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Separation of propene/1-alkene and ethylene/1-alkene copolymers by high-temperature adsorption liquid chromatography

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ABSTRACT

A high performance liquid chromatography column (HPLC) Hypercarb® packed with porous graphite has proven to discriminate polyolefin molecules due to differences in their adsorption and desorption behaviour. While linear polyethylene (PE) and syndiotactic polypropylene (sPP) are adsorbed on the graphite packing, isotactic polypropylene (iPP) is not adsorbed. The column operates at 160 °C with 1-decanol as sample solvent and mobile phase. We have now tested this HPLC system for separations of random propene/1-alkene and ethylene/1-hexene copolymers: While copolymers of propene with 1-butene, 1-hexene and 1-octene copolymers eluted in size exclusion mode without adsorption, propene/1-octadecene and ethylene/1-hexene copolymers are strongly retained and eluted only after application of a linear gradient starting from 1-decanol and ending with pure 1,2,4-trichlorobenzene. The retention of propene/1-alkene (>11 carbons in the side chain) copolymers increases with the concentration of comonomer, making this HPLC system suitable to separate these copolymers according to their chemical composition. In contrast, the retention of ethylene/1-hexene samples decreases with increasing 1-hexene content. Branching in this case shortens the length of continuous methylene sequences of the polymer backbone, which are expected to adsorb in a planar conformation to the graphite layers. This is the first report on the separation of short chain branched polyolefins by high-temperature adsorption liquid chromatography.

1. Introduction

In the current polyolefin industry, polyethylenes (PEs), polypropylenes (PPs), their copolymers, and blends are the most widely used thermoplastics. Their large range of applications is possible because of their facile ability to change crystallinity via altering chain structure. A common route to introduce defects into the linear homopolymer chain, and thus reduce crystallinity, is the copolymerization of the ethylene and propene monomers with relatively low contents of other 1-alkene comonomers. Moreover, the final product properties not only depend on the overall degree of crystallinity but on how the crystallinity develops during processing. The latter is strongly influenced by the inter and intra-chain comonomer distribution and by the molecular weight distribution.

Two common methods to characterize inter-molecular comonomer composition are temperature rising elution fractionation (TREF) and crystallization analysis fractionation (CRYSTAF) [1–3]. Both methods rely on the analysis of the crystallizability of these materials from dilute solution which in turn depends in the content of the comonomer and the branching microstructure on the basis of Flory's equilibrium theory [4,5]. TREF and CRYSTAF are effective due to their sensitivity in identifying even small differences in crystallinity distribution, and have been used to study the compositional distribution in ethylene/1-alkene [6–17] as well as in propene/1-alkene copolymers [18–21]. The results from TREF are often combined with data from DSC, FTIR, NMR, size exclusion chromatography (SEC), and other techniques to further understand the compositional heterogeneity in more detail [22–25]. However, CRYSTAF and TREF fail to characterize the comonomer distribution in samples with low levels of crystallinity or in amorphous ethylene- or propene-based copolymers.

Among all chromatographic methods only SEC is routinely used, and mainly for evaluation of the molar mass distribution of polyolefins [26–31]. Interactive liquid chromatography is widely used to

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characterize the chemical heterogeneity of copolymers and blends that are soluble at room temperature [32,33]. However, since most commercial PEs and PPs are insoluble at room temperature, high performance liquid chromatography (HPLC) has not been applicable to separate these copolymers according to their comonomer content. In addition to a limited choice of solvents for PEs and PPs, differences in the interaction between the polymer molecules in the mobile phase and the stationary phase were expected to be minimal at high temperature, restricting the fractionation applicability using HPLC techniques.

Only recently has HPLC been successfully applied to characterize blends of PE and PP [34–40]. The retention of PE was based on the fact that high molar mass PE precipitates in ethylene glycol monobutylether (EGMBE) at 140 °C in a HPLC column, while PP chains are fully soluble and elute in SEC mode [34,35,40]. Thus, blends of iPP and PE could be separated using a gradient of EGMBE and 1,2,4-trichlorobenzene (TCB) at 140 °C and bare silica gel as the stationary phase [34]. HPLC separation of ethylene-propylene copolymers [36] according to their chemical composition was also reported. In these cases the separation is based on a mechanism of precipitation and re-dissolution, i.e. no adsorption takes place. The first example of adsorption of non polar polyolefins is the adsorption of PE and PP in chromatographic columns packed with zeolites which has been described recently [37–39]. The adsorption on zeolites enabled removing either PE or PP from their blends [38], however, it was not possible to desorb the adsorbed PE and PP from the stationary phase.

