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Characterization of polyolefins by comprehensive high-temperature two-dimensional liquid chromatography (HT 2D-LC)

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ABSTRACT

Temperature rising elution fractionation hyphenated to size exclusion chromatography (TREF × SEC) is a routine technique to determine the chemical heterogeneity of semicrystalline olefin copolymers. A serious limitation is its applicability to non crystallizing samples. Comprehensive high temperature two-dimensional liquid chromatography (HT 2D-LC) gives an alternative to characterize the chemical heterogeneity of copolymers irrespective of their crystallizability. We have hyphenated interactive HPLC, which separates polyolefins according to their chemical composition, with high-temperature size exclusion chromatography (SEC), which distinguishes polyolefins with regard to their molar mass at 160 °C. The first separation step was based on a selective adsorption of macromolecules on a Hypercarb® column packed with porous graphite particles and subsequent desorption by a gradient 1-decanol → 1,2,4-trichlorobenzene at 160 °C. The SEC column was calibrated with polypropylene (PP) and polyethylene (PE) standards and it turned out that the injection solvent from the first dimension influenced the elution of PP in the SEC column, while the retention of PE was virtually constant. HT 2D-LC was then used to separate a broad variety of polyolefin blends containing PE, PP with different microstructure, ethylene–propylene (EP) and ethylene–propylene–diene (EP(D)M) rubber and ethylene/1-hexene copolymers. For the first time it has been shown that the elution of iPP in the gradient HPLC is molar mass dependent. The results from the HT 2D-LC separation were compared to those from TREF × SEC-experiments. The particular advantage of HT 2D-LC over TREF × SEC is the fact that HT 2D-LC is also applicable to non crystallizing polyolefin samples. The new technique therefore resolves the problem to analyze the chemical heterogeneity of non crystallizing olefin copolymers like EP and EP(D)M copolymers.

1. Introduction

During the last 70 years, polyolefins have become the most important synthetic polymers with the current annual world-wide production in excess of hundred million tons per year. This rapid growth was fuelled by a series of breakthroughs in catalysis and reactor technology. These made it possible to control the way how the monomers are incorporated in the macromolecules. The polymer chains differ in their composition and length which in turn influences the degree of crystallinity. As a result many physical properties of polyolefins are related to both the chemical composition distribution, CCD, and the molar mass distribution, MMD. It is, therefore, of paramount importance to characterize these parameters.

At the time being, the CCD of polyolefins is characterized by temperature rising elution fractionation, TREF,

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and crystallization analysis fractionation, CRYSTAF. Both techniques are based on the crystallization of macromolecules from a hot solution in a temperature gradient. On the basis of Flory's equilibrium theory [1,2], the crystallization temperature is explicitly related to the content of the comonomer. Consequently, the applicability of TREF and CRYSTAF is limited to well-crystallizing polyolefins and the methods fail in the case of amorphous samples. TREF and CRYSTAF have been used to study the compositional distribution of various ethylene/1-alkene copolymers [3–12] as well as propene/1-alkene copolymers [13,14]. However, the fractionations alone do not reveal information on the MMD.

Size exclusion chromatography (SEC) is a well-established method to determine the MMD of polyolefins [15,16] and requires in the case of semicrystalline polyolefins temperatures above 100 °C. The separation is entropy controlled and based on the differences in the size of the macromolecules in solution (hydrodynamic volume) and the extent to which they are excluded from the pores of a 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. Therefore macromolecules can differ in all these parameters but yet have the same elution volume. Consequently, it is not possible to distinguish between these copolymers, if only SEC is used.

High-performance liquid chromatography (HPLC) has been widely used to separate polymers with respect to their chemical composition. The majority of published HPLC separations of synthetic polymers have been realized at temperatures below 60 °C [17–21]. Dissolution and chromatographic separation of semicrystalline polyolefins, however, require temperatures of up to 130–160 °C. For the past few years, our group has discovered and elaborated the first chromatographic systems based on selective adsorption and desorption of polyethylene which can separate polyolefins according to chemical composition. The key for the successful separation is the use of a carbon based stationary phase, Hypercarb®, which was reported by Macko and Pasch. Using a gradient 1-decanol → TCB as mobile phase allows to separate linear PE from isotactic PP and also to distinguish PP according to tacticity [22–24]. In detail it was shown that at 160 °C linear PE and syndiotactic and atactic PP were fully adsorbed on the stationary phase from 1-decanol, while isotactic PP eluted isocratically. Thereafter, all retained components were desorbed from the column by a gradient 1-decanol → TCB. Later on, it was demonstrated that this system enables to separate various propene/1-alkene and ethylene/1-elkene copolymers with respect to their chemical composition [25].

