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Separation of Linear Polyethylene from Isotactic, Atactic, and Syndiotactic Polypropylene by High-Temperature Adsorption Liquid Chromatography

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ABSTRACT: For the first time polyolefins are separated according to tacticity by liquid chromatography. High-temperature gradient HPLC is shown to be suitable for the separation of polyethylene and polypropylene. As the stationary phase a porous carbon-based material is used; the mobile phase is composed of 1-decanol and 1,2,4-trichlorobenzene. It is shown that at an operating temperature of 160 °C linear polyethylene as well as syndiotactic and atactic polypropylenes are fully adsorbed on the stationary phase from 1-decanol. In contrast, isotactic polypropylene is fully eluted. This behavior provides a novel way for liquid chromatographic separation of polyolefins. After the isocratic elution of isotactic polypropylene with 1-decanol, all retained components are desorbed from the column packing in a gradient of 1-decanol/1,2,4-trichlorobenzene. Nearly baseline-separated peaks are obtained for all components even in the case where the components do not differ in their molar masses.

Introduction

Linear and branched polyethylenes (PE), isotactic polypropylene (PP), and polyolefin copolymers are the most important synthetic polymers. They are industrially produced for more than 70 years. In 2007, 48 million tons of PE and 47 million tons of PP materials have been produced worldwide.[1,2] Because of their technical importance, numerous groups investigated the separation, analysis, and characterization of these materials. Polyethylene and polypropylene are semicrystalline materials that are soluble only at high temperatures in solvents such as 1,2,4-trichlorobenzene, decalin, and 1,2-dichlorobenzene. Dissolution temperatures are typically between 130 and 160 °C.

Specific analytical techniques have been developed for the analytical separation of these polymers, such as Holtrup fractionation[3] and temperature rising elution fractionation (TREF).[4,5] While Holtrup fractionation separates mainly according to molar mass, TREF separates predominantly according to crystallinity, which is a function of the chemical composition and the microstructure of the polyolefin. Monrabal has developed a time-saving modification of TREF, which is known as crystallization analysis fractionation (CRYSTAF),[6] and an instrument for the Holtrup fractionation, referred to as PREP. CRYSTAF and PREP are automated instruments; however, they require long fractionation times. Holtrup fractionation and TREF are used mainly for the preparative fractionation of selected interesting samples. Between 7 and 16 fractions are typically collected, and each fraction is separately characterized by size exclusion chromatography (SEC), FTIR, NMR, differential scanning calorimetry, or other methods. As a result, information about the molar mass and the chemical composition distribution of the samples is obtained.[7−15] The drawback of both methods is that they require large amounts of solvents and long time for analysis. Moreover, the separation of amorphous materials, i.e., noncrystallizable polyolefins and their components, is not possible using TREF or CRYSTAF.

Different from TREF or Holtrup fractionation, the molar mass distribution of polyolefins is routinely measured by (fast) high-temperature SEC.[16] PS/DVB column packings and 1,2,4-trichlorobenzene (TCB) at temperatures of 130−160 °C are typically applied for HT-SEC. Typical detectors are differential refractometers, infrared, viscosimetric, and/or light scattering detectors.[17−20] Information about the chemical composition of the separated species may be obtained by coupling of HT-SEC online with FTIR[21−23] or NMR.[24] Since SEC is separating by hydrodynamic volume, chemically different polymers may coelute if they have the same size in solution. As a result, an average chemical composition corresponding to each volume increment is obtained by coupling of HT-SEC with FTIR or NMR. No information can be obtained, however, on the chemical composition distribution. The coupling of HT-SEC and TREF[25,26] may offer a comprehensive characterization; however, the separation of amorphous components is problematic and requires additional analyses.