Aiming to aid desorption from the stationary phase, the present work describes the use of porous graphite as a suitable column packing for the chromatographic separation of polyolefins and their copolymers. Porous graphite was first described as a stationary phase in chromatography in the mid 1970s by Kiselev et al. [41]. Various methodologies for its synthesis have been described since then [42–44]. The retention characteristics of porous graphite which were described by Knox et al. [44] and by Pereira [45] are based on London interactions, i.e. a temporal dipole of the molecule induces a mirrored dipole on the surface of the stationary phase. Attraction interactions, inducing enhanced nucleation in PE crystallization were further confirmed between PE and the surface of graphite [46,47]. As the adsorption liquid chromatography may be driven by similar surface interactions, thermally stable graphite should be considered as an attractive porous media for the separation of polyolefins, as demonstrated in a recent work [48], and for the separation of olefin copolymers containing non polar comonomer units. The adsorption selectivity of polyolefins to porous graphite was found to be controlled by the geometrical structure of the analyte molecules [48]. On this basis, the HPLC system recently described enabled separation of linear PE from isotactic polypropylene as well as separation of polypropylene according to its tacticity [48].

In this work we describe the use of interactive HPLC, with porous graphite as column packing, for the characterization and fractionation of ethylene/1-hexene as well as propene/1-alkene copolymers according to their comonomer content.

2. Materials and methods

2.1. Instrumentation

All measurements were carried out in a high-temperature chromatograph PL-GPC 210 (Polymer Labs, Church Stretton, England) connected to an evaporative light scattering detector (ELSD, model PL-ELS 1000, Polymer Labs, Church Stretton, England). The following parameters were used at the ELSD: gas flow rate 1.5 L/min, nebulizer temperature 160 °C, evaporator temperature 260 °C. A quaternary gradient pump (model Agilent 1200 Series) was used for all measurements. The flow rate of the mobile phase was 0.5 mL/min.

The characteristics of the column are as follows: 100 mm length x 4.6 mm i.d. packed with porous graphite particles with a particle diameter of 5 µm, a surface area of 120 m^2/g, and a pore size of 250 Å. Brand: Hypercarb®, Thermo Scientific, Dreieich, Germany. The column was placed in the column oven and thermostated at 160 °C.

2.2. Solvents, mobile phase

1-decanol and 1,2,4-trichlorobenzene (TCB, VWR, Darmstadt, Germany) were used as the mobile phases and to form a linear gradient 1-decanol/TCB. The composition of the mobile phase was changed in 10 min from 0 to 100% of TCB, subsequently, pure TCB was pumped for 10 additional minutes. A linear gradient from 100 to 0% of TCB followed in 2 min. Finally, the column was purged for 25 min with pure 1-decanol.

2.3. Polymer samples

The polymers analyzed were first dissolved in 1-decanol at 160 °C at a concentration of about 1–2 mg/mL. The time of dissolution for the samples varied between 30 and 100 min. 13 µL of each sample solution were injected in the column.

Linear PE standards with peak molar masses from 2 to 126 kg/mol were obtained from Polymer Standards Service GmbH, Mainz, Germany. Linear PE with $M_w = 260$ kg/mol was purchased from PSD Polymers, Linz, Austria. Isotactic PP (iPP) standards were purchased from American Polymer Standards Corp., Mentor, OH, USA. Samples of syndiotactic PP (sPP) with M_w of 18-193 kg/mol provided by Prof. S. Bo [49] were used for preparation of blends (Table 1). Each ternary blend was dissolved in 1.5 mL of 1-decanol.

The type and content of comonomer and the average molar masses of all copolymers analyzed by HPLC in this study are listed in Table 2.

