

Characterization of Ethylene-Propylene Copolymers with High-Temperature Gradient Adsorption Liquid Chromatography and CRYSTAF

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ABSTRACT: Blends of linear polyethylene (PE) and isotactic polypropylene (iPP) with different average molar masses and a series of ethylene-propylene (EP) copolymers with different chemical composition as well as blends of PE, iPP, and EP copolymers were separated using a carbon-column packing (Hypercarb®) and gradients of 1-decanol or 2-ethyl-1-hexanol → 1,2,4-trichlorobenzene (TCB). The separation is based on full adsorption of linear PE on the carbon sorbent at temperature 160°C. However, iPP is not adsorbed and elutes in size exclusion mode. The random EP copolymers have been adsorbed in the column packing and separated according to their average chemical

composition after application of the gradient starting with alcohol and ending with pure TCB. The elution volumes of the copolymers depended linearly on the average concentration of ethylene in the copolymers. The HPLC elution profiles were correlated with the CRYSTAF elution profiles. In contrast to CRYSTAF, fully amorphous polyolefin samples were separated with the high-temperature adsorption liquid chromatography. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 3211–3217, 2011

Key words: separation of polymers; adsorption; high performance liquid chromatography; polyolefins

INTRODUCTION

Goods produced from polyethylene (PE), polypropylene, and their copolymers have been found broad applications in every day life as well as in industry due to their advantageous properties and their economic performance/price ratio. As a consequence, there is a great interest to improve the properties of these polymer materials. The success in research and development of these materials depends on several factors; one of them is an efficient and detailed characterization of their molecular heterogeneity, that is, branching, tacticity, etc. The molar mass distribution of these polymers is obtained from high-temperature size exclusion chromatography,^{1–3} where in addition

to a refractometric index detector also either viscosimetric or light scattering detector is applied.^{4–11} The average chemical composition is determined mainly using FTIR or NMR spectroscopy. However, SEC separation may be combined with the on-line FTIR^{12–14} or NMR¹⁵ spectroscopic analysis. In such cases, information about the distribution of the chemical composition along the molar mass axis is obtained. Holtrup's fractionation,¹⁶ which is based on precipitation and dissolution of a polymer in a specific mixture of solvent/nonsolvent, enables to prepare larger fractions with different molar mass. Fraction temperature rising elution fractionation (TREF)¹⁷ can be used to evaluate the distribution of the chemical composition of semicrystalline polyolefins. The separation exploits the crystallizability of the macromolecules from a solution at elevated temperature, which in turn is related to the chemical composition and the architecture of macromolecules. However, a single measurement requires 1–2 days. The measurement time was pronouncedly reduced after introduction of Crystallization Analysis Fractionation, CRYSTAF, which is a modified version of TREF.¹⁸ Both, TREF and CRYSTAF, are widely used to characterize PE, PP, and their copolymers.^{7,12,18–26} The drawback of TREF and CRYSTAF is that non-crystallizable materials can not be analyzed. If a

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detailed analysis of a sample is required, TREF is used to prepare 7–15 fractions and each fraction is then individually characterized by FTIR, SEC, NMR, and DSC.^{22–27} Moreover, TREF may be coupled online with SEC analysis.^{14,28–30}

These time and labor consuming analytical procedures could be partially eliminated by the use of a liquid chromatographic separation according to chemical composition or microstructure. Although many chromatographic procedures were published for various polymers,^{31–35} solvent/sorbent systems for realization of the interactive liquid chromatography of polyolefins were unknown even 70 years after beginning of their industrial production. The group of Prof. H. Pasch (present address: University of Stellenbosch, Stellenbosch, South Africa) in Darmstadt has recently published the first HPLC procedures for the separation of PE and PP.^{36–43} PE or PP were selectively adsorbed in the zeolites^{40–43} or HPLC separation has been based on selective precipitation of PE.^{36,38} Lehtinen and Paukerri⁴⁴ found that ethylene glycol monobutyl ether (EGMBE) dissolves isotactic polypropylene (iPP) but not linear PE. The retained PE may then be eluted applying a gradient EGMBE → 1,2,4-trichlorobenzene (TCB).³⁶ Using this approach it was for the first time possible to separate ethylene-propylene (EP) copolymers according to their chemical composition.^{45,46} However, there is still a significant influence of the molar mass on the separation, which makes it unpractical for routine analysis.

