



Elution behavior of polyethylene and polypropylene standards on carbon sorbents

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ABSTRACT

The elution behavior of linear polyethylene and isotactic, atactic and syndiotactic polypropylene was tested using three different carbon column packings: porous graphite (Hypercarb), porous zirconium oxide covered with carbon (ZirChrom-CARB), and activated carbon TA95. Several polar solvents with boiling points above 150 °C were selected as mobile phases: 2-ethyl-1-hexanol, n-decanol, cyclohexylacetate, hexylacetate, cyclohexanone, ethylene glycol monobutyl ether and one non-polar solvent, n-decane. Polyethylene standards were completely or partially adsorbed in all tested sorbent/solvent systems. Polypropylene standards were partially adsorbed on Hypercarb and carbon TA95, but did not adsorb on ZirChrom-CARB. ZirChrom-CARB retained polyethylene pronouncedly when 2-ethyl-1-hexanol, cyclohexylacetate or hexylacetate were used as mobile phases at temperature 150 or 160 °C, while all three basic stereoisomers of polypropylene eluted in size exclusion mode in these sorbent/solvent pairs. This is very different from the system Hypercarb/1-decanol, which separated polypropylene according to its tacticity. The opposite elution behavior of polyethylene and polypropylene in system ZirChrom-CARB/2-ethyl-1-hexanol (polypropylene eluted, polyethylene fully adsorbed) enabled to realize separation of blends of polyethylene and polypropylene. Ethylene/1-hexene copolymers were separated according to their chemical composition using system Hypercarb/2-ethyl-1-hexanol/1,2,4-trichlorobenzene.

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1. Introduction

Polyethylene (PE) and polypropylene (PP) are basic types of polyolefins. The industrial production of polyolefins, which now exceeds 100 million tons per year, continues to grow exponentially [1]. Research, development, and production of polyolefin based materials require their analytical characterization. Among the available chromatographic methods, size-exclusion chromatography, SEC, is routinely used to measure the molar mass distribution of polyolefins. SEC of polyolefins is carried out at temperatures between 130 and 160 °C, because only at these conditions the semicrystalline polymers are soluble. The ability of polyolefins to crystallize from diluted solutions is basic principle of the temperature gradient elution fractionation (TREF [2]) and crystallization analysis fractionation (CRYSTAF [3]). The both methods are routinely used for separation and characterization of polyolefin materials [2–10]. The crystallization temperature measured by TREF or CRYSTAF correlates with the chemical composition of the polyolefins, i.e., for example, with the chemical composition

of copolymers [2–4,9]. TREF and CRYSTAF require for one analysis relatively long time, i.e., 10–24 h. Moreover, parts of a polyolefin sample, which do not crystallize are not selectively separated. HPLC, on the other hand, has potential to analyse crystallizable as well as amorphous samples in short time and selectively. However, although polyolefins have been industrially produced for more than 70 years, chromatographic systems which enable to separate polyolefins according to their chemical composition were unknown until recent years. The first such chromatographic systems have been developed only in the last few years. PP was separated from PE using liquid chromatography under limiting conditions by Macko et al. [11]. The separation in this chromatographic system was based on differences in the solubility of PE and PP in ethylene glycol monobutyl ether (EGMBE) which selectively dissolves PP but not PE [12]. A substantial improvement in the recovery of the separated PE and PP was achieved by Heinz and Pasch [13] by a gradient elution using EGMBE → 1,2,4-trichlorobenzene (TCB). While isotactic PP eluted in pure EGMBE as mobile phase, PE precipitated onto the column and eluted only when TCB in the gradient reached a certain concentration, which dissolved the precipitated PE. The same HPLC system enabled to separate ethylene–propylene copolymers according to their chemical composition [14].

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Moreover, it was found that PE and PP can be adsorbed on specific zeolites even from eluents which are typically used for SEC of polyolefins, such as TCB and decalin [15,16]. However, the attempts to desorb the adsorbed PE or PP from zeolites were not successful.