To completely unravel the structure of complex polyolefins being disperse in more than one mutually dependent distribution a combination of separation methods (multidimensional separations) is necessary. The concept of two-dimensional separation was introduced into the characterization of polymers by Balke [26,27] and elaborated by others for review, see [17,21,28]. The combination of methods should be chosen in a way that their orthogonality (minimum correlation between two properties) is as large as possible, in order to maximize the separation performance [28]. The coupling of TREF and HT-SEC, where the sample is first fractionated by TREF with respect to chemical composition and the obtained TREF fractions are then analyzed by HT-SEC, offers the required comprehensive characterization. Wild et al. [29] were the first to combine a preparative fractionation by TREF off-line with HT-SEC analysis of the fractions. Other groups have constructed similar apparatuses for off-line TREF × SEC [30–35]. Automation in TREF × SEC was first reported by Nakano and Goto [36] and a fully automated instrument has been commercialized by Ortin et al. in the meanwhile [37]. But still, as the separation according to chemical composition is achieved via TREF, it can only be applied to samples which crystallize sufficiently.

The hyphenation of two chromatographic modes, 2D-LC has been realized for many synthetic polymers at room temperature. In the majority of 2D-LC separations of polymers, the first separation step distinguishes the macromolecules of different chemical composition, while the second step separates the macromolecules according to molar mass or the other way around. The advantages and disadvantages of using either HPLC × SEC or SEC × HPLC sequences were discussed in detail by van der Host and Schoenmakers [38,39]. From the practical point of view, a preferred 2D-LC set-up is HPLC × SEC because HPLC is less sensitive towards molar mass effects and SEC as the second dimension allows the use of different detectors. Many successful 2D-LC separations of synthetic polymers have been reported [40–53]. However, at the time being, the published 2D-LC methods and available instrumentation are still limited to separation at ambient temperatures. The first communications regarding high-temperature two-dimensional liquid chromatography of synthetic polymers emerged only recently [54–56]**.** In [54,55] the high-temperature 2D-LC of EVA copolymers was announced and in [56] the HPLC × SEC separation of ethylene/1-octene copolymers using porous graphite/1-decanol → TCB was described. In this paper we want to show that HT 2D-LC making use of the recent progress in HT-HPLC is very useful to separate polyolefin blends. In particular we want to demonstrate that blends containing amorphous and crystallizing components, which cannot be separated by TREF × SEC can be fractionated by HT 2D-LC. The calibration of SEC axis will be addressed and the challenges originating from the injection in a mixed solvent be discussed.

2. Experimental section

2.1. Instrumentation

2.1.1. High-temperature HPLC × SEC

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). 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

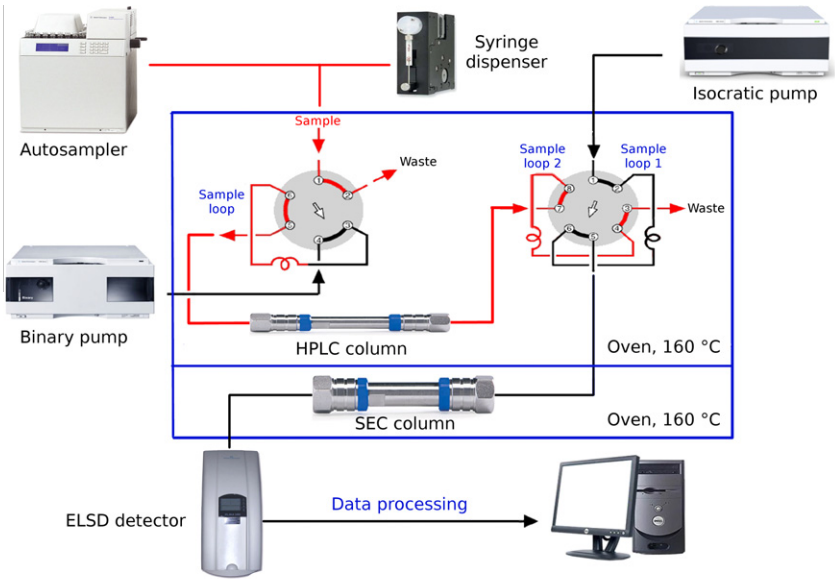

Fig. 1. Setup for HT 2D-LC.

thermostat the HPLC column. A scheme of the HT 2D-LC setup is shown in Fig. 1.

The coupling of HT-HPLC and HT-SEC was achieved by using an electronically controlled eight-port valve EC8 W (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.

First dimension separations were carried out on a Hypercarb® column packed with porous graphite particles with the following parameters: column size 250 × 4.6 mm i.d., average particle size diameter 5 μm, surface area of 120 m^2/g and pore size of 250 Å (Thermo Scientific, Dreieich, Germany). A column PL Rapide H, 150 × 7.5 mm (Polymer Laboratories, Church Stretton, England) was used in the second dimension (SEC).