In this article, we describe the HPLC separation of PE/PP-blends and EP copolymers based on the selective adsorption of PE on a column packing at high temperature. In this HPLC system, a chromatographic column packed with porous particles of graphite as stationary phase is used. The characteristics and applications of this column packing material has been recently summarized by Pereira⁴⁷ and Michel and Buszewski.⁴⁸ The porous graphite column has superior ability to discriminate analytes, which differ only a little in their structure, that is, isomers, including stereoisomers of PP.⁴⁹ Moreover, propene/1-alkene copolymers were separated with the column packed with porous graphite particles.⁵⁰ The separation of ethylene-propylene copolymers is reported in this work.

EXPERIMENTAL

Instruments

A high-temperature chromatograph HT GPC 210 (Polymer Laboratories, Church Stretton, England) was used for injection and analysis of samples at temperature 160°C. The sample injection volume was 13 μ L. The samples were injected into the col-

umn Hypercarb® 100 \times 4.6 mm, particle diameter 5 μ m, pore diameter 200 Å (Thermo Fisher Scientific, Waltham, MA). A quaternary gradient pump (Agilent 1200 Series, Waldbronn, Germany) was used to form the mobile phase. The flow rate was 0.5 mL/min. An evaporative light scattering detector (ELSD, Polymer Laboratories, Church Stretton, England) was used for detection of polymers in the mobile phase. The following parameters were selected for ELS-detection: air flow rate 1.5 L/min; temperature of nebulizer 160°C; temperature of evaporator 260°C; temperature of transfer line 160°C. The gas phase leaving the ELSD was condensed in a cooler at temperature 10°C. WinGPC-software (Polymer Standard Service GmbH, Mainz, Germany) was used for data collection and processing.

CRYSTAF analysis was carried out using a model CRYSTAF-TREF 300, Polymer Char, Valencia, Spain. Polymer solutions with a concentration close to 0.5 mg/mL were prepared by dissolving about 20 mg of polymer in 40 mL of TCB at 160°C. The crystallization was carried out in the temperature range 95–30°C with a cooling rate of 0.1°C/min.

Solvents

1-decanol, TCB, and 2-ethyl-1-hexanol (synthesis quality, Merck, Darmstadt, Germany) were used.

Polymer samples

Linear PE standards (Polymer Standard Service GmbH, Mainz, Germany), isotactic PP standards (American Polymer Standards, Mentor), linear PE with M_w 260 kg/mol, iPP 200 kg/mol, and EP copolymers were dissolved in 1-decanol at a concentration of 1–2 mg/mL at 160°C.

Samples of EP copolymers were prepared by Suarez^{51,52} and described by Coto et al.^{53,54} The copolymerization reactions were carried out in a stirred tank reactor operating in semicontinuous mode at 70°C and 5 bar. Their molecular characterization data obtained with high-temperature SEC and NMR spectroscopy are summarized in Table I. Our previous study with MALS did not revealed presence of long chain branching in these samples.

RESULTS AND DISCUSSIONS

Interactive liquid chromatography of PE and iPP

All chromatographic separations reported here were obtained using the following procedures. The sample was first dissolved in 1-decanol at 160°C and injected into the column kept at the same temperature. The mobile phase used initially was same as the sample solvent, 1-decanol, and then switched to