3. Results and discussion

Building from prior data on binary blends of iPP/sPP, sPP/aPP and sPP/PE that used the same Hypercarb® column [48], we first test the separation capabilities of this column with ternary mixtures of iPP, sPP and linear PE with different average molar masses. The elugrams of the mixtures (Table 1) analyzed are shown in Fig. 1.

The chromatograms of Fig. 1 show that iPP is eluted in 1-decanol, while sPP and linear PE are fully retained (adsorbed) in the column packing and elute (desorb) only with the gradient. Although the molar mass of the components influences the elution volume, i.e., PE 2 kg/mol is eluted before PE 22 kg/mol and PE 260 kg/mol, and the same trend is observed for sPP, the separation is mainly driven by the type of polyolefin and its tacticity. Isotactic

Table 1
Composition of blends.

	iPP M_w; weight[a]	sPP M_w; weight[a]	PE M_w; weight[a]
Blend 1	8.5 kg/mol 3.4 mg	18.8 kg/mol 2.2 mg	2 kg/mol 2.6 mg
Blend 2	52.3 kg/mol 1.7 mg	36.3 kg/mol 1.9 mg	22 kg/mol 2.0 mg
Blend 3	198 kg/mol 2.5 mg	193 kg/mol 1.8 mg	260 kg/mol 1.7 mg

[a] Weight average molar mass; weight of polymer per 1.5 ml of 1-decanol.

Table 2
Molecular characterization of copolymers analyzed. Listed are average comonomer content, weight average molar mass, M_w, polydispersity, PDI, and data source.

Sample name and sample code[a]	Comonomer	Comonomer content [mol %]	M_w [kg /mol]	PDI	Reference
Propene/1-butene copolymer iPP/C2	1-butene	5.8	147	2.10	[50]
		18.8	262	2.04	
Propene/1-hexene copolymer iPP/C4	1-hexene	1.4	125	1.70	[51]
		5.9	107	2.00	
		8.6	226	1.80	
Propene/1-octene copolymer iPP/C6	1-octene	1.3	130	1.80	[50]
		5.6	150	2.10	
		7.2	220	2.05	
Propene/1-tetradecene copolymer iPP/C12	1-tetradecene	0.26	283	2.29	[18,52]
		0.68	554	2.54	
		0.89	639	2.51	
		2.33	416	2.15	
		2.76	395	2.31	
Propene/1-octadecene copolymer iPP/C16	1-octadecene	1.5	126	1.80	[53]
		4.5	104	1.80	
		7.6	193	1.80	
Propene/1-pentene copolymer sPP/C3	1-pentene	0.7	184.5	1.77	[54]
		1.5	139.2	1.85	
		2.4	113.1	1.93	
		4.5	104.4	1.90	
Ethylene/1-hexene copolymer PE/C4	1-hexene	3.6	–	–	[55]
		9.2	–	–	
		19.0	–	–	
		43.0	–	–	
		62.1	–	–	

[a] Symbols: C2 – ethyl, C4 – butyl, C6 – hexyl, C12 – dodecyl, C16 – hexadecyl.

PP elutes in SEC mode, i.e., the elution volume decreases with increasing molar mass of iPP, with small differences in the elution volumes. The small peak at ~10.5 mL in Fig. 1 is associated with the fraction of atactic polypropylene molecules present in the iPP. Atactic PP is adsorbed on graphite from 1-decanol and eluted in the gradient [48].

The Hypercarb® column contains fully porous spherical carbon particles consisting of flat sheets of hexagonally arranged carbon atoms. The adsorption of long chain alkanes on graphite from solvents was studied by Findenegg et al. [57,58]. Measurements of adsorption isotherms and enthalpies of adsorption of alkanes on graphite led to conclusion that only a single monomolecular layer of alkane adsorb onto highly ordered pyrolytic graphite surfaces at room temperature [57,58]. Reports of imaging alkane monolayers on graphite with scanning tunneling microscopy [59] confirmed this assertion. Electron microscopy observations of crystallization of PE on graphite [60] have shown that the PE chains lie flat on the graphite surface (adsorbed with their long axis paralel to the graphite surface) and exhibit a high degree of order. Chain molecules with side groups, however, cannot form closely packed layers with the graphite surface because of steric hindrance and show different adsorption behaviour [57]. Such effects were observed for PE and iPP, and are expected to influence the adsorption behaviour of propene/1-alkene and ethylene/1-alkene copolymers.

