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Separation and Characterization of Ethylene-Propylene Copolymers by High-Temperature Gradient HPLC Coupled to FTIR Spectroscopy

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Summary: The chromatographic separation of ethylene-propylene (EP) copolymers with regard to chemical composition was accomplished by a new technique - high-temperature gradient HPLC. Using a mobile phase of ethylene glycol monobutylether (EGMBE) and 1,2,4–trichlorobenzene (TCB), and silica gel as the stationary phase, copolymers with different ethylene contents were separated according to their chemical compositions. Using a sample solvent of n-decanol and a column temperature of 140 °C, chromatographic conditions were established that correspond to separation in a precipitation-redissolution mechanism. With the aim to obtain further information on the separation process, the HPLC system was coupled to FTIR spectroscopy through a LC-Transform interface. The FTIR data confirmed that the copolymers were separated according to the ethylene content of the eluted samples.

Keywords: ethylene-propylene copolymers; FTIR; high performance liquid chromatography; polyolefins

Introduction

Ethylene-propylene (EP) copolymers are important polymeric materials. Depending on the comonomer content of the EP copolymers their properties change from crystalline (low comonomer content) to amorphous (high comonomer content). The determination of the chemical composition distribution (CCD) of EP copolymers requires fast and efficient analytical methods. The analysis of EP copolymers and blends of polyethylene and polypropylene by DSC is a well established and simple method;[1–6] however, it is not a separation method and, thus, cannot provide a CCD.

For separations according to chemical composition, temperature rising elution fractionation (TREF) is used.[7–14] In a TREF experiment the sample is dissolved at high temperature and precipitated using a slow cooling process. In a second step, fractions of the precipitated material are eluted at increasing elution temperatures. The fractionation occurs mainly regarding sample crystallinity and cannot be used for amorphous samples. In addition, the long analysis times and the complexity of the method prevent a routine use on a daily basis. With crystallization analysis fractionation (CRYSTAF), which is partially similar to TREF but requires less analysis time, determinations of the CCD of EP copolymers, high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE) and polypropylene (PP) were accomplished.[15–19] It should be noted that amorphous EP copolymers that do not crystallize cannot be separated using the mentioned fractionation techniques. Other techniques that separate polyolefins according to chemical composition are selective extraction with appropriate solvents and solution-precipitation techniques.[20–22] These

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techniques, however, require significant amounts of solvents, time and labour.

Within the large variety of liquid chromatographic techniques, only size exclusion chromatography (SEC) has been used so far for the analysis of polyolefins. High temperature SEC enables a more or less correct determination of molar mass distributions of olefin copolymers, but components with different chemical compositions may co-elute. Even by coupling SEC with FTIR spectroscopy, only average chemical compositions corresponding to each elution volume, but not CCDs, can be determined.[23–25]

High performance liquid chromatography (HPLC) is an important tool for fast separation of complex polymers with regard to chemical composition.[26,27] Different separation mechanisms such as adsorption-desorption or precipitation-redissolution are used.[28,29] Typical concentration detectors like differential refractive index (DRI) and evaporative light scattering detectors (ELSD) do not provide information on the chemical composition of the separated species. When HPLC is coupled to FTIR, however, information on the chemical composition of the chromatographic fractions can be obtained.[30–32]

Unfortunately, up to now, HPLC techniques for the separation of polymers have been used only at temperatures below 100 °C. For polyolefins, however, temperatures between 130–160 °C are necessary for keeping the polymer samples in solution. In our previous work,[33] a gradient HPLC system was developed that enables to separate blends of olefin homopolymers (PE and PP) according to their chemical composition at high temperatures. Polar silica gel, as the stationary phase, and a mobile phase comprising ethylene glycol monobutylether (EGMBE) and 1,2,4-trichlorobenzene (TCB) were used. The separation was based on the fact that EGMBE is a non-solvent for linear polyethylene (above ~20 kg/mol) and a solvent for isotactic polypropylene. Thus, polyethylene precipitates on the column while polypropylene is eluted when pure EGMBE is used as the mobile phase. With a gradient of EGMBE and TCB, the separation of polypropylene and polyethylene can be achieved, where polypropylene elutes in the SEC mode and polyethylene elutes with the solvent gradient, respectively.[33]

In the present paper, the separation of EP copolymers by high temperature gradient HPLC according to chemical composition is reported. For the first time the coupling of gradient HPLC with FTIR spectroscopy at temperatures that are suitable for the characterization of polyolefins is described.