A carbon based stationary phase (Hypercarb) enabled for the first time to fractionate PE and PP by a mechanism of adsorption and desorption [17]. Using 1-decanol as mobile phase PP eluted from the Hypercarb column in SEC mode while linear PE, atactic as well as syndiotactic PP were fully adsorbed. These adsorbed polymers were desorbed only after applying a gradient from 1-decanol to 1,2,4-trichlorobenzene. The separation was carried out at temperature 160 °C. With the same chromatographic system copolymers of propene/1-alkene and ethylene/1-alkene were separated by Macko et al. [18] according to their comonomer content.

A number of carbon sorbents are commercially available and some varieties of carbon are industrially produced on a large scale: activated carbon is made from coke and charcoal by controlled oxidation and contains functional groups like –OH, –COOH, >C=O. Acting as polar sorbents with hydrophilic nature their adsorption properties depend on the origin of the raw material and the temperature and atmosphere used during production [19]. Carbon black is made by pyrolysis of oils in an oxygen free environment and is generally hydrophobic. It is used in the tire industry and in the production of various rubber articles.

Since the pioneering work of Kiselev et al. [20,21], carbon sorbents have been increasingly applied in gas and liquid chromatography. However, in most cases these supports had some serious drawbacks like poor mechanical stability, low surface area for interaction, lack of energetically homogeneous surface, and non-uniform pore structure which limited their applications in liquid chromatography (LC). To meet the requirements of LC various procedures for the preparation of carbon sorbents were proposed [22–32] and their adsorption properties studied [33–38]. Hypercarb is a porous graphitic carbon whose application in HPLC and GC was for the first time demonstrated by Gilbert and Knox [24,25]. Its production includes several steps: impregnating a silica gel template with a phenol-hexamine mixture, polymerizing this mixture within the pores of the silica gel, pyrolyzing the resin in nitrogen, dissolving out the silica template, and finally heating the remaining porous carbon to a temperature in excess of 2000 °C. Graphitized carbon black called Carbo-pack is produced by Supelco for application in gas chromatography. Carbon-clad zirconia was prepared by chemical vapour deposition of carbon onto a porous zirconia by Weber and Carr [30,31]. It was also shown that this sorbent is a good alternative to chemically bonded reversed-phase supports as it resolved the isomer mixtures to a greater extent and in a shorter time than ODS column.

Leboda et al. [39] reviewed applications of various carbon sorbents in liquid chromatography. Hypercarb is the most widespread carbon sorbent as the column packing in LC and its applications were recently surveyed by several authors [40–42]. However, chromatographic separations of synthetic polymers using a carbon sorbent were not known with the exception of Eltekov's work [43]. Eltekov studied the extent of adsorption of polychloroprene, polybutadienes, polyoxyethylenes and polydimethylsiloxanes from solvents onto carbon black. Similar measurements were reported by Vuillaume et al. for polybutadienes/toluene on carbon black [44,45].

N-alkanes are oligomers of ethylene and several authors demonstrated that linear or branched alkanes are retained on carbon column packings. Either the retention of alkanes in liquid chromatography [33,36,38] or adsorption isotherms of alkanes [46–48] were studied. Methanol–water, i.e., a polar solvent, was used as

the mobile phase in most cases. Such polar mobile phase is non-solvents for high molar mass alkanes and dissolve only alkanes with low molar mass (<C₃₂). Due to their semicrystalline nature PE and PP require solvents with boiling point above 130 °C for their dissolution. A series of polar liquids, which dissolve PE and PP, was identified experimentally [49]. These solvents represent potentially suitable mobile phases to realize interactive liquid chromatography of polyolefins.

The system Hypercarb/1-decanol/1,2,4-trichlorobenzene is the first and only one sorbent/solvent system published [17], which enables adsorption as well as desorption of PE and PP. Considering the ability of the carbon sorbent, Hypercarb, to fractionate PP, PE and propene/1-alkene copolymers [17,18], two additional carbon based sorbents namely Zirchrom CARB and activated carbon TA 95 along with Hypercarb were tested in combination with several polar solvents as mobile phase. The focus of this study was to find new sorbent/solvent systems for the separation of PE or PP with the adsorption liquid chromatography. Such systems may enable in the future to separate also polyolefins which are not retained in the first published chromatographic system enabling adsorption/desorption of polyolefins, i.e., in Hypercarb/1-decanol/1,2,4-trichlorobenzene [17]. Moreover, new sorbent/solvents systems may possess separation selectivity, which would differ from selectivity of Hypercarb/1-decanol/1,2,4-trichlorobenzene, for example that tacticity of PP will play no role in the separation.