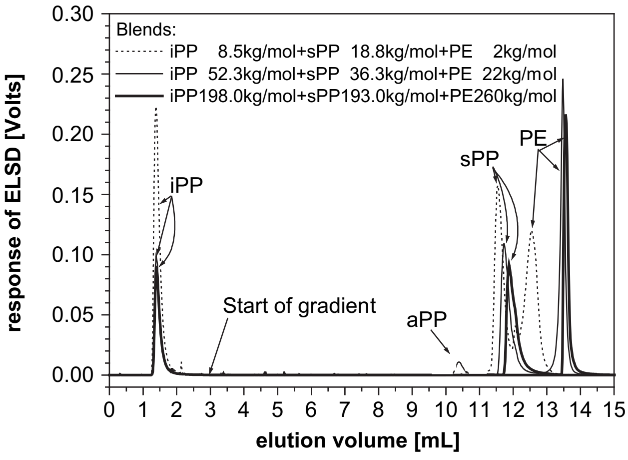

Fig. 1. Overlay of chromatograms corresponding to mixtures of isotactic PP, syndiotactic PP and linear PE. The molar mass is given in the inset, see text for blend composition. Column: Hypercarb®, 100 x 4,6 mm. Isocratic elution of iPP in the mobile phase 1-decanol. Gradient: From 100% 1-decanol to 100% 1,2,4-TCB in 10 min. Temperature: 160 °C. Flow rate: 0.5 mL/min. Notice: Start of the gradient in pump is shown in the figure [56].

An interesting question is how the concentration and the length of 1-alkene type comonomers influence the retention of random copolymers. This point is now probed by analyzing the retention behaviour of propene/1-alkene copolymers with a branch length changing from 2 to 16 carbons. Only samples with uniform interchain comonomer concentration distribution, such as those of metallocene-made copolymers are initially analyzed. Fig. 2 shows the chromatograms of copolymers of propene with 1-butene, 1-hexene and 1-octene (iPP/C2, iPP/C4, iPP/C6).

The samples iPP/C2 and iPP/C4 elute before the start of the gradient, indicating that the copolymer is not adsorbed. Differences in the elution volumes of Fig. 2 only reflect differences in the molar mass distribution. For the copolymers of propene with 1-octene (iPP/C6) a small portion of the sample with the highest comonomer content elutes with the gradient while the majority of the polymer elutes before the start of the gradient (Fig. 2 c).

The chromatograms of random copolymers of propene with 1-tetradecene and 1-octadecene (iPP/C12, iPP/C16) are shown in Fig. 3. Compared with the behaviour of branches <C7, copolymers with longer alkyl branches are clearly adsorbed eluting mainly with the gradient (Fig. 3). Moreover, the elution volume of the propene/1-tetradecene and propene/1-octadecene copolymers increases with increasing concentration of alkyl side chains (branches) in the copolymer. This indicates that the long alkyl chains grafted on the isotactic main chain are adsorbed, i.e., the incorporation of long alkyl branches to the iPP chain enables the retention of these copolymers proportionally to the comonomer content. We summarise that the iPP chains with the short alkyl branching (iPP/C2, iPP/C4, iPP/C6) are not retained, while samples with the long alkyl branching (iPP/C14, iPP/C16) are pronouncedly adsorbed.

We found in Fig. 1 that retention of propene units is stereospecific, sPP chains are retained, while iPP molecules are not. This tacticity effect on adsorption is also found in copolymers. While isotactic propene units are not retained in the iPP/1-alkyl samples, the syndiotactic propene units in samples sPP/C3 are strongly attracted to the graphite surface. An example is given in Fig. 4 for propene/1-pentene copolymers in a comonomer content range from 0.7 to 4.5 mol%.