Experimental Part

High-Temperature Chromatograph PL XT-220

A prototype high-temperature gradient HPLC system PL XT-220 (Polymer Laboratories, Varian Inc, Church Stretton, England) was used.[34] The stationary phase was silica gel Nucleosil 500, column size 25 × 0.46 cm I.D., average particle diameter 5 μm (Macherey Nagel, Düren, Germany). For dissolution and injection of the samples a robotic sample handling system PL-XTR (Polymer Laboratories) was used. The temperature of the auto sampler with the sample block and the injection needle, the injection port and the transfer line between the auto sampler and the column compartment was set to 140 °C. The mobile phase flow rate was 1 mL/min and 50 μL of sample solutions were injected. The polymers were dissolved in TCB at a concentration of 1–1.2 mg/mL at a temperature of 150 °C. The column outlet was connected either to an evaporative light scattering detector (ELSD, model PL-ELS 1000, Polymer Laboratories) or to a LC-Transform FTIR Interface (Series 300, Lab Connections, Carrboro, USA). The ELSD was operated at a nebulisation temperature of 160 °C, an evaporation temperature of 270 °C and an air flow of 1.5 mL/min. The LC-Transform was operated at a stage temperature of 164 °C and a temperature

Table 1.
Average molar masses, polydispersities (PD) and ethylene contents of the copolymers.

Sample	M_w (SEC) [g/mol]	M_n (SEC) [g/mol]	PD	Ethylene (FTIR) wt [%]
EP1	277,000	77,600	3.57	49
EP2	270,000	49,000	5.52	32
EP3	757,000	97,700	7.76	26
EP4	277,000	72,400	3.82	38

of the transfer line of 150 °C. A temperature gradient of the nozzle was used due to the different boiling points of the mobile phase components. The rotation velocity of the Germanium disc was 10 degree/min. FTIR spectra of the deposited fractions were recorded using a Nicolet Protegè 460 (Thermo Electron, Waltham, USA). For data collection and processing, the WinGPC-Software (Polymer Standards Service, Mainz, Germany) was used.

Crystaf

A Crystaf model 200 (Polymer Char S.A, Valencia, Spain) was used for the fractionation. For the analysis, 20 mg of the sample were dissolved in 30 mL of 1,2-dichlorobenzene in a stirred vessel. A cooling rate of 0.1 °C/min was used for the fractionation of the samples.

Solvents

1,2,4-Trichlorobenzene (TCB), n-decanol and ethylene glycol monobutylether (EGMBE), all of synthesis quality (Merck, Darmstadt, Germany) were used as received in this study.

Samples

Linear polyethylene (PE) with a weight-average molar mass of M_w 126 kg/mol was obtained from Polymer Standards Service (Mainz, Germany). Moplen HP 400R (M_w: 305 kg/mol) is a commercial polypropylene of BASELL Polyolefine GmbH, Frankfurt, Germany. A blend of 2.52 mg PP and 2.26 mg PE was used for developing a coupling method HT-gradient HPLC-FTIR.

EP copolymers were obtained from BASELL Polyolefine GmbH and their characteristic data are summarized in Table 1. The samples were prepared by the gas phase process.

Results and Discussion

Separation of EP copolymers

The fractionation of amorphous EP copolymers with regard to chemical composition is difficult. These samples do not crystallize and, hence, TREF or CRYSTAF cannot be used for fractionation. The CRYSTAF curves of samples EP1-EP4 are presented in Figure 1. As can be seen, there are no crystallizing fractions indicating that the samples are fully amorphous. On the other hand, the CRYSTAF results indicate that the samples do not contain any PE or PP homopolymers. These components would crystallize producing peaks in the CRYSTAF curves of Figure 1.