The separations were done by applying a linear gradient 1-decanol/TCB. Starting with 100% of 1-decanol for 40 min, the volume fraction of TCB was linearly increased to 100% within 80 min and then held constant for 80 min. Finally, the initial chromatographic conditions were re-established. Because of the system void volume and the system dwell volume, the gradient reached the detector with a delay of 48.4 min. The void volume (3.4 mL) of the system was determined by using a low molar mass PS standard (M_w = 0.687 kg/mol) which was injected in 1-decanol into the entire 2D system. The dwell volume (1.44 mL) was measured according to the method described by Ginzburg et al. [55].

The system was coupled to an evaporative light scattering detector (ELSD, model PL-ELS 1000, Polymer Laboratories, Church Stretton, England) to monitor the effluent from the SEC column. The following parameters were set on the ELSD: air flow rate 1.5 L/min, nebulizer temperature 160 °C, evaporation temperature 260 °C. Both ovens, the autosampler and all transfer lines, were thermostated at 160 °C. 2D-LC system handling was done 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.

2.1.2. 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 five 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. The procedure described by Ortin et al. [37] was used to perform TREF × SEC fractionation. A sample is first dissolved in the stainless steel vessel. Once the sample is dissolved, an aliquot is 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 0.5 °C/min. Then a discontinuous elution process is followed by increasing the temperature in 5 °C-steps. TREF fractions with volume 100 μl are then alternatively injected one after other into the SEC column flushed with 1,2,4-trichlorobenzene at flow rate 2.5 mL/min. The SEC column was calibrated with PS standards.

2.1.3. Solvents

1-decanol and 1,2,4-trichlorobenzene (TCB) (Merck, Darmstadt, Germany) were used as the mobile phases and the components of a linear gradient 1-decanol → TCB in the first separation stage at a flow rate of 0.1 mL/min. TCB was used as the mobile phase in SEC with a flow rate of 2.5 mL/min. TCB was freshly distilled, 1-decanol was used, as delivered.

Table 1
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, 8.68 mg; 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 hexene, 8.06 mg; polyhexene 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, 8.85 mg; EP(D)M (6.3 wt.% of ENB, 60 wt.% of ethylene), 14.00 mg; PE 1.18 kg/mol, 7.90 mg	
5	iPP 1.1 kg/mol, 11.78 mg; 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	

2.1.4. Polymer samples

Linear polyethylene (PE) standards with peak molar masses (M_p) in the range of 1.18–126 kg mol^{-1} (PD = 1.12–1.59) and isotactic polypropylene (iPP) with weight average molar mass (M_w) of 1.1 kg/mol were obtained from Polymer Standard Service (Mainz, Germany). Linear PE with M_w = 260 kg·mol^{-1} was obtained from PSD Polymers (Linz, Austria). Samples of linear PE with M_n = 316 kg mol^{-1} (PDI = 1.03) and M_n = 985 kg mol^{-1} (PDI = 1.17) were donated by Prof. S. Mecking (University of Konstanz, Germany). A sample of syndiotactic polypropylene (sPP) with M_w = 196 kg/mol was purchased from Sigma–Aldrich (Munich, Germany). A sample of atactic polypropylene (aPP) with M_w = 211 kg/mol was provided by Dr. I. Mingozzi (LyondellBasell, Ferrara, Italy). Isotactic iPP standards with peak molar masses (M_p) in the range of 60–350 kg mol^{-1} were purchased from American Polymer Standards Corp. (Mentor, OH, USA). iPP with M_w = 45 kg/mol was synthesized at the University of Stellenbosch [57].

A sample of ethylene/hexene (EH) copolymer (18.6 mol.% of hexene) was donated by Dr. Y. Thomann (University of Freiburg, Germany). A sample of ethylene/propylene (EP) rubber (M_w = 165 kg/mol, PDI = 2.1, C2-content = 10.4 wt.%) was provided by Dr. K. Remerie (Sabic-Europe, Netherlands). A sample of ethylene/propylene copolymer (81.3 wt.% of ethylene, M_w = 164 kg/mol, PDI = 3.01) prepared with metallocene catalyst [58,59] was given by Dr. B. Coto (Universidad Rey Juan Carlos, Madrid, Spain). A sample of ethylene/propylene/diene rubber (EP(D)M, diene type – ethylene norbornene 6.3, 60 wt.% of ethylene) was provided by Dr. G. van Doremaele (DSM, Geleen, Netherlands). The individual samples were dissolved in 1-decanol at 160 °C and at a concentration of 2–3 mg/mL. The samples were blended into mixtures (Table 1) and dissolved in 1-decanol at a temperature of 160 °C at a concentration of about 2–3 mg/mL for each component. The dissolution time was between 30 and 180 min depending on the type of the sample or the mixture.