These copolymers are strongly retained from the 1-decanol mobile phase and elute only in the gradient with TCB. Interestingly, the incorporation of increasing contents of comonomer decreases the ability of the syndiotactic PP segments to adsorb on the graphitic surface. When the concentration of alkyl branches in the macromolecule is increased, the average length of the syndiotactic segments decreases, and the retention volume decreases accordingly. Therefore, branching is acting against the adsorption of these copolymers. This is in contrast to the trend observed for propene/1-alkene copolymers with the iPP backbone (Fig. 3) where the iPP units are not adsorbed and only long alkyl side groups (dodecyl or hexadecyl) enable the retention. Naturally, the adsorption is stronger, when the concentration of these alkyl groups in the copolymer increases.

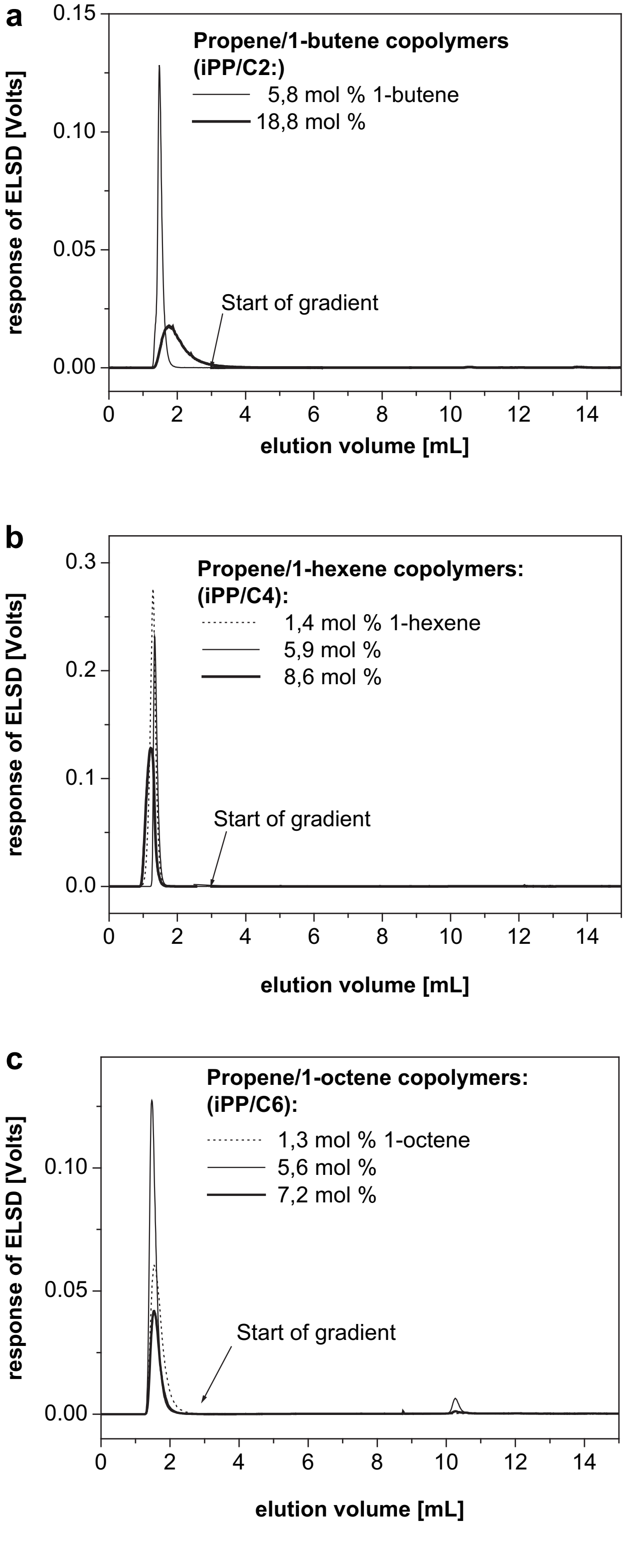

Fig. 2. Overlay of chromatograms corresponding to a) propene/1-butene, b) propene/1-hexene and c) propene/1-octene copolymers. The comonomer content is indicated. Experimental conditions as in Fig. 1.