For the chromatographic separation of the copolymer samples regarding chemical composition, gradient HPLC is the method of choice. In gradient HPLC experiments, very frequently the sample is dissolved in a good solvent and then injected into a mobile phase of low solvent strength or even a non-solvent. This causes the sample to precipitate on the column. By stepwise or continuously increasing the solvating power of the eluent, the precipitate is re-dissolved and separated by adsorptive or solubility effects. These adsorptive or solubility effects correlate with the chemical composition of the sample and separation according to chemical composition can be achieved.

As has been shown previously, PE-PP blends can be separated by high-temperature gradient HPLC using silica gel as the stationary phase. A mobile phase of TCB as the thermodynamically good solvent and EGMBE as the poor solvent is used. TCB is a good solvent for both PE and PP, while EGMBE is a good solvent for PP and a non-solvent for PE.[21,35] Starting with 100% EGMBE for 2 min, the volume

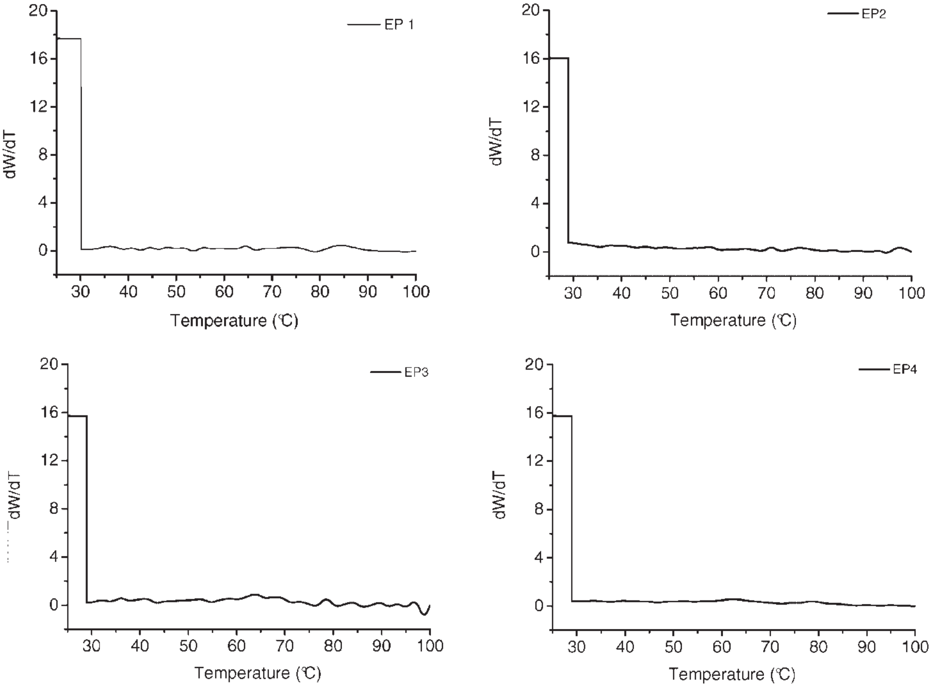

Figure 1.
CRYSTAF curves of samples EP1, EP2, EP3 and EP4.

fraction of TCB is increased linearly to 100% in 3 min and held constant for 3 min. Finally, the initial chromatographic conditions are re-established. The corresponding gradient profile is shown in Figure 2.

Because of the column void volume and the dwell volume of the chromatographic system, the gradient reaches the detector with a delay of 5.03 min, i.e., the gradient reaches the detector at 7.03 min. For the EP copolymers, chromatograms are obtained that are presented in Figure 3. Qualitatively similar chromatograms are obtained for all samples. All samples elute in three different elution regions. These can be attributed to different separation mechanisms and

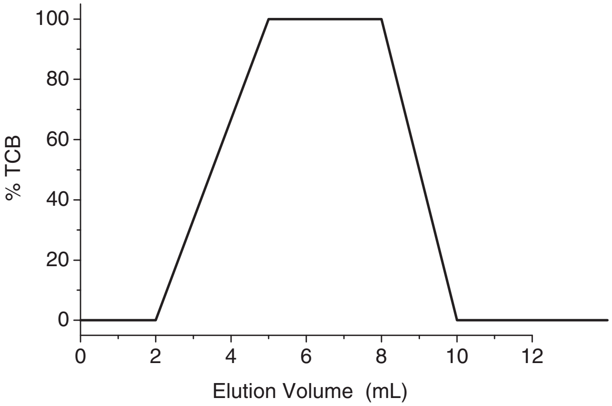

Figure 2.
Gradient profile, stationary phase: Nucleosil 500, mobile phase: linear gradient EGMBE-TCB.