2. Experimental

2.1. Instruments

A high-temperature liquid chromatograph PL XT-220 (Polymer Laboratories, Varian Inc., Church Stretton, United Kingdom) was used. Dissolution and injection of samples were performed using a robotic sample handling system PL-XTR (Polymer Laboratories). The temperature of the sample block, injection needle, injection port and the transfer line between the autosampler and the column compartment was set at 160 °C for 2-ethyl-1-hexanol, cyclohexylacetate, 1-decanol and n-decane, at 165 °C for EGMBE, at 150 °C for n-hexylacetate and at 140 °C for cyclohexanone. The column outlet was connected to an evaporative light scattering detector (ELSD, model PL-ELS 1000, Polymer Laboratories). The ELSD was run at a nebulization temperature of 160 °C for cyclohexanone, 1-decanol, 2-ethyl-1-hexanol, TCB and cyclohexylacetate, 170 °C for n-hexylacetate, EGMBE and n-decane, an evaporation temperature of 200 °C for cyclohexanone, n-hexylacetate, EGMBE and n-decane, 270 °C for cyclohexylacetate, 1-decanol, 2-ethyl-1-hexanol and TCB and with an air velocity of 1.5 L/min. The mobile phase flow rate was 1 mL/min. WinGPC-Software (Polymer Standards Service GmbH, Mainz, Germany) was used for data collection and processing.

A part of measurements was realized using the high-temperature liquid chromatograph PL-GPC 210 (Polymer Laboratories, Varian Inc., Church Stretton, United Kingdom). As detector a second ELSD (model PL-ELS 1000, Polymer Laboratories) was used. The gas leaving this ELSD was cooled in a metal tube (10 m × 1 cm i.d.), which was poured into circulating water at temperature 10 °C. This cooling ensured the condensation of 1-decanol. All other experimental parameters were the same as described for the chromatograph PL XT-220.

We notice that the used ELSD detectors may have very different responses, which depends on the selected output signal (1/1 or 1/10 of the original signal), on the adjustment of a needle in the evaporator as well as on the purity of the glass lenses and the evaporator tube.

Table 1
Elution behavior of PE and PP standards in tested sorbent/solvent systems.

Polymer/solvent and temperature	Sorbent											
	ZirChrom-CARB				Hypercarb				Activated carbon TA 95			
	PE	iPP	aPP	sPP	PE	iPP	aPP	sPP	PE	iPP	aPP	sPP
2-Ethyl-1-hexanol, 160 °C	FR	E	E	E	FR	PR	PR	PR	PR	PR	PR	PR
1-Decanol, 160 °C	FR	E	E	E	FR	E	FR	FR	PR	E	PR	PR
Hexylacetate, 150 °C	FR	E	E	E	PR	PR	PR	PR	PR	PR	PR	PR
Cyclohexylacetate, 160 °C	FR	E	E	E	FR	PR	PR	PR	PR	PR	PR	PR
Cyclohexanone, 140 °C	PR	E	E	E	PR	PR	PR	PR	FR	PR	PR	PR
n-Decane, 140 °C	PR	E	E	E	FR	PR	PR	PR	FR	PR	PR	PR
EGMBE, 165 °C	NS	E	PS	PS	NS	PR	PS	PS	NS	PR	PS	PS

Symbols: FR, fully retained (all PE or PP standards fully retained, i.e., they eluted exclusively after the start of the gradient elution); PR, partially retained (PE or PP standards eluted in two peaks, i.e., not adsorbed macromolecules eluted isocratically, the retained macromolecules eluted after the start of the gradient elution); E, eluted; NS, not soluble; PS, partially soluble (only a part of sample with small molar mass was soluble).