A similar trend for the retention on graphite as found for samples sPP/C3, was also found in random ethylene/1-hexene copolymers. An example is given in Fig. 5. These copolymers are of interest because both, the polyethylene main chain and the alkyl branches can be potentially adsorbed.

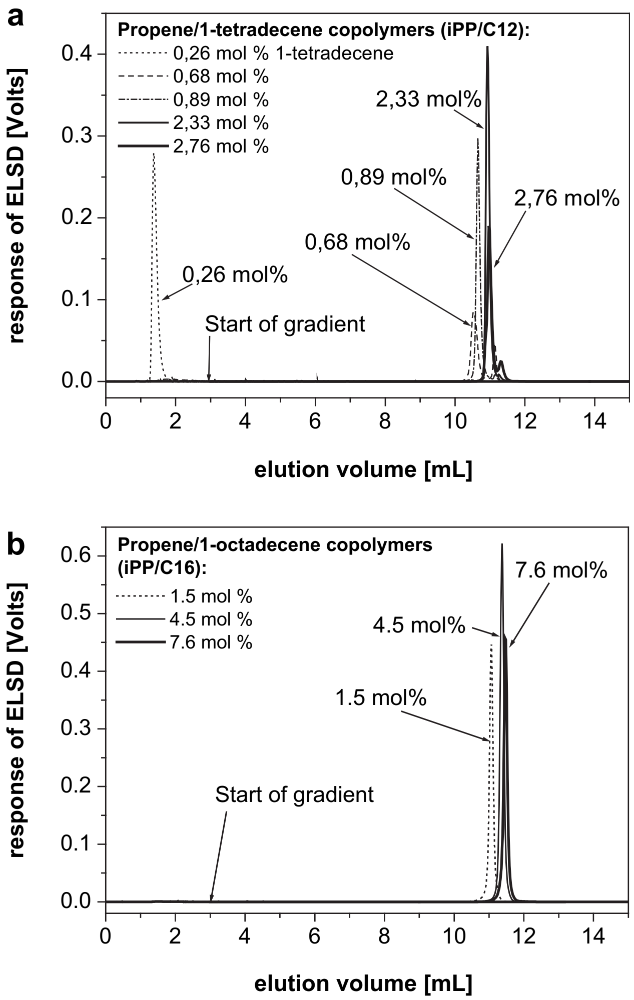

Fig. 3. Overlay of chromatograms corresponding to a) propene/1-tetradecene and b) propene/1-octadecene copolymers. The comonomer content is indicated. Experimental conditions as in Fig. 1.

At relatively low 1-hexene content, the adsorption is expected to be driven by the backbone ethylene runs. Accordingly, we found that the probability of adsorption of the main chain on the graphitic surface decreases as the comonomer content increases,

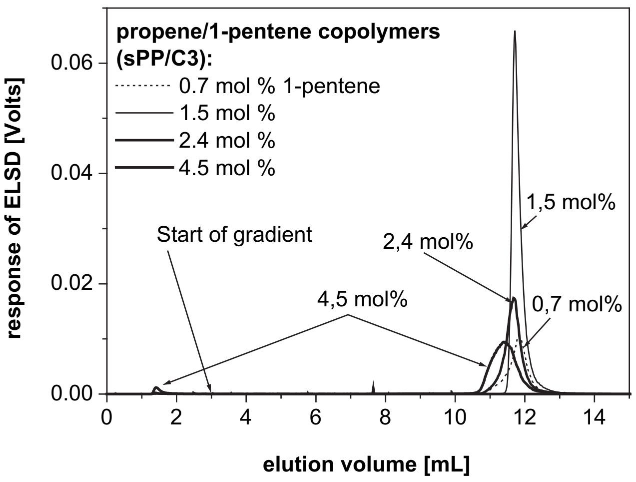

Fig. 4. Overlay of chromatograms corresponding to propene/1-pentene copolymers. The 1-pentene content is indicated. Experimental conditions as in Fig. 1.