different chemical compositions. The polymer fractions that appear between 1.5 and 2.2 mL elute with the initial mobile phase and, thus, are soluble in EGMBE at 140 °C. Taking into account the results of our previous investigations[33] these fractions can be assumed to be EP copolymers with low ethylene contents. In addition, these fractions could contain some atactic PP. The next elution region correlates with the solvent peak (n-decanol) at an elution volume of 2.3 mL. The polymer fractions that elute with the sample solvent n-decanol are assumed to be EP copolymers with medium ethylene contents. Polymers that are insoluble in EGMBE and do not elute with n-decanol appear later in the chromatograms. They elute with the TCB gradient in the elution volume region of 7–9 mL. These polymer fractions are supposedly EP copolymers with higher ethylene contents. As has been shown by the CRYSTAF experiments (see Figure 1) the samples do not contain PP or PE homopolymer fractions.

Coupling of HT-gradient HPLC and FTIR

As is shown in Figure 3 the chromatograms indicate that the EP copolymer samples are separated with regard to chemical composition by high-temperature gradient HPLC. To prove that this is the case and to get more information on the separation mechanism, the HPLC system was coupled to FTIR spectroscopy. The most suitable way of combining the two techniques is by using the LC-Transform interface where the eluate coming from chromatography is sprayed on a rotating Germanium disc. Under high temperature spraying conditions the mobile phase evaporates and the polymer fractions are deposited as solid layers at different positions of the disc. Subsequently, the disc is placed in a FTIR spectrometer and spectra are taken from all polymer fractions.

One major issue of the spray deposition procedure is the boiling point of the mobile phase. In particular, when conducting gradient HPLC separations, problems arise

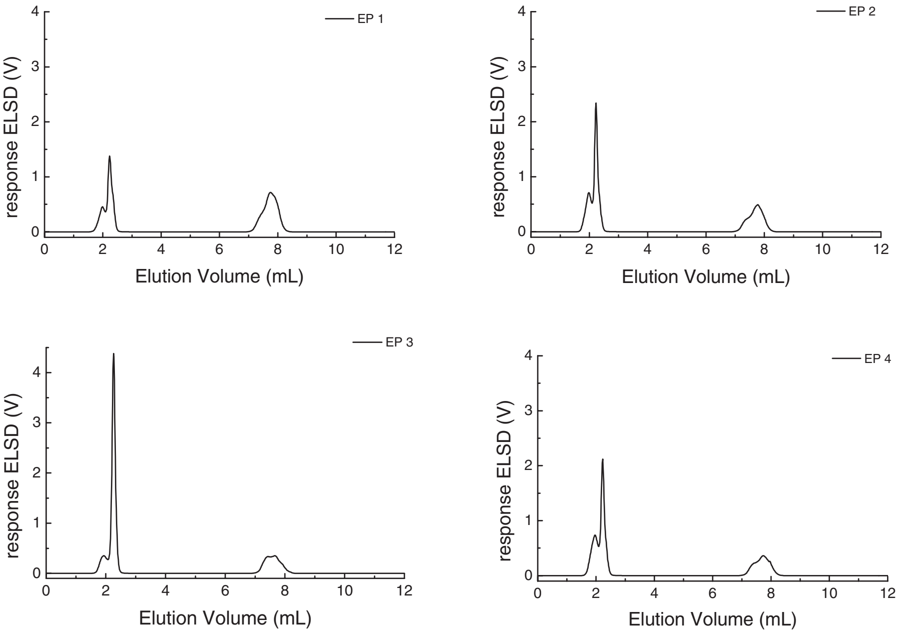

Figure 3.

Gradient HPLC chromatograms of samples EP1-EP4, stationary phase: Nucleosil 500, mobile phase: linear gradient EGMBE-TCB, column temperature: 140 °C, detector: ELSD, sample solvent: n-decanol, sample concentration ~ 1.3 mg/mL.