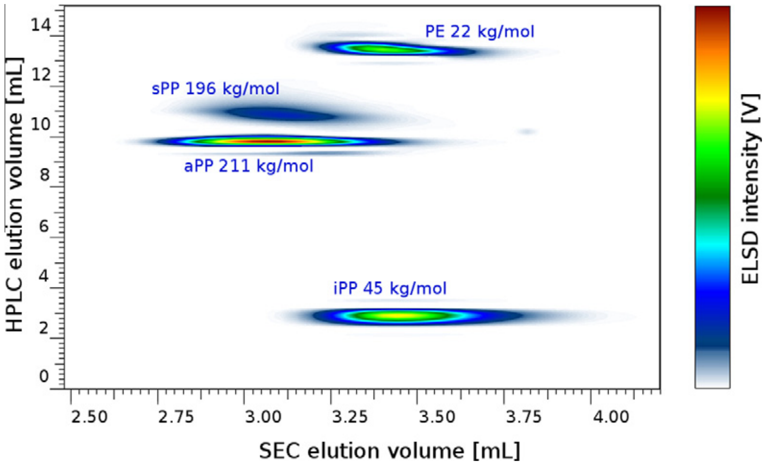

Fig. 2. Contour plot obtained by HT 2D-LC of a blend of iPP 45 kg/mol, aPP 211 kg/mol, sPP 196 kg/mol and PE 22 kg/mol; Columns and flow rates: HPLC: Hypercarb®, 0.1 mL/min; SEC: PL Rapide H, 2.5 mL/min. Temperature: 160 °C.

3. Results and discussion

The separation performance of the HT 2D-LC system was tested by injecting a quaternary mixture of iPP, sPP, aPP and PE. The 2D-contour plot is shown in Fig. 2 where the gradient separation is represented along the *Y*-axis while the elution along the *X*-axis corresponds to the SEC separation. 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 [22].

In order to study the influence of the molar mass of the components on the elution volume in HPLC, a blend consisting of iPP 1.1 kg/mol, iPP 45 kg/mol, aPP 211 kg/mol, sPP 196 kg/mol, PE 1.18 kg/mol and PE 22 kg/mol was analyzed by 2D-LC. The corresponding contour plot is presented in Fig. 3. Isotactic PP 60 kg/mol is separated from the blend of aPP, sPP and PE, however, it elutes in two peaks (Fig. 3). The lower molar mass one elutes in 1-decanol while a fraction with higher molar mass is retained and elutes only after addition of TCB into the mobile phase, i.e., after the start of the gradient elution. This effect is new because it was reported in [22,25] that iPP eluted solely in 1-decanol, independently of its molar mass. This effect will be described in more detail later. We notice that the elution volume of PE standards with $M_w < 14$ kg/mol depends in system Hypercarb/1-decanol/TCB pronouncedly on the molar mass, while the elution volume of PE with larger molar mass is constant [22].

Fig. 4 illustrates the separation of a blend, which contains ethylene/1-hexene copolymer, PE and polyhexene. As can be seen, baseline separation was achieved for all components and even the bimodal molar mass distribution of the polyhexene is clearly reflected. We have shown recently that the elution volumes of ethylene/1-hexene copolymers from 1-decanol on the graphitic surface decreases with increasing comonomer content [25]. It is assumed that the backbone ethylene units adsorb on the graphitic surface and the sterically hindering alkyl branching acts against the adsorption. Consequently the elution volume decreases with the increasing content of 1-hexene in the copolymers. This behaviour is also reflected in Fig. 4: While the ethylene/1-hexene copolymer is retained and

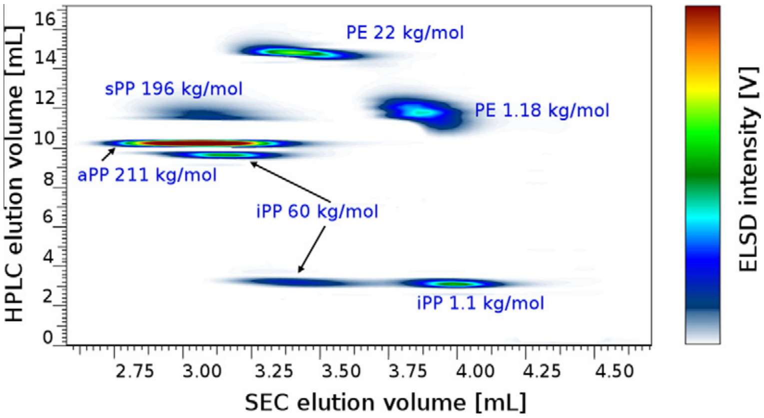

Fig. 3. Contour plot obtained by HT 2D-LC of a blend of iPP 1.1 kg/mol, iPP 60 kg/mol, aPP 211 kg/mol, sPP 196 kg/mol, PE 1.18 kg/mol and PE 22 kg/mol; Exp. conditions as in Fig. 2.