TABLE I
Molecular Characterization Data of the
Ethylene-Propylene Copolymers

Sample code	Content of ethylene [wt %]	M_w [g/mol]	M_w/M_n
EP-2	2.3	112,200	2.45
EP-4	4.0	118,800	2.44
EP-15	14.6	70,000	2.42
EP-23	22.6	61,600	2.08
EP-49	49.0	62,000	2.86
EP-74	73.5	54,700	2.54
EP-81	81.3	163,900	3.01
EP-91	91.0	268,500	2.78
EP-99	98.6	260,800	3.63

a linear gradient ending with 100% TCB. The start of gradient (at 3 mL) is marked in the chromatograms. Figure 1 shows the chromatographic separation of isotactic PP- and linear PE-standards with different average molar masses. As we have shown previously,⁴⁹ peaks corresponding to iPP standards eluted before the start of the solvent gradient because isotactic PP was not retained on the column and elutes in SEC mode [Fig. 1(a)]. The difference in the elution volume of iPP 1 kg/mol and iPP 200 kg/mol is only 0.2 mL, which is likely because the carbon packing has a small specific pore volume (0.7 mL/g).⁴⁷ However, PE samples are fully retained on the column packing from 1-decanol, that is, no peaks appeared in the chromatogram [Fig. 1(b)]. Only after applying a linear gradient from 100% 1-decanol to 100% TCB, peaks corresponding to PE appeared in the chromatogram [Fig. 1(b)].

Several groups^{55–57} have studied adsorption isotherms of alkanes, that is, oligomers of PE, on graphite from different solvents. Groszek⁵⁶ studied the adsorption of *n*-dotriacontane (*n*-C₃₂H₆₆) from heptane onto graphite and observed a very strong adsorption of the long-chain paraffin. This was attributed to a lattice fit between the graphite basal plane and the chain molecules in their extended *trans*-conformation.^{55,56} The adsorption is supported by the homogeneity of the graphitized carbon packing—the individual graphite sheets might be regarded as very large aromatic molecules consisting almost exclusively of carbon.⁴⁸ A schematic representation of tetradecane adsorbed on graphite is shown in Figure 2 for illustration.⁵⁷

Investigations of PE-crystallization⁵⁸ via electron microscopy from highly diluted solutions on graphite confirmed the existence of attractive interactions between PE and the graphite substrate. Due to these interactions, orientation of PE chains at crystallization upon the graphite is oriented (so-called epitaxial crystallization). The carbon atoms of the chains were arrayed in a perfectly ordered way on the graphite substrate. In contrast, they were ordered randomly

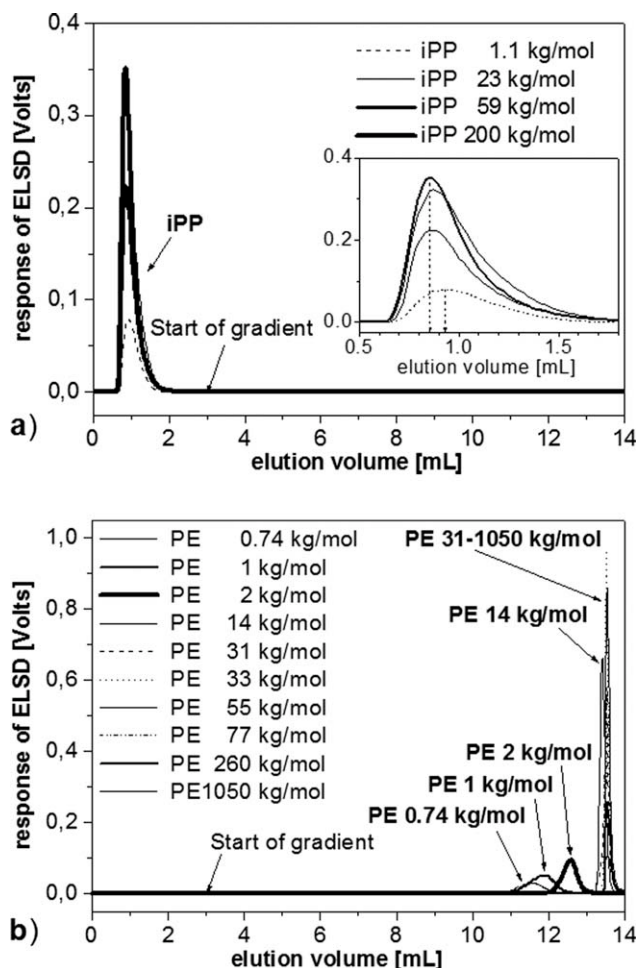


Figure 1 Overlay of chromatograms for isotactic PP-standards (a) and PE-standards (b). Column: Hypercarb. Mobile phase: 1-decanol and linear gradient: In 10 min from 0 to 100% TCB. Flow rate: 0.5 mL/min. Temperature: 160°C. Start of the gradient in the pump is indicated in the figure.