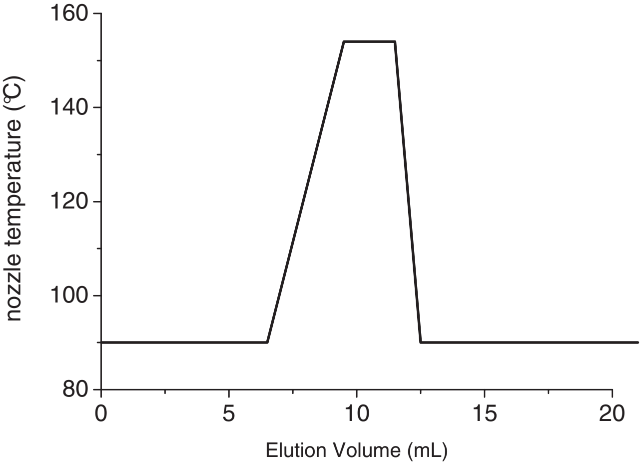

Figure 4.
Temperature gradient for the spray nozzle of the LC-Transform interface.

from the fact that the components of the mobile phase have different boiling points. In the present case these are 220 °C for TCB and 170 °C for EGMBE. Therefore, the evaporation temperature in the LC-Transform interface has to be changed continuously and corresponding to the actual mobile phase composition. A linear temperature gradient for the LC-Transform nozzle has been found to be the optimum, see Figure 4. Starting with a nozzle temperature of 90 °C for 6.5 min, the nozzle temperature is raised linearly to 151 °C in the following 3 min and than kept constant for another 3 min. Finally, the nozzle temperature is decreased back to 90 °C.

To prove that the system is working properly, a model PP-PE blend was fractionated and analyzed by HPLC-FTIR. The concentration profile of this separation obtained by the ELS detector is shown in Figure 5.A, indicating that a perfect separation into two components was obtained. The first peak eluting at 2 mL corresponds to PP and the later eluting peak corresponds to PE. The Gram-Schmidt plot resulting from summarizing all FTIR peak intensities in the range of 2800–3200 cm^{-1} as a presentation of the concentration profile is given in Figure 5.B. The comparison of the Gram-Schmidt plot (Figure 5.B) with the concentration chromatogram

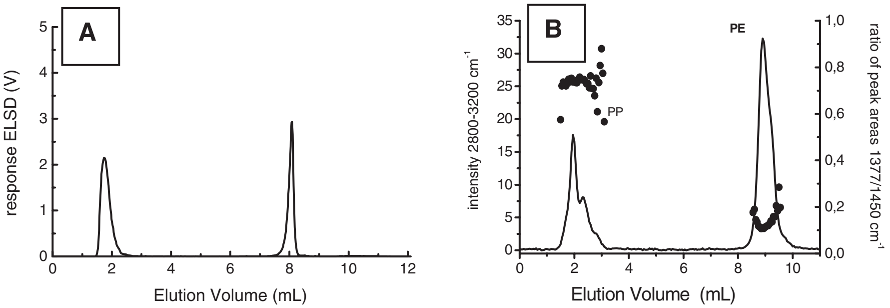

Figure 5.
HT-HPLC separation of a PP-PE blend (A) and HPLC/FTIR analysis (B), full line ELSD trace (A) or Gram-Schmidt plot (B), ■ relative amount of CH_3 groups (peak ratio CH_3/CH_2), chromatographic conditions see Figure 3.

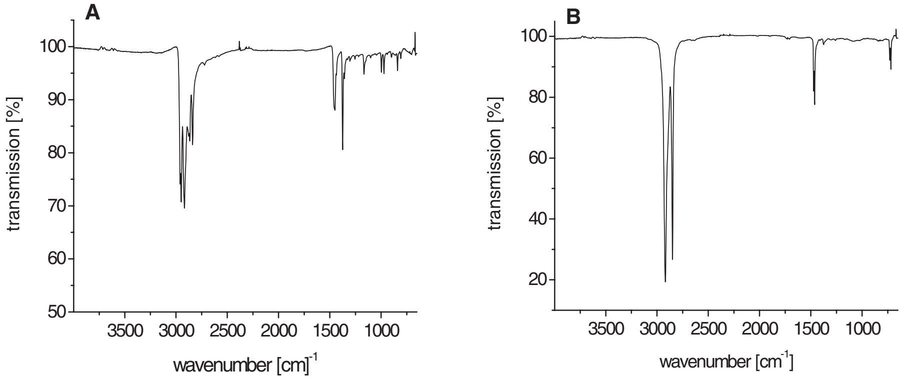

Figure 6.
FTIR spectra of the PP and PE peaks (in Figure 5) taken at peak maximum.