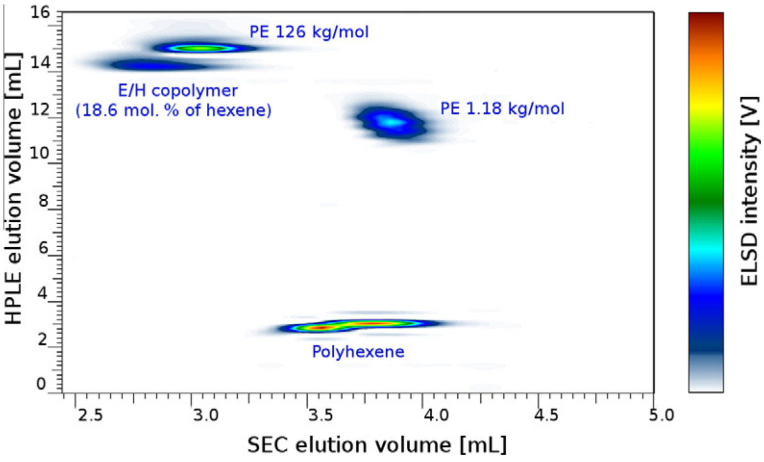

Fig. 4. Contour plot obtained by HT 2D-LC of a blend containing polyhexene, ethylene/1-hexene copolymer (18.6 mol.% of hexene), PE 1.18 kg/mol and PE 126 kg/mol; Exp. conditions as in Fig. 2.

elutes only in the gradient, polyhexene 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. 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 molecular structure–property relationships.

The separation of a model blend containing iPP, low molar mass polyethylene and ethylene/propylene/diene rubber (EP(D)M) rubber is shown in Fig. 5. As can be observed, all components are baseline resolved. EP(D)M rubber 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.

The separation of another amorphous material, ethylene/propylene (EP) rubber, from a blend with PE and iPP is illustrated in Fig. 6. The rubber elutes before the low molecular PE along the HPLC axis. The EP rubber exhibits a bimodal CCD, where 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. 7 shows the 2D-LC separation of a model mixture 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.

3.1. Calibration of SEC separation in 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

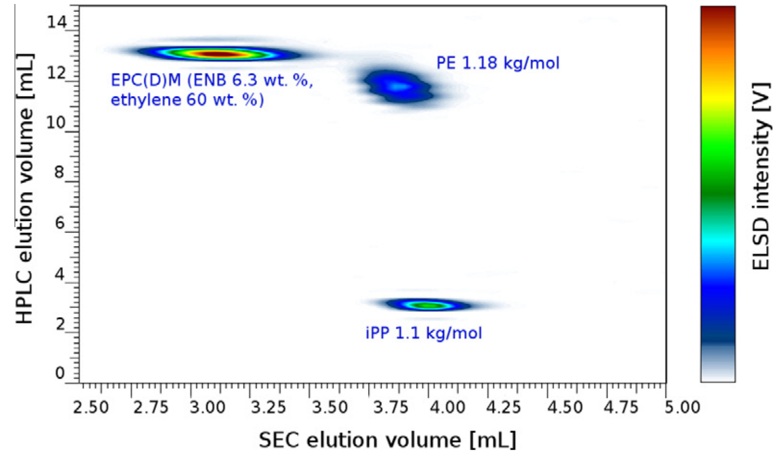

Fig. 5. Contour plot obtained by HT 2D-LC of blend of iPP 1.1 kg/mol, PE 1.18 kg/mol and EP(D)M (6.3 wt.% of ENB, 60 wt.% of ethylene); Exp. conditions as in Fig. 2.

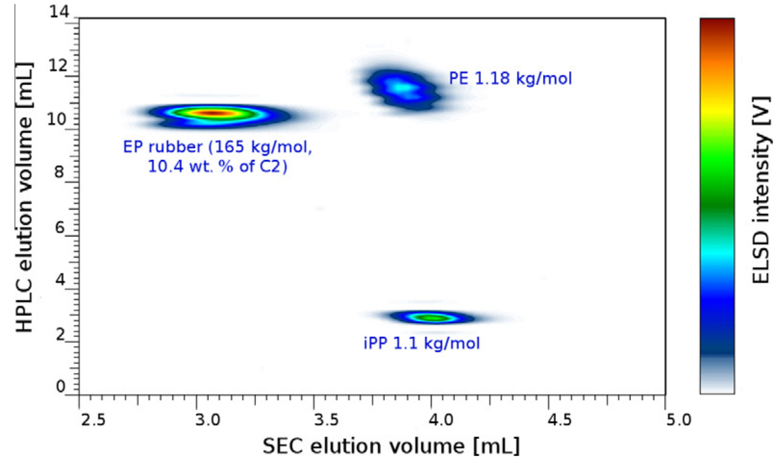

Fig. 6. Contour plot obtained by HT 2D-LC of blend of iPP 1.1 kg/mol, PE 1.18 kg/mol and EP rubber (10.4 wt.% of ethylene, M_w = 165 kg/mol); Exp. conditions as in Fig. 2.