2.2. Stationary phases

Three different carbon containing sorbents were used as the column packing:

Porous graphite Hypercarb (Thermo Scientific, Dreiech, Germany) with a particle diameter of 5 μm , a surface area of 120 m^2/g , a pore size of 250 \AA and the column with dimensions 100 $\text{mm} \times 4.6 \text{ mm i.d.}$

Carbon-clad zirconia particles, ZirChrom-CARB (ZirChrom Separations, Anoka, MN, USA), with a particle diameter of 5 μm packed in column 100 $\text{mm} \times 4.6 \text{ mm i.d.}$

Activated carbon TA 95 (PICA, Vierzon, France) with particle diameter about 1 mm, a surface area 1585 m^2/g and an average pore diameter of about 8 \AA [47]. The elemental composition of TA 95 determined by elemental analysis is: H: 0.63%, N: 0.00%, S: 0.10%, O: 4.99%, and Cl: 0.00% [48]. The carbon particles were dry-packed in a column with dimensions 150 $\text{mm} \times 4.6 \text{ mm i.d.}$

2.3. Mobile phases

2-Ethyl-1-hexanol, cyclohexylacetate, n-hexylacetate, cyclohexanone, ethylene glycol monobutylether (EGMBE), n-decane, n-decanol, and 1,2,4-trichlorobenzene (TCB), all of synthesis quality were obtained from Merck, Darmstadt, Germany. The mobile phase was either a single solvent or a binary gradient. In such case after injection of a sample an isocratic elution follows for 3 min before starting a 10 min linear gradient to reach 100% TCB in all the gradient runs. The gradient reaches the detector with a delay of 3.7 min with Hypercarb and 3.5 min with both ZirChrom-CARB and activated carbon TA 95 (after starting the gradient in pump) in the chromatograph PL XTR 220.

2.4. Polymer samples

Linear PE standards with weight average molar masses, M_w , from 2 to 181 kg/mol and isotactic PP (iPP) 1.1 kg/mol were obtained from Polymer Standards Service (Mainz, Germany). Their polydispersity (M_w/M_n) was in the range of 1.2–1.7. PE with weight average molar mass of 260 kg/mol was purchased from PSD Polymers (Linz, Austria). Isotactic PP (iPP) standards with M_w in the range of 6–136 kg/mol and polydispersity range 2.0–3.7 were purchased from American Polymer Standards (Mentor, OH, USA). A sample of atactic PP (aPP) with M_w of 315 kg/mol was provided by Dr. I. Mingozzi (LyondellBasell, Ferrara, Italy). Syndiotactic PP (sPP) with M_w of 196 kg/mol was obtained from Sigma–Aldrich (Munich, Germany). The random ethylene/1-hexene copolymers were obtained from Dr. Y. Thomann (University of Freiburg, Freiburg, Germany). The samples were dissolved in the respective mobile phase at a concentration of about 1–3 mg/mL . The disso-

lution temperature and time varied with solvent from 140 °C to 160 °C and 60 min to 180 min respectively. 40 μL of each sample solution were injected.

3. Results and discussion

The polymer samples were dissolved in the respective mobile phase and injected separately into a capillary (without column) before injecting into columns packed with the carbon sorbents. Comparison of peak areas obtained with the column and without the column indicates the extent of adsorption of the polymer sample. Every time before using another solvent as the mobile phase, adsorbed polymer was removed from the column by purging with pure TCB. In the selected sorbent/solvent systems each adsorbed polymer was desorbed by a linear gradient starting with the polar solvent and ending with pure TCB. Because a repeated desorption with TCB did not generate any peak on chromatogram and the measurements were reproducible in long period of time, it is supposed that the adsorbed polymers were fully desorbed by TCB. All tested sorbent/solvent systems and the corresponding elution behavior of PP and PE standards are summarized in Table 1.

The basic types of the elution behavior of PE and PP standards are illustrated in the figures. Fig. 1 shows the chromatograms obtained with the system ZirChrom-CARB/2-ethyl-1-hexanol. While PE was fully retained in the column (i.e., no peaks of PE appeared on chromatograms as shown in Fig. 1a), all stereoisomers of PP were eluted in SEC mode (Fig. 1b). The SEC separation in this column packing is, however, quite poor due to the small pore volume of the sorbent. As a result, the difference in the elution volumes for the biggest and the smallest macromolecules is small, only about 0.2 mL. PE standards were fully retained on Hypercarb (Table 1) and partially retained on carbon TA 95 from 2-ethyl-1-hexanol, i.e., in this case the peak areas obtained with the columns were smaller than the peak areas obtained without the columns in the column oven (Fig. 2). In contrast to the elution of PP in ZirChrom-CARB/2-ethyl-1-hexanol (Fig. 1b), PP samples were partially retained in Hypercarb/2-ethyl-1-hexanol and carbon TA 95/2-ethyl-1-hexanol (Table 1).