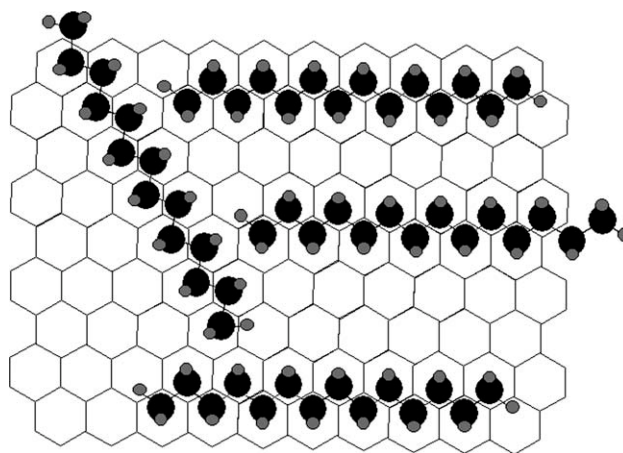


Figure 2 Schematic representation of the monolayer crystal structures for tetradecane adsorbed on graphite. The plane of the carbon skeleton is found parallel to the graphite surface.⁵⁷

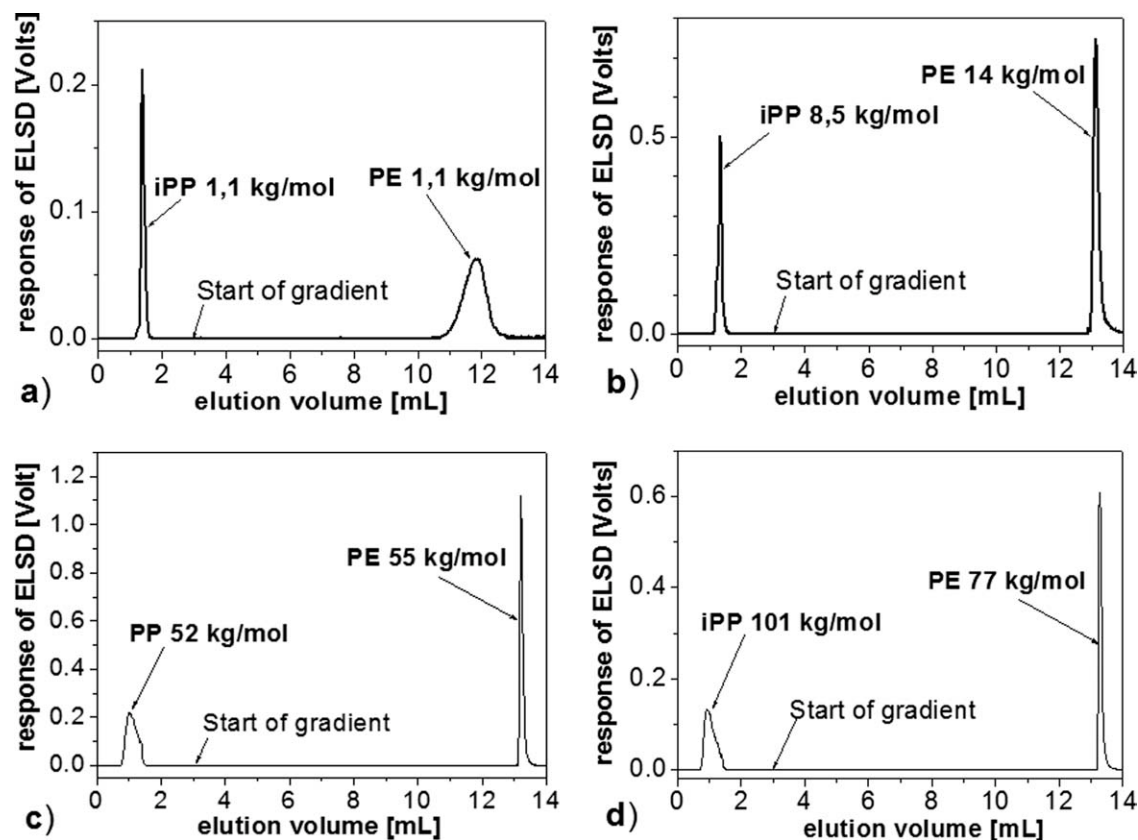


Figure 3 Overlay of chromatograms. Separation of mixtures of linear PE and iPP with different molar mass: (a) i-PP 1.1 kg/mol and PE 1.1 kg/mol; (b) i-PP 8.5 kg/mol and PE 14 kg/mol; (c) i-PP 52.3 kg/mol and PE 55 kg/mol; (d) i-PP 101 kg/mol and PE 77 kg/mol. Experimental parameters as in Figure 1.

on amorphous carbon. We suppose that these interactions play a role in HPLC of polyolefins.

Separation of PE-PP blends

Figure 3 illustrates that the described chromatographic system enables to separate PE-PP blends. Peaks of isotactic PP and linear PE are excellently baseline separated, also in the case that their average molar mass is only about 1 kg/mol. For comparison, a separation of PE from PP with molar mass below about 20 kg/mol was not possible using precipitation-redissolution chromatography with EGMBE as the mobile phase.^{36,37} We note that oligomers of PE and PP with smaller molar mass evaporate at 260°C in the ELSD and therefore do not yield a detector response.

The opposite adsorption behavior of PE (adsorbed from 1-decanol) and iPP (not adsorbed) is illustrated in Figure 3.

Therefore, it is an interesting question if how EP copolymers are separated in this chromatographic system. This was probed in the following measurements.

Separation of EP copolymers

The chromatograms corresponding to EP-samples are shown in Figure 4. In general, the elution volume of the samples increases with the average concentration of ethylene in the copolymers, although the average molar mass of these samples differ about four times (see Table I). This proves that the separation is not governed by the molar mass, but mainly by the chemical composition of the samples. Samples with a higher content of ethylene (EP15-EP99) are eluted mainly or exclusively in the gradient mode in the system Hypercarb/1-decanol → TCB. However, the samples with a low concentration of ethylene (EP2 and EP4) are eluted prevalingly before the gradient like isotactic PP, because the adsorption interactions in the system Hypercarb/1-decanol are not strong enough to adsorb copolymers with such a small content of ethylene. If 1-decanol is replaced by 2-ethyl-1-hexanol, all copolymer samples are adsorbed (Fig. 5). As the interactions between the copolymers and the sorbent are stronger when 2-ethyl-1-hexanol is used, the retention volume is larger (about 16 mL in Fig. 5 vs. 13 mL in Fig. 4).