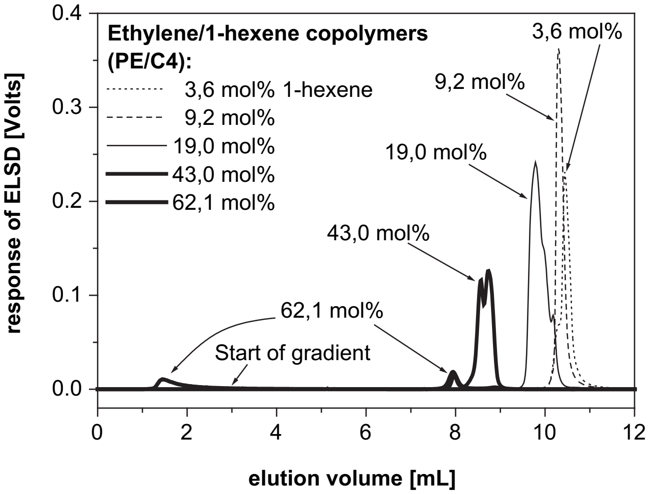

Fig. 5. Overlay of chromatograms corresponding to ethylene/1-hexene copolymers. The 1-hexene content is indicated. Experimental conditions as in Fig. 1.

in parallel with the behaviour of syndiotactic propene/1-pentene copolymers. The sample PE/C4 with 62.1 mol % of hexene eluted in two peaks: It is supposed that the peak with smaller elution volume (1.5 mL) contains chains with a lot of branching (i.e., not adsorbed) while the peak with larger retention volume contains chains with a smaller extent of branching (i.e., adsorbed). The work of Möckel et al. [61] on linear and branched alkanes supports the above conclusion. Using a Hypercarb® HPLC column, they found a lower retention for branched alkanes than for the corresponding linear isomers with identical chain length [61]. They concluded that the selectivity of Hypercarb® for isomer separation is clearly superior over silica gel C18 columns despite the fact that the retention volumes are small.

Notice in Fig. 5 the high sensitivity of the retention (elution volume) in HPLC with comonomer content, including amorphous ethylene/1-hexene copolymers (>15 mol % 1-hexene). These differences open the possibility to characterize copolymers with a broad distribution of the comonomer content by analyzing the shape and breadth of their HPLC elugrams.

In the chromatograms of Fig. 5, the ethylene/1-hexene samples were injected at a comparable concentration, yet the peak heights decrease systematically. This is due to the fact that the response of the ELSD detector is a function of the chemical composition of the copolymers. The comonomer composition dependence of the detector's response has been observed by Albrecht et al. for ethylene/vinylacetate copolymers [62]. Moreover, the ethylene/1-hexene samples studied here elute in the gradient, and the same authors have also observed that the response of ELSD depends on the composition of the mobile phase [62]. Both effects combined may complicate any quantitative evaluation of branching content and distribution based on a ELSD response in the chromatograms.

The retention behaviour as a function of type of copolymer and branching length and content is summarized in Fig. 6. The elution volume is plotted vs. comonomer content for samples iPP/C12, iPP/C16, sPP/C3 and PE/C4.

Isotactic propene/1-alkene copolymers show strong retention at branch lengths >11 carbons. For these copolymers the elution volume increases with branching content (Fig. 6b). This indicates that alkyl branches longer than C11 attached to non adsorbed backbones lead to a retention of the macromolecule on the graphite packing. In contrast, a high concentration of branches in adsorbable backbones (i.e. PE or sPP backbone) act against adsorption. As seen in Figs. 6a and 6b, the retention of the samples PE/C4 or sPP/C3 is indirectly proportional to the amount of comonomer in the copolymer (Fig. 6a).