On the other hand, liquid chromatography enables to separate many polymers according to their chemical composition fast and efficiently.[27−31] The corresponding HPLC methods are usually based on a selective precipitation or adsorption. A HPLC method for separation of polyolefin materials according to their chemical composition, however, has not been available for a long time for three reasons: (1) the samples are soluble only at high temperatures, (2) a dedicated high-temperature HPLC instrument was not in the market, and (3) no information was available about the adsorption properties of polyolefins on HPLC stationary phases. Recently, we have published a series of works about interactive HPLC of polyolefins.[32−40] PE has been separated from PP, when ethylene glycol monobutyl ether (EGMBE) has been used as the mobile phase and the polymers have been injected in 1-decanol.[32] PP eluted isocratically in EGMBE[32,33] and PE eluted in a gradient consisting of EGMBE/1,2,4-trichlorobenzene.[32,33] In addition to PE and PP blends, even ethylene−propylene copolymers have been separated in this HPLC system according to their chemical composition.[35] Paukerry and Lehtinen[41] have found

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that isotactic PP is soluble in EGMBE, while EGMBE is a nonsolvent for linear PE. This means that selective precipitation of PE was mainly responsible for the separation of the blends.[32-36]

Strong adsorption of linear PE and isotactic PP from dilute solutions on specific zeolites has also been described.[37-40] Unfortunately, the adsorption was irreversible, and thus, the adsorbed polymer could not be recovered. The application of chlorinated mobile phases (1,2,3-trichloropropane and 1,1,2,2-tetrachloroethane) enabled strong retention (adsorption) and also desorption of PE and PP samples.[40] Under these conditions, however, PE and PP may be chlorinated. Moreover, these solvents cause corrosion of the HPLC instrumentation.

Fast analytical HPLC separations of polyolefins would perfectly fit into high-throughput experimentation for research on new polyolefins[42,43] Not only the fast separation of PE from PP but also the separation of PP according to tacticity is of major interest. There have been reports on the separation of stereoregular polymers by various interaction chromatography modes. Inagaki and co-workers were the first to report on the separation of poly(methyl methacrylate) according to tacticity by thin layer chromatography.[44] Liquid chromatography at critical conditions was applied by Berek et al. to separate poly(methyl methacrylate)[45-47] and poly(ethyl methacrylate)[48,49] according to tacticity. Such separations have also been realized by temperature gradient interaction chromatography.[50] CRYSTAF separates a polypropylene mixture into the highly crystalline isotactic PP, the lower crystalline syndiotactic PP, and the amorphous atactic PP.[51] A mixture of syndiotactic PP, isotactic PP, and linear PE has been separated by CRYSTAF as well.[12] The CRYSTAF separation for a set of five samples takes, however, 6−10 h. A chromatographic separation of PP or other polyolefins according to tacticity has not been published yet.

In this paper a new chromatographic system for the adsorption and desorption of PE and PP is described. It has been observed several times that the retention of *n*-alkanes (i.e., oligomers of PE) on specific stationary phases increases with molar mass.[52-56] As the mobile phases, frequently alcohols and mixtures of alcohols and water have been applied. Möckel et al.[56] found that *n*-alkanes are retained from methanol on a carbon column more strongly than on a reverse-phase silica gel. In agreement with ref 56, preferential adsorption of *n*-alkanes from alcohols on a carbon sorbent has been found by Kalies et al.,[57] who studied adsorption isotherms. The retention characteristics of carbon sorbents have been summarized by Knox et al.[58] and by Pereira.[59]

Alkanes are oligomers of polyethylene; thus, their adsorptive interactions were assumed to be comparable to the adsorptive interactions of polyethylene chains. On the basis of this working hypothesis, the chromatographic behavior of polyolefins has been investigated on a porous carbon-based stationary phase.

Experimental Section

Instrument. A high-temperature chromatograph PL-GPC 210 (Polymer Laboratories, Church Stretton, England) equipped with an evaporative light scattering detector (model PL-ELS 1000, Polymer Laboratories, Church Stretton, England) has been used for all measurements. The following parameters have been 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. Flow rate was 0.5 mL/min.

A column Hypercarb, 100 × 4.6 mm i.d. with a particle diameter of 5 μm, a surface area of 120 m^2/g, and a pore size of 250 Å (Thermo Scientific, Dreieich, Germany), has been placed in a column oven and thermostated at 160 °C.