In the system Hypercarb/1-decanol only iPP eluted in SEC mode, while sPP, aPP and PE were fully retained [17]. They eluted only after the application of a linear gradient from 1-decanol to TCB [17]. Under the same conditions the elution behavior of PE and PP was tested using ZirChrom-CARB and activated carbon TA 95. The results are summarized in Table 1 and chromatograms of PE are shown in Figs. 3 and 4.

In difference to the elution of PP in Hypercarb/1-decanol all isomers of PP eluted in SEC mode in both ZirChrom-CARB/1-decanol and activated carbon TA 95/1-decanol i.e., no influence of the tacticity was observed on the elution. PE with 2 kg/mol was not retained

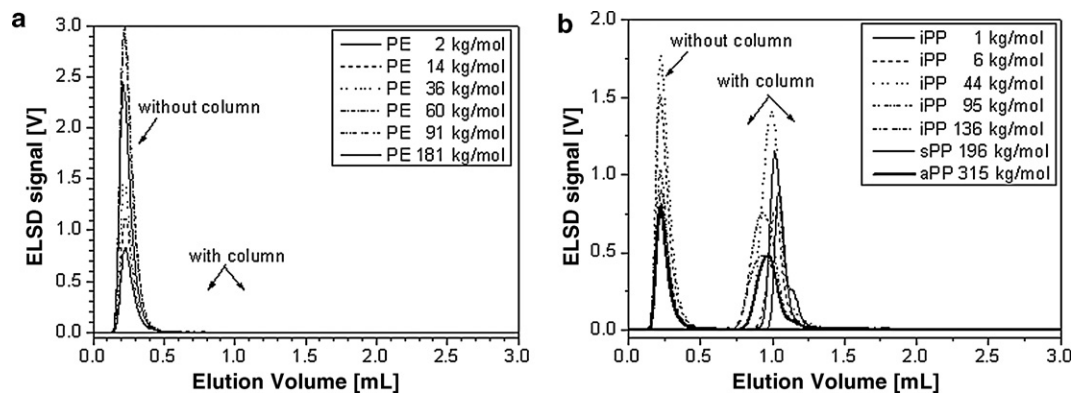


Fig. 1. Overlay of chromatograms (a) PE standards and (b) PP standards. Sorbent: ZirChrom-CARB. Mobile phase: 2-ethyl-1-hexanol. Temperature: 160 °C. Chromatograph: PL XT-220.

in ZirChrom-CARB/1-decanol, but PE standards with higher molar mass were fully retained (Fig. 3), i.e., almost all PE standards were fully retained. The elution volumes of PE with $M_w > 16$ kg/mol are almost identical. It indicates that the separation is governed mainly by the chemical composition of the polymers (PE contra PP) and the molar mass of the samples play a secondary role.

Fig. 4 illustrates a partial adsorption of PE on the activated carbon TA 95 from n-decanol: One part of the PE standard elutes in

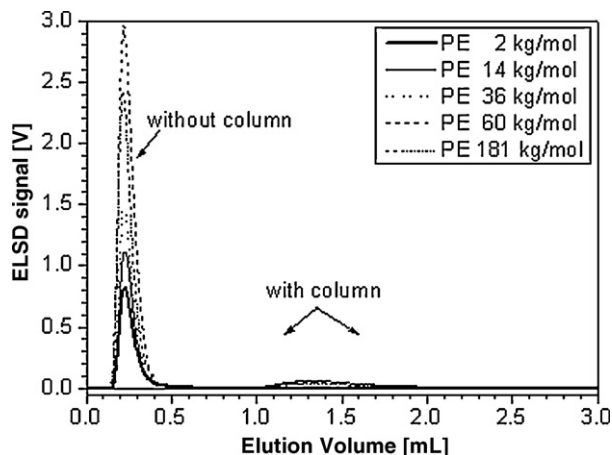


Fig. 2. Overlay of chromatograms illustrating full adsorption of PE standards. Sorbent: activated carbon TA 95. Mobile phase: 2-ethyl-1-hexanol. Temperature: 160 °C. Chromatograph: PL XT-220.