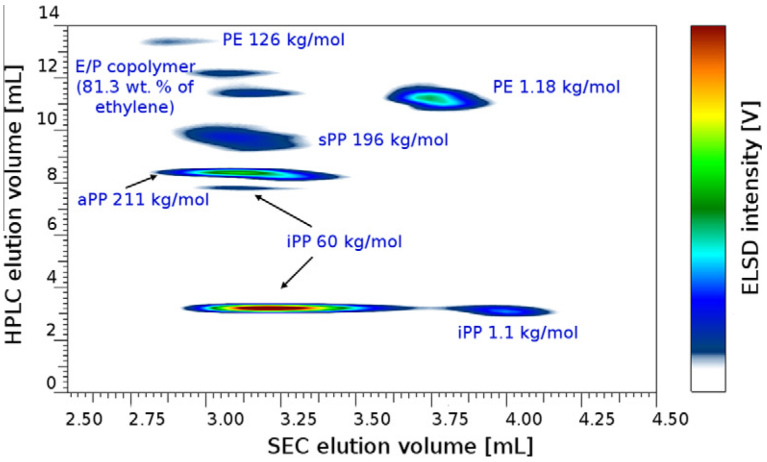

Fig. 7. Contour plot obtained by HT 2D-LC of blend of iPP 1.1 kg/mol, iPP 60 kg/mol, aPP 211 kg/mol, sPP 196 kg/mol, PE 1.18 kg/mol, PE 126 kg/mol and EP copolymer (81.3 wt.% of ethylene, M_w = 164 kg/mol, PDI = 3.01); Exp. conditions as in Fig. 2.

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 to 1-decanol/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 the 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. Figs. 8 and 9 show an overlay of two SEC calibration curves constructed for iPP and PE standards of the various average molar masses. As can be seen, the calibration curves obtained with iPP standards corresponding to the different injection solvents are different (Fig. 8). 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. 9).

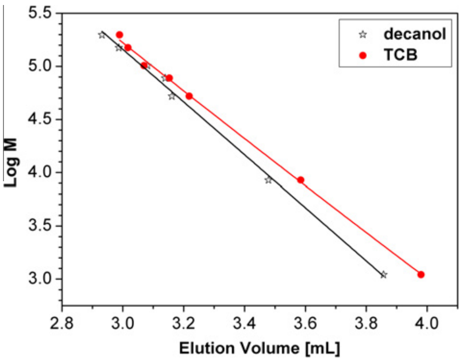

Fig. 8. Overlay of the isotactic PP calibration curves corresponding to two different injection solvents. Stationary phase: PL Rapide H, mobile phase: TCB, 2.5 mL/min, temperature: 160 °C.

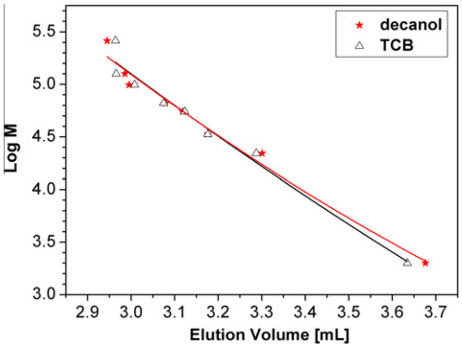

Fig. 9. Overlay of the PE calibration curves corresponding to two different injection solvents. Exp. conditions as in Fig. 8.

The shift between the calibration curves in Fig. 8 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. 9) 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 the PE can exchange its solvating solvent 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 to the entire gradient region.

The molar mass calibration in Fig. 9 corresponds to the SEC column alone. In order to apply this to the 2D-LC, the PE calibration standard should also undergo the HPLC separation and then enter the SEC system via an automated injection [17]. Therefore nine PE standards were injected into the 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. 10.

In contrast to the calibration curve shown in Fig. 9, the points in Fig. 10 are rather scattered. We notice that the

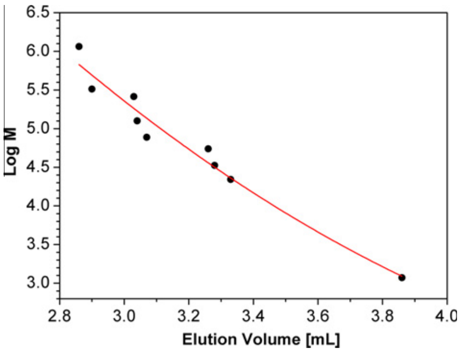

Fig. 10. Calibration curve obtained by injecting PE standards (M_w = 1.18, 22, 33.5, 55, 77.5, 126, 260, 325 and 1152 kg/mol) into the entire HT 2D-LC system (elution volumes at the peak maximum); Exp. conditions as in Fig. 2.

scattering of points for PE standards using the identical SEC column and 2D-LC instrument was observed also in our previous work [55]. On the other hand, a nice calibration line was measured with this SEC column for PS standards in TCB with 2D-LC [55]. The polyethylene standards available on the market are quite broad in comparison with PS standards. 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 SEC column, i.e., increases broadening of peaks. The broadening itself is a function of various parameters, including the type of polymer. This could eventually influence the determination of elution volumes for PE peaks.