(Figure 5.A) indicates that the first eluting peak appears to be broader in the Gram-Schmidt plot. An explanation for this behaviour is the use of n-decanol as the sample solvent (boiling point 233 °C) that cannot evaporate as fast as EGMBE at the present conditions. Traces of n-decanol that were not evaporated were detected even on the Germanium disc.

The quantitative analysis of the FTIR spectra was carried out by analyzing the absorption bands for the CH_3 groups at 1376 cm^{-1} and the CH_2 groups at 1462 cm^{-1}.[36] The presence of CH_3 groups indicates branching and is characteristic for propylene units while the concentration of CH_2 groups is a measure for total polymer concentration. In Figure 5.B the ratio of CH_3/CH_2 (1394–1328 cm^{-1}/1394–1488 cm^{-1}) is plotted against the elution volume.

For the PP-PE blend in Figure 5, peak area ratios of 0.75 for the PP peak and 0.10 for the PE peak were detected. The low concentration of CH_3 groups in the PE fraction indicates that the material is slightly branched. The corresponding FTIR spectra at the peak maximum verify the chemical composition of the first peak as PP and of the second peak as PE, respectively, see Figure 6.

Analysis of EP copolymers by HPLC-FTIR

As has been demonstrated, PP-PE blends can be separated by HT-gradient HPLC with regard to chemical composition. The quantitative analysis of the fractions is conducted by FTIR spectroscopy using the LC-Transform approach. A similar procedure shall be used also for the analysis of the EP copolymers. Using the same experimental conditions for the LC-Transform and the FTIR measurements, the EP copolymers are analysed with regard to chemical composition as is shown in Figure 7.

A comparison of the Gram-Schmidt plots and the elution profiles obtained with the ELS detector shows that the Gram-Schmidt peaks are slightly broader. This is due to the fact that a certain spreading cannot be avoided in the spraying procedure of the LC-Transform interface. This, however, does not affect the quality of separation with regard to chemical composition.

The peak area ratios CH_3/CH_2 for the different elution peaks show clearly that early eluting peaks exhibit a higher peak area ratio than late eluting peaks. This clearly indicates that the early eluting fractions have lower ethylene contents than the late eluting fractions. Over the entire elution volume range the ratio of CH_3/CH_2 decreases with an increase in the elution volume. This is in full agreement with the proposed separation mechanism.

If the ethylene content in the copolymer increases, a decrease in solubility is observed. Copolymers with high propylene content (peak area ratio >0.55) elute in EGMBE or