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

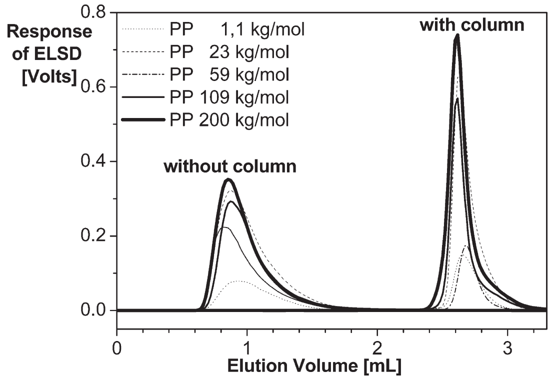

Figure 1. Overlay of chromatograms for isotactic polypropylene standards. The samples have been injected either into the column or into a capillary. Column: Hypercarb, 100 × 4.6 mm i.d. Mobile phase: 1-decanol. Temperature: 160 °C. Flow rate: 0.5 mL/min.

Polymer Samples. Linear PE standards with peak molar masses from 1.1 to 126 kg/mol have been obtained from Polymer Standards Service GmbH, Mainz, Germany. Linear PE with $M_w = 260$ kg/mol and isotactic PP with $M_w = 200$ kg/mol were obtained from PSD Polymers, Linz, Austria. All other isotactic PP samples have been synthesized at the University of Stellenbosch.[60] One sample of syndiotactic PP ($M_w = 196$ kg/mol) was delivered by Sigma-Aldrich (Munich, Germany), and five samples of syndiotactic PP with M_w of 18−193 kg/mol have been obtained from Dr. S. Bo.[61] A sample of atactic PP with $M_w = 315$ kg/mol has been a gift from Dr. I. Mingozzi (LyondellBasell, Ferrara, Italy). The polymers have been dissolved in 1-decanol at 160 °C at a concentration of about 1 mg/mL. The time of dissolution for the samples varied between 30 and 100 min. 13 μL of each sample solution has been injected.

Results and Discussion

In continuation of our previous work where we tested silica- and zeolite-based stationary phases the present work is dedicated to using a porous carbon-based stationary phase. The Hypercarb material consists of fully porous spherical carbon particles comprised of flat sheets of hexagonally arranged carbon atoms. The carbon atoms have a fully saturated valence and exhibit completely different retention and selectivity behavior than silica- and polymer-based phases. Hypercarb can be used for reversed and normal phase chromatography at extremes of temperature. For low molar mass compounds Hypercarb exhibited some stereoselectivity that was not found for conventional sorbents. In polymer applications this material has never been tested.

In order to investigate the chromatographic performance of this stationary phase, polyolefins of different chemical structures and molar masses were separated. Standards of five linear PE, five isotactic PP, one sample of atactic PP, and five samples of syndiotactic PP have been dissolved in 1-decanol at 160 °C and injected individually into the Hypercarb column. With the aim to evaluate the sample recovery, alternatively the column was replaced by a capillary, and the samples have been again injected. The overlays of the obtained chromatograms are shown in Figures 1 and 2. Figure 1 illustrates that isotactic PP elutes from the column with full recovery. This indicates that isotactic PP does not undergo adsorptive interactions with the stationary phase. Samples of isotactic PP elute like it is typical in SEC; however, the difference in their elution volumes is small (maximally ca. 0.2 mL).

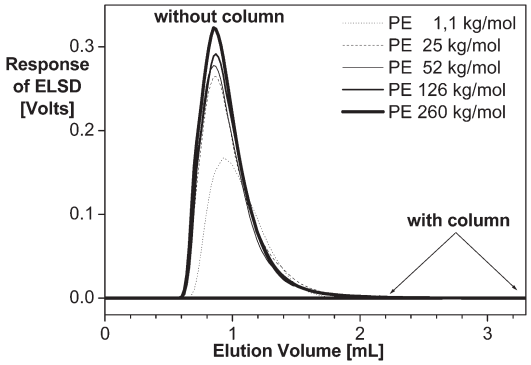

Figure 2. Overlay of chromatograms for linear polyethylene standards. Experimental conditions as in Figure 1. Notice: polyethylene is fully retained on the stationary phase.