It is known that PS standards are most frequently used to calibrate SEC chromatography [16]. We found that PS standards with a molar mass less than 30 kg/mol were adsorbed on Hypercarb® from 1-decanol and can be eluted in a 1-decanol → TCB gradient. 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.

3.2. Separation of isotactic polypropylene in 2D-LC

As mentioned above, it was previously observed that iPP eluted in the system Hypercarb/1-decanol → TCB exclusively in 1-decanol [22,25] while the contour plot in Figs. 3 and 7 indicates that iPP elutes in two peaks, namely one in 1-decanol, the second one after the start of 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. 11 shows the results of these experiments.

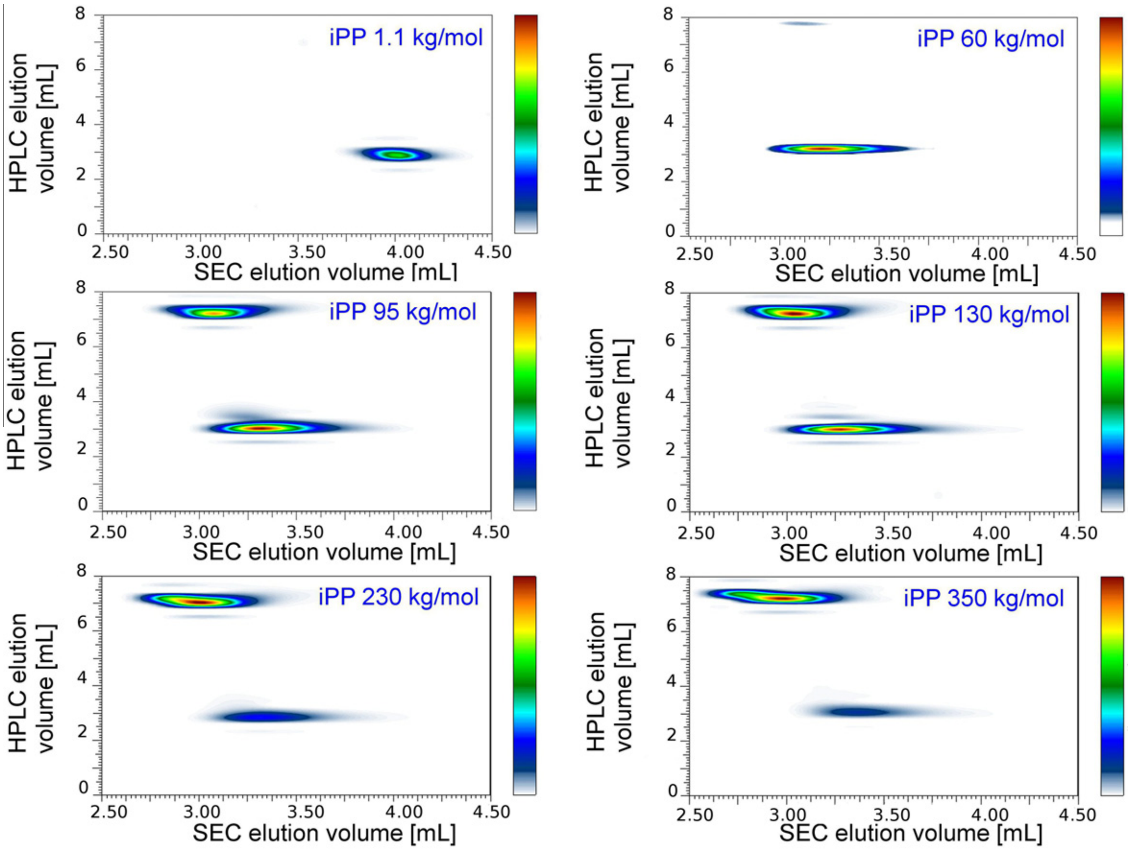

Fig. 11. Contour plots of the HT 2D-LC of iPP with different average molar masses. Exp. conditions as in Fig. 2.

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. Moreover, the higher the molar mass of the injected iPP standard, the larger the part 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 [22–25]. 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 literature (for references, see [22]). It is known that differences in interactions of streoisomeric polymers with a stationary phase may be very delicate [60,61]: For example Berek et al. [60] found that poly(methylmethacrylate) 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 strongly retained. 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.

Response of ELSD, at constant instrumental parameters (gas flow rate, nebulization and evaporation temperature, flow rate of effluent) is proportional to 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 [62,63]. 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 chemical composition distribution will require a calibration of the response of ELSD detector. The influence of these parameters on the response of ELSD for polyolefins has not been described yet in the literature. Alternatively, an infrared detector or a refractometric index detector could be applied instead of ELSD under conditions of HT 2D-LC.