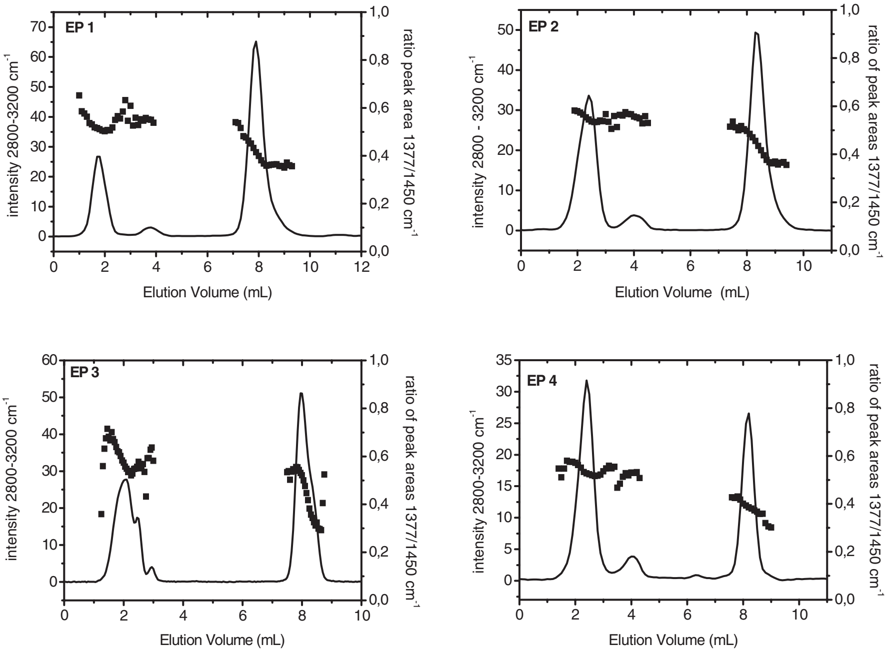

Figure 7.
Gram-Schmidt plots of the HT-gradient HPLC separation of EP copolymers 1–4, full line Gram-Schmidt plots, ■ relative amount of CH_3 groups (peak ratio CH_3/CH_2), chromatographic conditions see Figure 3.

with the sample solvent peak. From the fact that the peak area ratio is less than for pure PP (0.75 in Figure 6) it can be concluded that the early eluting peaks do not contain PP but EP copolymer with low ethylene contents. This is in a good agreement with the CRYSTAF measurements, where no isotactic PP and no PE were detected. With increasing PE content the EP copolymer becomes less and less soluble in EGMBE and elutes with the solvent gradient according to the solvent strength. The EP copolymers start to elute close to the starting point of the gradient between 7.1 and 7.5 mL. Apparently, there is a solubility threshold at a certain copolymer composition. Accordingly, rather similar CH_3/CH_2 ratios are obtained for the end of the first peak and the beginning of the second peak. For the EP copolymer fractions with the lowest propylene content, peak area ratios of 0.25 to 0.35 are measured. Compared to the blend separation in Figure 5 a shift to lower elution volumes is observed for the late eluting peaks. This additionally indicates that the peaks are due to EP copolymer and not PE homopolymer. Finally, the decreasing peak area ratio with increasing elution volume within the late eluting peaks clearly confirms the separation with regard to chemical composition. Due to the steep gradient it is not surprising that the peak positions of the EP copolymers do not vary much. For a better separation of the fractions A more shallow gradient has to be chosen.

As mentioned earlier, the higher boiling point of n-decanol compared to EGMBE results in a certain spreading of n-decanol on the Germanium disc. The elution peak appearing at an elution volume of 4 mL corresponds to the solvent peak in Figure 3. This peak contains small amounts of EP copolymer with medium ethylene content as can be seen in Figure 7.

As indicated in Figure 7, the analyzed EP copolymers exhibit broad distributions with chemical compositions ranging from 0.7 to 0.3 (relative amount of CH_3/CH_2). The differences between the samples can be understood from the chemical compositions of the different eluting fractions. Sample EP1 has the highest average ethylene content (49%) while sample EP3 has the lowest average ethylene content (26%), see Table 1. The results in Figure 7 indicate the same trend: in EP1 the first eluting (propylene-rich) fraction shows a peak area ratio of 0.63–0.5 while for EP3 this ratio is higher with 0.72–0.5. This indicates that the propylene content of this fraction is higher for sample EP3. In addition to the higher propylene content, the area of this peak is higher as compared to EP1. This is a clear proof that the average propylene content of EP3 is higher as compared to EP1.

The aim of forthcoming investigations is the exact calibration of the FTIR system for a strict quantitative analysis of the ethylene content of the EP copolymers. To achieve this goal NMR data of model EP copolymers will be correlated with corresponding FTIR bands for PP and PE. By using a fully calibrated system, absolute chemical composition values of amorphous EP copolymers can be obtained and the chemical composition distribution of these copolymers can be described.

Conclusions

High temperature gradient HPLC is the first chromatographic method that enables separation of EP copolymers with regard to their chemical composition. Using a polar stationary phase and a solvent gradient of EGMBE/TCB it is possible to fractionate complex copolymers in the direction of increasing ethylene content. The separation of a PE-PP blend and EP copolymers into components of different chemical compositions was confirmed by coupling of the gradient HPLC with FTIR. This is the first time that a LC-Transform FTIR interface was used for gradient-HPLC at temperatures suitable for the separation of polyolefins.

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