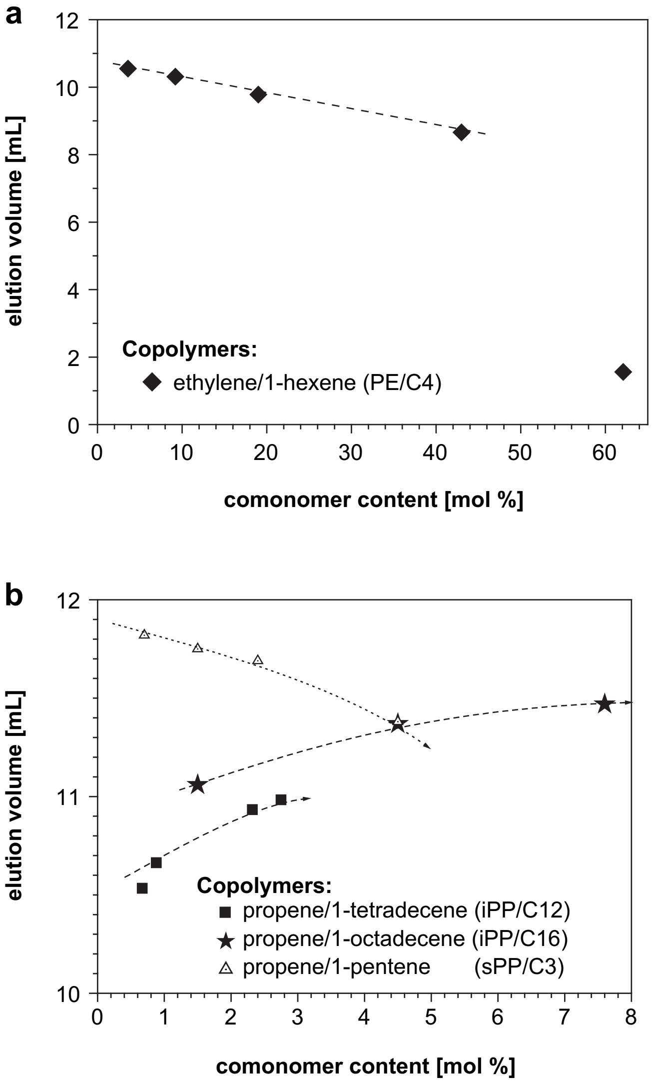

Fig. 6. Dependence of the elution volume on the comonomer composition for random copolymers.

The results presented in Fig. 6 indicate that using a porous graphite column packing, HPLC may be a sensitive fractionation technique to discriminate polyolefins with regard to their branching microstructure.

4. Conclusions

Analytical or preparative fractionation of branched polyolefins according to their chemical composition, i.e. branching, are presently carried out by crystallinity dependent techniques, such as TREF and CRYSTAF. A novel type of analytical separation technology for branched polyolefins is described in this work: The separation is based on the adsorption and desorption of the macromolecules in a chromatographic column operating at high temperatures (up to 160 °C). The HPLC technique uses a Hypercarb® column packed with porous graphite particles. The graphite packing enables a selective adsorption of polyolefins with long methylene sequences (>11 carbons) and syndiotactic poly(propylenes). While isotactic poly(propylene) and propene/1-alkene copolymers with alkyl branches C6 and shorter (iPP/C2, iPP/C4, iPP/C6) are not retained, copolymers with longer branches (iPP/C12, iPP/C16) are strongly adsorbed. Moreover, the retention time of propene/1-tetradecene and propene/1-octadecene copolymers increases with increasing comonomer content, opening the possibility of using the HPCL technique for the characterization and fractionation of copolymers with comonomer compositional heterogeneity.

Ethylene/1-hexene copolymers and propene/1-pentene copolymers with sPP in the backbone are separated according to their chemical composition. Contrasting the adsorption behaviour of propene/1-alkene copolymers with iPP in the backbone, an increased concentration of the comonomer in these copolymers leads to a decreased retention volume for ethylene/1-hexene copolymers and samples sPP/C3. The branching in the PE/C4 and sPP/C3 samples decreases the probability of backbone adsorption in a flat conformation on the graphite surface. The precise spatial orientation of the adsorbed polyolefins from 1-decanol on graphite is at the present unknown. However, the experimental results enable to formulate comprehensible correlations between the retention volume and the chemical composition of branched polyolefins.

The common methods used to separate branched polyolefins, i.e., CRYSTAF and TREF, do not enable to study amorphous polyolefin samples. The high-temperature sorbent-solvents system described here enable to separate amorphous as well as crystallizable polymer samples. Moreover, with the HPLC technique described polyolefin separations can be accomplished faster and the consumption of solvents and samples per analysis is smaller. These features make the HPLC system described here especially suitable for the fast screening of samples in a high throughput research and development of polyolefin materials [63,64].

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