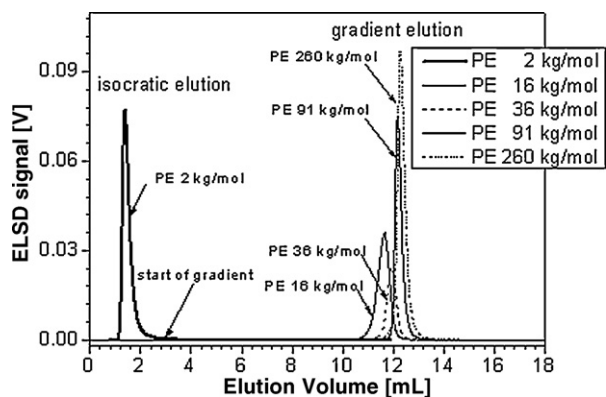


Fig. 3. Overlay of chromatograms illustrating partial adsorption of PE standards. Sorbent: ZirChrom-CARB. Mobile phase: n-decanol and gradient n-decanol → TCB. Temperature: 160 °C. Start of gradient in pump is indicated in the figure. Chromatograph: PL-GPC 210.

1-decanol (i.e., is not retained in the carbon TA 95) and the other part elutes only after the start of the gradient 1-decanol → TCB (i.e., after desorption of the retained macromolecules). Comparison of the peak heights in Fig. 4 indicates that PE standards with smaller molar mass were adsorbed to a larger extent. This effect for PE and PP was found also in system carbon TA 95/cyclohexylacetate. As the pores in carbon TA 95 are very small (8 Å), it is expected that the accessibility of pores for polymers with higher molar mass is limited, which influences the extent of their interaction with sorbent. Carbon TA 95 contains polar groups [48], which are not present in both Hypercarb and Zir-Chrom CARB. We suppose that due to these features of the carbon TA 95 PE and PP are either pronouncedly retained (Fig. 2, 2-ethyl-1-hexanol) or the extent of the polymer adsorption decreased with increasing molar mass (Fig. 4, 1-decanol) depending on the mobile phase used.

EGMBE was the first solvent which enabled the partial retention by precipitation–dissolution of PE, while eluting isotactic PP in SEC mode [11,13]. Isotactic PP is soluble in EGMBE at 140 °C, but PE with higher molar mass ($> \sim 20$ kg/mol) is not [12]. EGMBE is a polar solvent and therefore it could enhance the adsorption of PP. Unfortunately atactic PP and syndiotactic PP with higher molar mass is not completely soluble in EGMBE. Isotactic PP standards eluted in SEC mode from the ZirChrom-CARB column. Smaller peak areas and a slight increase in elution volume with molar mass from the column Hypercarb indicated that partial adsorption of iPP onto Hypercarb from EGMBE took place. Pronounced adsorption of iPP on activated carbon TA95 was observed from EGMBE (Table 1).

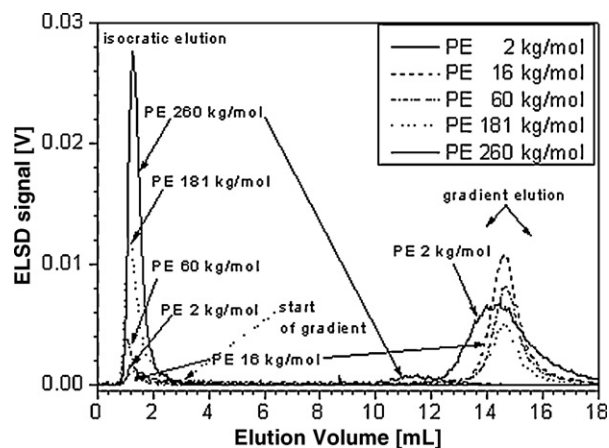


Fig. 4. Overlay of chromatograms illustrating partial retention of PE standards. Sorbent: activated carbon TA 95. Mobile phase: n-decanol and gradient n-decanol → TCB. Temperature: 160 °C. Start of gradient in pump is indicated in the figure. Chromatograph: PL-GPC 210.