3.3. High-temperature two-dimensional liquid chromatography (HT 2D-LC) vs. TREF × SEC

In order to compare the chromatographic results with the conventional technique, the blends 1, 2, and 5 (Table 1) were cross-fractionated by TREF × SEC. Fig. 12 shows the contour plot of the TREF × SEC of blend 1. The *X*-axis represents the separation in SEC mode, while the *Y*-axis shows the elution temperature in TREF.

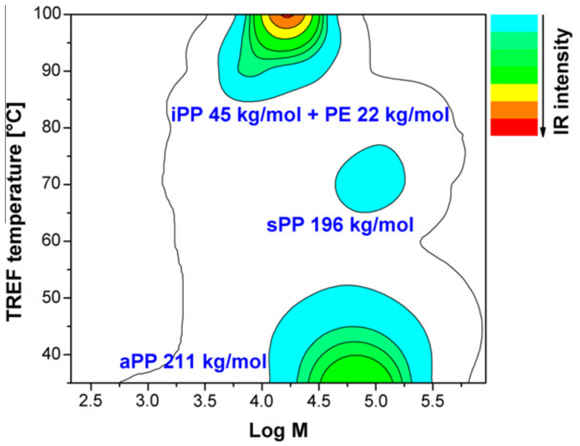

Fig. 12. Contour plot obtained by TREF × SEC of blend 1.

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.

The result of the cross-fractionation of blend 2 is presented in Fig. 13. 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 molecular polyethylene. iPP 60 and PE 22 kg/mol are observed to coelute in temperature range from 105 to 140 °C.

Fig. 14 shows the TREF × SEC separation of mixture 5 containing iPP 1.1 kg/mol, PE 1.18 kg/mol and EP rubber. Low molecular iPP and the EP rubber do not crystallize and, therefore, elute at 35 °C. Low molecular PE crystallizes at 80 °C. Considering the broadness of the elution spot assigned to PE, it can be hypothesized that it contains also a part of the EP rubber which exhibits some degree of crys-

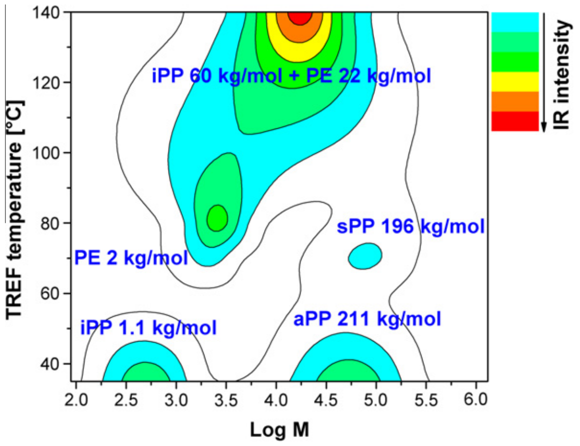

Fig. 13. Contour plot obtained by TREF × SEC of blend 2.

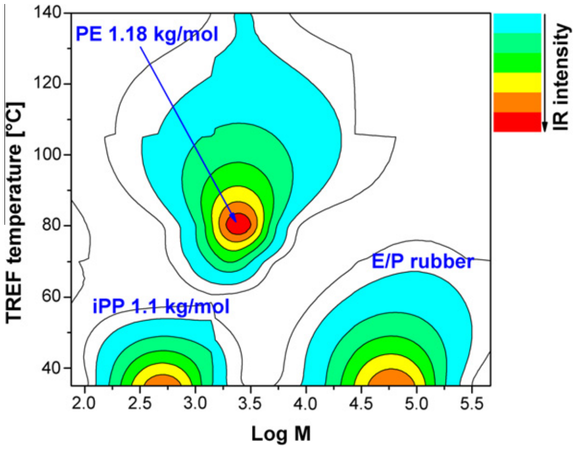

Fig. 14. Contour plot obtained by TREF × SEC of blend 5.

tallinity. However, CRYSTAF analysis of the rubber alone showed that it did not crystallize.

Comparison of the contour plots, which were obtained via TREF × SEC, with the figures 2,3,6 demonstrates that the same blends were perfectly separated in the single components by HT 2D-LC irrespective of their crystallinity.

4. Conclusions

High-temperature two-dimensional liquid chromatography (HT 2D-LC) of polyolefins as well as olefin copolymers has been realized by coupling of interactive high-performance liquid chromatography (HPLC) with SEC at 160 °C. In the first step, the polyolefins were separated with regard to the differences in their chemical composition, while in the second step the obtained fractions were distinguished according to the molar mass distribution. The Hypercarb® column packed with porous graphite particles was used as the stationary phase in the HPLC separation stage. Polystyrene divinyl-based column (PL Rapide H) was used for SEC separations. It could be demonstrated that the sample solvent has an influence on 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. Polyolefin blends, which contained 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 automated TREF × SEC. Comparison of the new developed method with the TREF × SEC revealed that the separation by HT 2D-LC is independent on the crystallinity of the polyolefin samples. As a result, HT 2D-LC is a technique which 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.

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