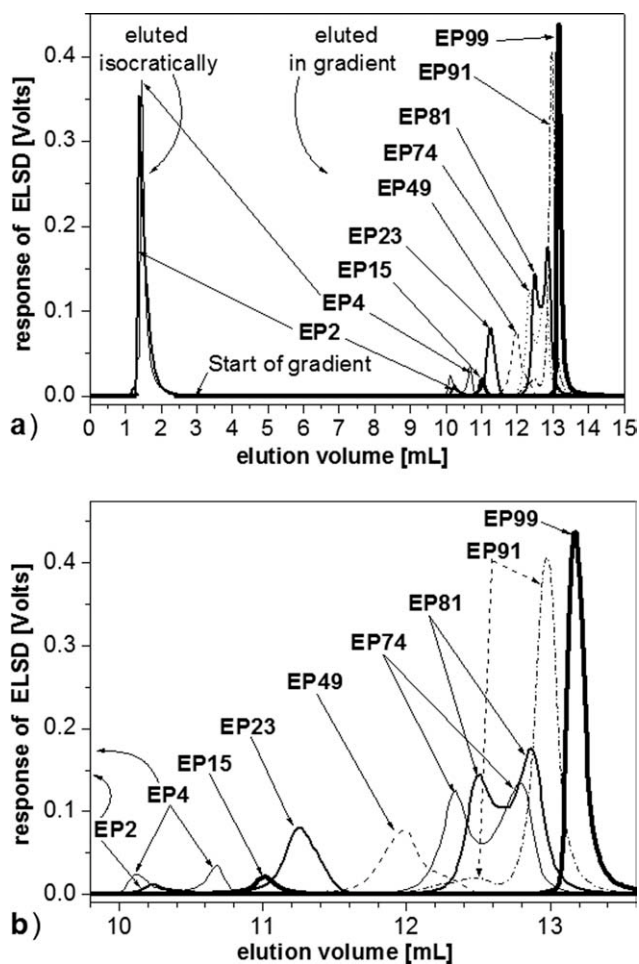


Figure 4 Overlay of chromatograms obtained with the system Hypercarb/1-decanol → TCB. The average chemical composition of random EP copolymers is indicated in the figure. b: shows an enlarged part of (a). Experimental parameters as in Figure 1.

Comparison of CRYSTAF and HPLC for the analysis of copolymers

CRYSTAF separates the components present in a sample based on their crystallizability. The first derivatives of the concentration profiles of these samples are shown in Figure 6.

CRYSTAF separates the EP copolymers according to their crystallizability, which is related to the chemical composition of macromolecules and their microstructure, that is, arrangement of branches along a chain (random, blocks, tacticity). Several samples (i.e., EP4, EP74, and EP81) show crystalline and amorphous portions and sample EP 91 contains two crystallizable fractions (Fig. 6). Samples EP2 and EP99 do not contain a pronounced amorphous fraction. Corresponding HPLC chromatograms show a single peak for EP2 and EP99 (sample EP2 has also a small peak, which probably corresponds to an amorphous portion). The samples, which show two separate fractions in CRYSTAF (EP4, EP74, EP81, and

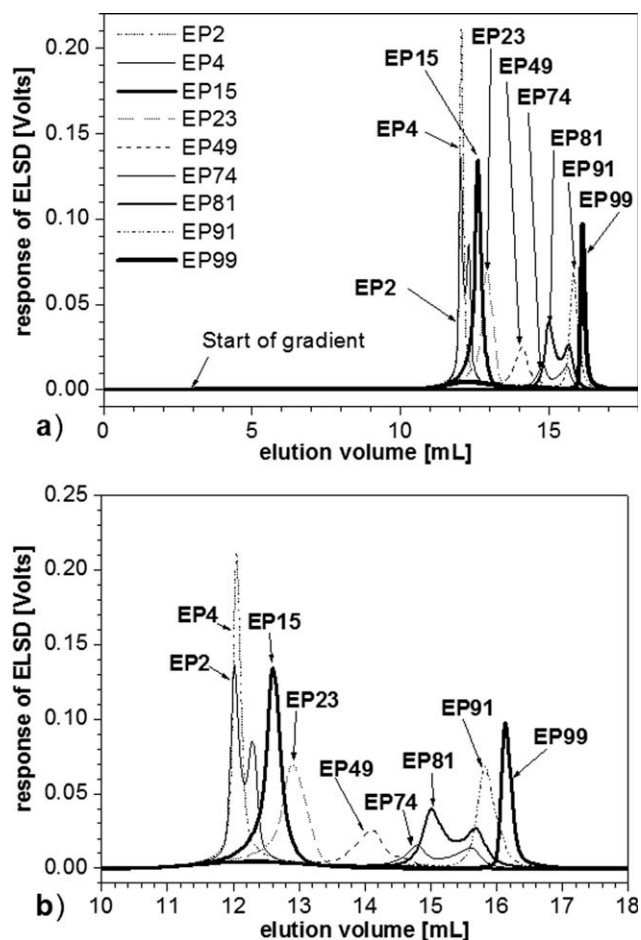


Figure 5 Overlay of chromatograms obtained in system Hypercarb/2-ethyl-1-hexanol → TCB. b: shows an enlarged part of (a).