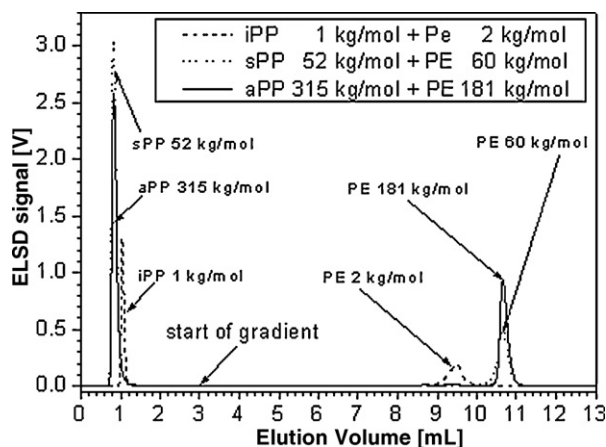


Fig. 5. Overlay of chromatograms obtained after injection of PE and PP blends. Sorbent: ZirChrom-CARB. Mobile phase: 2-ethyl-1-hexanol and gradient 2-ethyl-1-hexanol → TCB. Temperature: 160 °C. Start of gradient in pump is shown in the figure. Chromatograph: PL XT-220.

It is known that n-alkane with a higher molar mass is adsorbed preferentially on a carbon sorbent from a mixture of the two n-alkanes [46,48]. Taking this into account, the retention behavior of PE and PP from a non-polar solvent, n-decane, was tested. It was found that PE standards were fully retained on activated carbon TA 95, i.e., all PE standards eluted only in the gradient and partially retained on ZirChrom-CARB and Hypercarb from n-decane. PP standards were almost fully retained on carbon TA 95, partially retained on Hypercarb and eluted in SEC mode from ZirChrom-CARB with n-decane (Table 1). We found previously that linear PE may be strongly adsorbed on zeolites from specific non-polar solvents (for example, from decalin [15]), however, the attempts to desorb the polymer were not successful. N-decane is the first non-polar solvent from which PE and PP were adsorbed on a sorbent as well as desorbed (Table 1).

All the tested carbon sorbents contain ideally (atomic) flat structures of graphite. The conductive nature makes it possible to visualize molecules adsorbed on graphite by scanning tunneling microscopy with a very high resolution (atomic) [50–52]. It was found that alkanes (i.e., oligomers of ethylene) adsorb and form single monomolecular layers on graphite [50–52]. The adsorbed molecules appear to be oriented with their carbon skeleton parallel to the graphite surface plane [50–53]. A lattice fit between the graphite basal plane and the chain molecules in their extended conformation causes strong attractive interactions of the chains with the graphite surface. We suppose that these conclusions may be applied also for PE chains adsorbed on the tested carbon sorbents, such as Hypercarb and ZirChrom-CARB. In the case of carbon TA 95, however, functional groups (–OH, =CO, –COOH) present in the sorbent [48] could influence the conformations of PE chains.

Three chromatographic systems, i.e., ZirChrom-CARB in combination with 2-ethyl-1-hexanol, n-hexylacetate and cyclohexylacetate as mobile phase seem to be particularly suitable for HPLC of polyolefins. Unlike the chromatographic behavior described by Macko and Pasch [17], where iPP eluted in SEC mode and sPP and aPP eluted in adsorption mode, the tacticity of PP does not influence the elution behavior of PP in these three sorbent/solvent systems. All PP standards eluted in SEC mode irrespective of their tacticity. As this chromatographic system shows contrast behavior for both PP and PE standards, blends of these polymers were injected into ZirChrom-CARB using a gradient from 2-ethyl-1-hexanol to TCB. The obtained chromatograms are shown in Fig. 5.