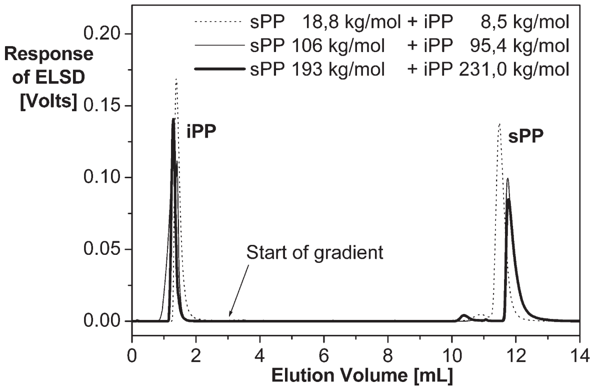

Figure 3. Overlay of chromatograms for blends of isotactic and syndiotactic polypropylene standards with various weight-average molar masses obtained after isocratic and gradient elution. Column: Hypercarb, 100 × 4.6 mm i.d. Isocratic elution in the mobile phase 1-decanol. Gradient: from 100% 1-decanol to 100% 1,2,4-trichlorobenzene in 10 min. Temperature: 160 °C. Flow rate: 0.5 mL/min. Notice: the gradient start at the pump is shown.

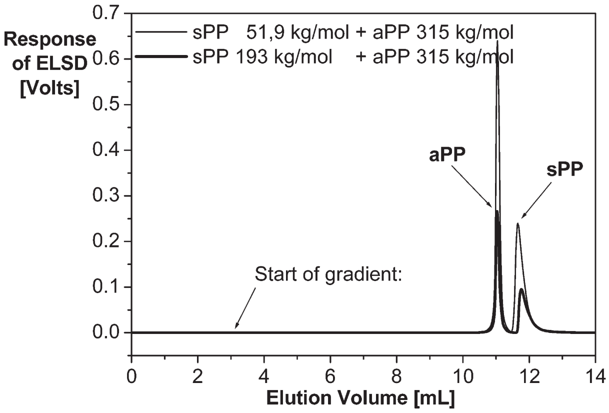

Figure 4. Overlay of chromatograms for blends of atactic and syndiotactic polypropylene standards with various weight-average molar masses. Experimental conditions as in Figure 3.

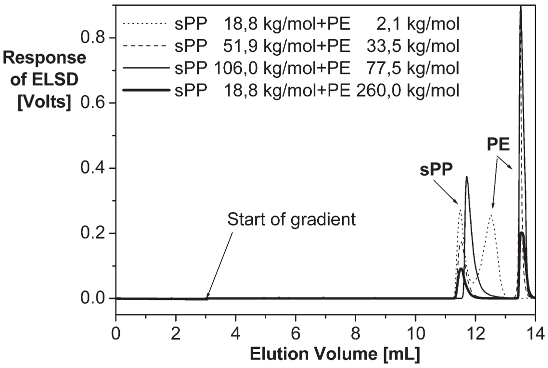

Figure 5. Overlay of chromatograms for blends of syndiotactic polypropylene and linear polyethylene standards. Experimental conditions as in Figure 3.

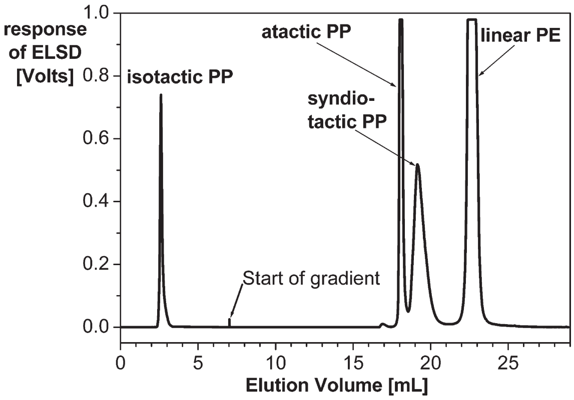

Figure 6. Chromatogram obtained after isocratic and gradient elution. Peaks in the chromatogram correspond to isotactic-PP (M_w = 200 kg/mol), atactic-PP (315 kg/mol), syndiotactic-PP (196 kg/mol), and five samples of linear PE (14−260 kg/mol). Experimental conditions as in Figure 3.

Testing linear PE under the same conditions revealed that irrespective of molar mass all PE samples were fully retained on the column packing, and no peaks of PE were detected when the column was used (see Figure 2).