EP91), also elute in two peaks (EP74, EP81, and EP91) or three peaks (EP4) from the Hypercarb column. Moreover, fully amorphous samples EP15, EP23, and EP49 elute from the column at elution volumes, which correlate with their average

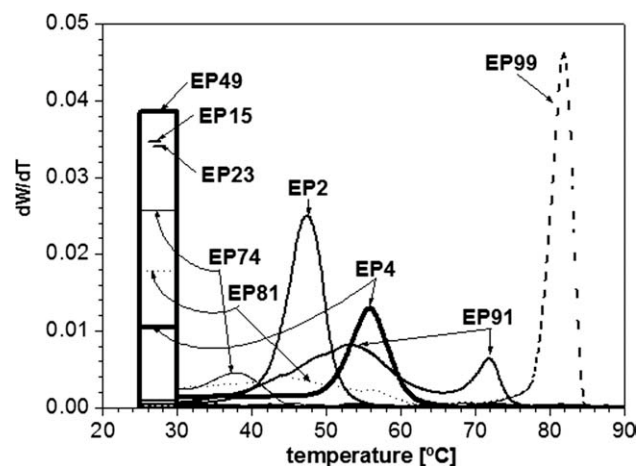


Figure 6 First derivative of the concentration profiles obtained from CRYSTAF analysis of EP-copolymers.

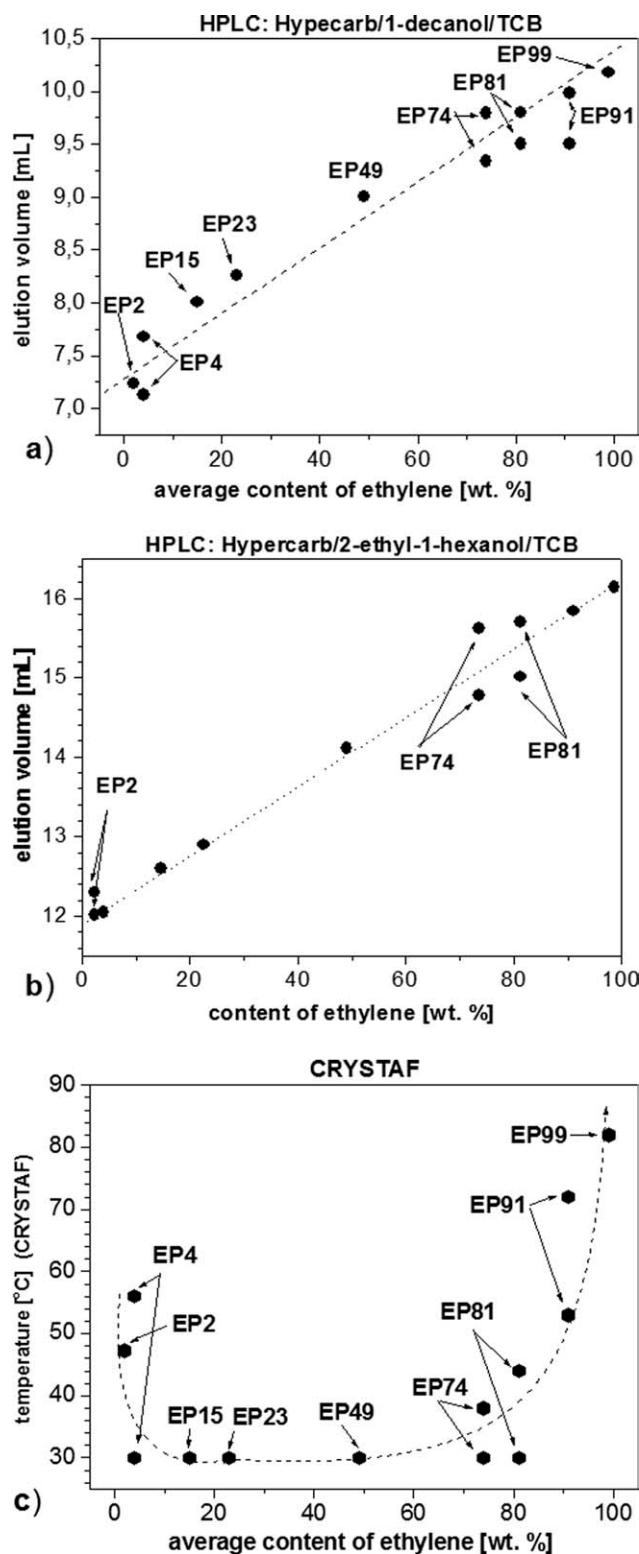


Figure 7 Relationship between the elution volume in the system Hypercarb/1-decanol \rightarrow TCB (a), Hypercarb/2-ethyl-1-hexanol \rightarrow TCB (b), the CRYSTAF temperature (c), and the average chemical composition of the copolymers. Notice to Figure 7(a): EP2, EP4 elute also at 1.4 mL.