As it is shown in Fig. 5, PE with a wide range of average molar mass were perfectly separated from PP, while the tacticity of PP

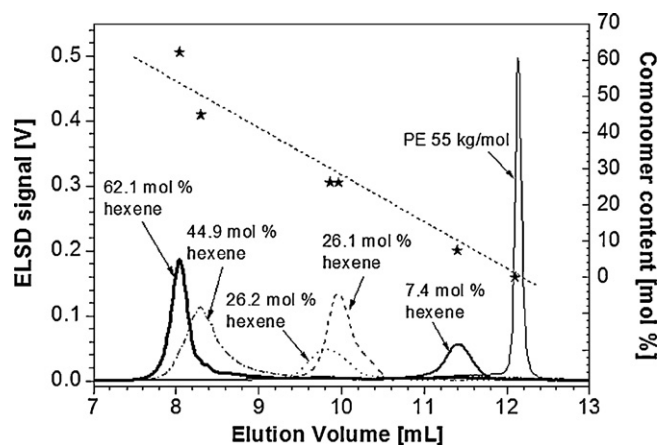


Fig. 6. Overlay of chromatograms of random ethylene/1-hexene copolymers and correlation between the elution volume and the comonomer content. Sorbent: Hypercarb. Mobile phase: 2-ethyl-1-hexanol and gradient 2-ethyl-1-hexanol → TCB. Temperature: 160 °C. Start of gradient in pump is shown in the figure. Chromatograph: PL XT-220.

does not influence the separation. PP standards elute in SEC mode (i.e., iPP 1 kg/mol eluted after sPP 52 kg/mol and aPP 315 kg/mol; both PP with higher molar mass were sterically excluded from the pores of the column packing), however the difference between the elution volumes is very small. PE standards elute only after the start of the gradient. This chromatographic system separates also PE < 20 kg/mol from PP, which was not possible with the first HPLC systems which were applied for the separation of PP and PE blends [11,13].

Using the same chromatographic conditions mentioned in Fig. 5 ethylene/1-hexene copolymers eluted with respect to the concentration of 1-hexene in the copolymers (Fig. 6). Copolymers containing above 46 mol.% of 1-hexene were not retained on ZirChrom-CARB from 2-ethyl-1-hexanol. On the other hand, the copolymers in range between 0 and 62 mol.% hexene were fully retained on Hypercarb from 2-ethyl-1-hexanol and desorbed after the start of the gradient elution. The retention of the copolymers increases linearly with the concentration of ethylene in the copolymers indicating that the incorporation of butyl branches leads to a decrease in the adsorption. The branching decreases the probability of the chains to localize near the carbon surface in planar conformation [46], which is a prerequisite for the intense interactions between sorbent and macromolecules.

4. Conclusion

Three carbon based sorbents were tested as stationary phase for liquid chromatography of linear PE and PP. It was found that all of them adsorb PE and/or PP to different extent, depending on the solvent used. PE was most pronouncedly adsorbed on ZirChrom-CARB from 2-ethyl-1-hexanol, cyclohexylacetate, n-hexylacetate; on Hypercarb from 2-ethyl-1-hexanol, cyclohexylacetate and n-decane; on activated carbon TA95 from n-decane. While the system Hypercarb/1-decanol/TCB enabled to separate PP with different tacticity [17], Hypercarb with other solvents (Table 1) lead to partial adsorption of all PP isomers. On the other hand, ZirChrom-CARB when combined with the mobile phase 2-ethyl-1-hexanol, n-hexylacetate or cyclohexylacetate did not retain isotactic, syndiotactic or atactic PP. PP eluted in SEC mode and this enabled to realize superior separation of PP from PE, as it was demonstrated using ZirChrom-CARB and gradient from 2-ethyl-1-hexanol to TCB. Thus the described new sorbent/solvent systems have different selectivity from previously known HPLC systems for the separation of PE and PP [11,13,17]. Pronounced adsorption of PE enabled

to realize also the separation of ethylene/1-hexene copolymers in this chromatographic system. The copolymers eluted according to their chemical composition.

HPLC is a new method for separation of PE, PP and other polyolefins. The presented work enlarges substantially number of HPLC sorbent/solvent systems suitable for realization of high-temperature adsorption liquid chromatography of polyolefins. In comparison with the commonly used methods, i.e., TREF and CRYSTAF, HPLC analysis requires smaller amount of both time and solvents. Moreover, the crystallizable as well as amorphous polyolefin samples may be selectively analyzed. Thus high-temperature interactive liquid chromatography of polyolefins has potential to be used in R&D laboratories similarly like high-temperature SEC, which is the most used method for determination of molar masses of polyolefins.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chroma.2010.10.036](https://doi.org/10.1016/j.chroma.2010.10.036).

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