Similar chromatograms as shown in Figure 2 have been obtained, when one sample of atactic PP and several samples of syndiotactic PP have been individually injected. This indicates clearly that atactic and syndiotactic PP are adsorbed on the stationary phase from 1-decanol. In a subsequent elution step, the retained polymers have been desorbed from the stationary phase using a gradient of 1-decanol/trichlorobenzene. It is known that aromatic compounds (i.e., TCB) are more strongly adsorbed on carbon adsorbents than aliphatic compounds (i.e., decanol).[54] Accordingly, TCB displaces both the polymer chains and 1-decanol from the carbon surface of the stationary phase.

With the aim to demonstrate the separation ability of the carbon column, mixtures of two polymers with different molar masses have been injected into the column. After isocratic elution in pure 1-decanol, the retained samples have been desorbed and eluted in the linear gradient 1-decanol/TCB. The corresponding chromatograms are shown in Figures 3−5.

Figures 3−5 show that the binary mixtures of polymers are separated into their individual components. Despite the fact that the molar masses of the components influence their retention volume, the separation is governed mainly by the chemical composition or tacticity of samples; i.e., nearly baseline-separated peaks are obtained for all components.

Figure 6 shows the chromatogram of a blend of the polymers that have been injected into the Hypercarb column as previously described. First, the isotactic PP elutes isocratically followed by the retained components that are desorbed by the gradient. Atactic PP, syndiotactic PP, and linear PE are first fully retained due to their selective adsorption on the column packing and finally desorbed by the linear gradient. PE standards with molar masses in the range of 1−10 kg/mol are eluted with smaller elution volumes than PE in the range of 14−260 kg/mol, which elute at almost identical elution volumes (see Figures 5 and 6). It is concluded that polymers with different molar masses eluted in narrow zones with slightly different elution volumes. However, the effect of chemical composition and tacticity on the elution volume is much more dominant. This makes the identification of the eluted components an easy task.

Findenegg and Liphard[62] studied the adsorption of higher *n*-alkanes ($C_{16}-C_{32}$) on graphitized carbon from dilute solutions. The interpretation of the adsorption isotherms suggests a close packing of the long-chain alkane molecules parallel to the graphite surface. Chain molecules with side groups cannot form closely packed layers because of steric hindrance and show quantitatively different adsorption behavior. Such effects may be expected for PE and PP. These effects may be supported by the homogeneity of the graphitized carbon packing which offers a three-dimensional spatial selectivity.[59]

The studies of crystallization of PE on graphite confirm that attractive interactions between PE and the surface of graphite are active.[63,64] Carbon atoms of PE are arrayed in a perfectly ordered way on a surface of highly oriented pyrolithic graphite;[63,64] i.e., the crystallization of PE on the surface of graphite is surface-controlled due to interactions of PE with the graphite substrate. It is supposed that the adsorption liquid chromatography of polyolefins presented in this paper utilizes such interactions.

The isocratic elution plus the gradient of decanol/1,2,4-trichlorobenzene and the reconditioning of the stationary phase require about 50 min. This indicates the fast kinetics of the adsorption and the desorption processes. The drawback of the Hypercarb material is the significantly higher price as compared to a reversed phase silica gel material. It should be noticed that 1-decanol and the sample solutions in 1-decanol have changed their color from clear to yellow or light brown, when they have been kept at 160 °C for several hours. A reason for this change of the color is not known yet. Differences in the retention behavior of clear and the colored sample solutions have not been observed. A change of the ELSD baseline through the gradient elution has not been detected.

In future work the separation selectivity of the described HPLC system toward other types of polyolefins will be tested.

Conclusion

The Hypercarb column with 1-decanol as the mobile phase adsorbs atactic polypropylene, syndiotactic polypropylene, and linear polyethylene at a temperature of 160 °C, while isotactic polypropylene is eluted without a pronounced retention. The retained polymers are eluted from the column in a gradient of 1-decanol/1,2,4-trichlorobenzene. A similar separation of the mentioned polymers, by e.g. TREF, CRYSTAF, or Holtrup fractionation, requires larger amounts of samples, solvents, and time. The described HPLC system enables faster separation of the linear polyethylene from isotactic polypropylene as well as separation of polypropylene according to its tacticity. Such separations could find applications especially in high-throughput experimentation for polyolefin research and development.

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