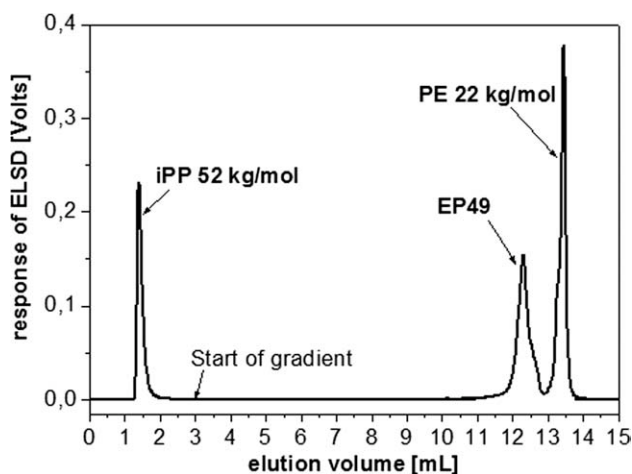


Figure 8 Chromatogram corresponding to separation of a mixture PE, isotactic PP, and EP copolymers. The HPLC experimental setup is the same as in Figure 1.

chemical composition: The samples EP15 and EP23 elute in one peak, while EP49 in one deformed peak.

We conclude that the retention volumes from HPLC correlate with the chemical composition of the copolymers: The elution volumes increase with the amount of ethylene in the copolymers [Fig. 7(a,b)]. However, temperatures corresponding to the CRYSTAF profiles do not show such correlation in range 2–91 wt % ethylene [Fig. 7(c)].

Unfortunately these samples are not ideal to establish a relationship between the elution volume and the chemical composition because they are in the majority of cases not chemically homogeneous. Finally, a chromatogram illustrating the separation of a blend containing iPP, PE, and EP copolymer is shown in Figure 8.

The copolymers are separated from both homopolymers. Thus, presence of homopolymers in the products may be monitored.

We notice that the signal of the ELSD may be a function of the chemical composition of the copolymers. Albrecht et al.⁵⁹ have shown that the ELSD response of ethylene vinyl acetate copolymers depends on the composition of the mobile phase (i.e., it changes through a gradient elution) and the chemical composition of EVA copolymers. These two effects may eventually complicate a quantitative evaluation of the chromatograms recorded by ELSD and their evaluation will require a calibration of the ELSD.

CONCLUSIONS

A commercially available carbon column packing Hypercarb was used to separate blends of PE and iPP. iPP elutes from the column in SEC mode, while linear PE in the molar mass range from 1000 to

100,000 g/mol is fully retained (adsorbed) on the column packing when flushed with 1-decanol or 2-ethyl-1-hexanol at 160°C. The retained PE was eluted by a linear gradient alcohol → TCB. The same HPLC system enables to separate EP copolymers according to their chemical composition. The pronounced adsorption of the copolymers from 2-ethyl-1-hexanol enabled that all copolymers eluted exclusively in the gradient in system Hypercarb/2-ethyl-1-hexanol → TCB. The average chemical composition of the copolymers correlated linearly with the elution volume. The molar mass of the PE and the copolymers plays a negligible role in the separation. The advantage of the described HPLC method is that information about the distribution of the chemical composition of the samples may be obtained within a shorter time than using the conventional methods (CRYSTAF and TREF). Moreover, the HPLC method can also be used for the noncrystallizable portion of the samples.

This reported interactive HPLC system has potential to be, in the foreseeable future, a complimentary method for analysis of the distribution of the chemical composition of polyolefins and be implemented in high-throughput research and the development of new polyolefin materials.^{60–62}

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