour plot of the mother sample in Figure 9. Thus, a TREF analysis prior to HT 2D-LC strongly enhances the information obtainable from the chromatographic separation.

It is shown above that lowering the temperature favors the interaction of PE with the PGC, and the retention increases more for large molecules (Figure 1). This could be utilized to improve the separation in HT 2D-LC. The contour plot of HDPE 1 at 140°C is shown in Figure 12. To take the effect of the temperature into account, a calibration of the compositional axis was carried out at 140°C (Figure 7). As can be noticed, the relationship between the elution volume and the degree of branching is steeper at 140°C than at 160°C, which means the interaction of the macromolecules is stronger at θ-conditions.

As can be observed, lowering the temperature to the θ value leads to a contour plot with a bimodal population. Figure 13 overlays the elution diagrams as reconstructed for the (a) SEC and (b) HPLC separation at 160 and 140°C.

Lowering the temperature leads to a more pronounced shoulder in the HPLC elugram while at the same time a bimodal MMD becomes clearly recognizable. This is the result of co-elution of
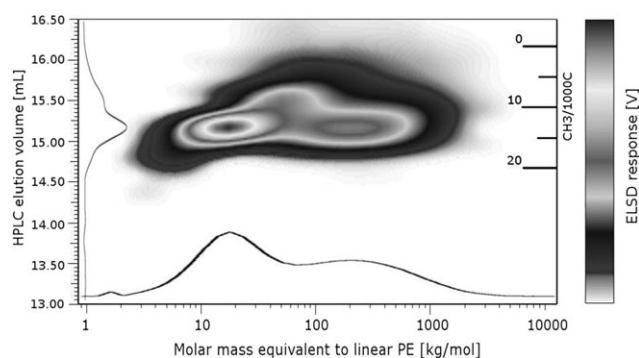

Figure 12. Contour plot including projections of CCD and MMD obtained with HT 2D-LC of HDPE 1. Temperature in HPLC and SEC: 140°C. Further experimental conditions as in Figure 6.
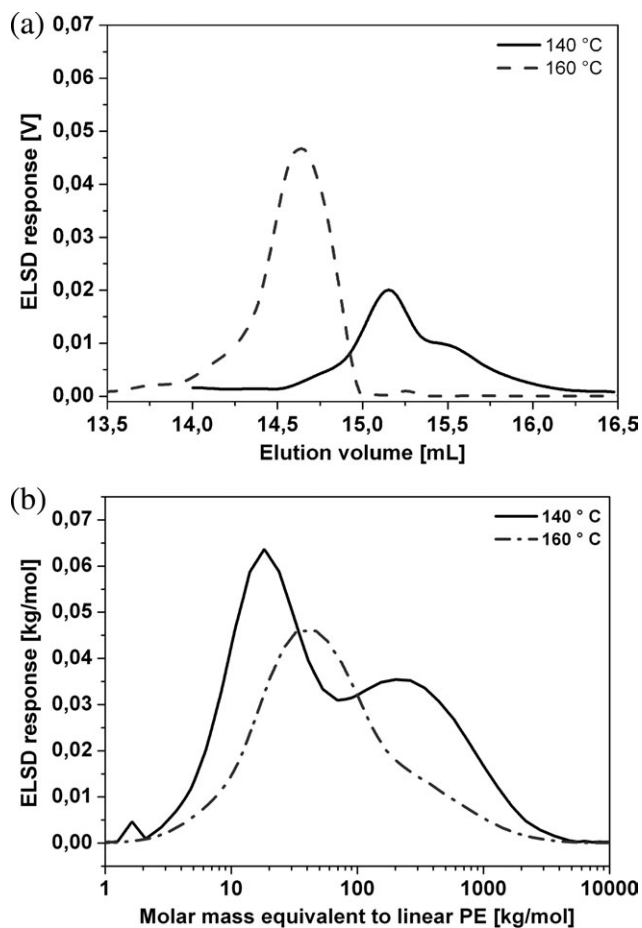

Figure 13. Overlay of reconstructed curves from Figures 7 and 9: (a) HPLC and (b) SEC.

short linear with strongly branched macromolecules. These results show that temperature in 2D-LC must be carefully chosen to achieve optimum separation.

The components separated by HT 2D-LC are eluted and detected in TCB.

Thus, detectors, which are used in high-temperature SEC, could in principle be applied (refractive index detector, IR, MALLS). In this study, we used an ELS-detector, because it offers a much higher response for polyolefins, compared to RI or IR. Moreover, an ELS-detector eliminates solvent peaks, because the mobile phase is evaporated (in our case, 1-decanol is present in the majority of the HPLC fractions, which are analyzed by SEC, that is, 1-decanol elutes in SEC with other small molecules). It is known that the response of an ELSD depends on several experimental parameters. However, it has to be kept in mind that the response of this detector for PE (and other polyolefins) has not been extensively studied yet. It is our aim to calibrate the ELSD-response for PE, PP, and other polyolefins in the future and results will be communicated soon.

If HT 2D-LC would be realized in a preparative manner, that is, a larger amount of separated sample would be collected in fractions, then additional methods (e.g., NMR, DSC, X-ray, and rheology) could be used to obtain qualitative and quantitative data about the separated components.

CONCLUSION

The effect of temperature on the compositional separation of linear PE-standards using a Hypercarb® column as stationary phase and a solvent 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 the low molar mass ones increases linearly. Simultaneously, the broadness of the peaks of high molar mass PE standards increases when approaching the θ-temperature. This effect of temperature can be explained by the influence the temperature exerts on the hydrodynamic volume and the interactions between macromolecules and the sorbent surface in the Hypercarb® column. A bimodal HDPE pipe grade was separated using HT 2D-LC for the first time; both axes were calibrated using compositionally narrowly distributed ethylene/1-butene samples and linear PE standards, respectively. The temperature's effect on the compositional separation is manifested in the contour plots from HT 2D-LC and proves that temperature may be used to enhance the selectivity of the 2D separation of bimodal HDPE. A prefractionation of the bulk sample using TREF prior to HT 2D-LC analysis and subsequent analysis of the individual TREF fractions by HT 2D-LC further enhances the information obtained from the 2D analysis. An advantage from the practical point of view is that HT 2D-LC requires less time per analysis than TREF × SEC and that also amorphous polyolefins may be selectively separated.

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