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High-temperature gradient HPLC for the separation of polyethylene–polypropylene blends

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Abstract

A high-temperature gradient HPLC method has been developed for the analysis of polyethylene–polypropylene blends. For the first time it was possible to separate these polyolefin blends by a chromatographic technique which is operating at 140 °C. Blends of a commercial polypropylene and a medium molar mass linear polyethylene were separated using a mobile phase of ethylene glycol monobutylether (EGMBE) and 1,2,4-trichlorobenzene (TCB) and silica gel as the stationary phase. With the use of *n*-decanol as sample solvent, a precipitation–redissolution mechanism for polyethylene (PE) was established while polypropylene (PP) is eluted in size exclusion mode.

Keywords: High performance liquid chromatography; Blends; Polyethylene

1. Introduction

Polymer blends are an important part of commercial polymeric materials. The identification and the quantification of the blend components require fast and efficient analytical methods. Blend analysis by DSC has the advantage of being simple to carry out and using widely available equipment [1–5]. Temperature rising elution fractionation (TREF) can effectively be used for blend and copolymer separation [6–12]. However, the operational complexity of this technique and the very long analysis times have prevented an extensive use. Crystallization analysis fractionation (CRYSTAF) separates through slow cooling of a polymer solution based on crystallinity. With this technique the separation of polymer blends as well as the determination of chemical composition distributions of various polyolefins, including linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE) and polypropylene (PP) were accomplished [13–17]. Other techniques to separate polymer blends are selective extraction with appropriate solvents, solution-precipitation, or size exclusion chromatography (SEC) [18–22].

High performance liquid chromatography (HPLC) is an important tool for the fast separation of complex polymers with regard to chemical composition [23,24]. HPLC separations can be achieved via different mechanisms, including adsorption–desorption and precipitation–redissolution [25,26]. In gradient HPLC, frequently precipitation and adsorption processes are combined [27–30]. An overview of different techniques and applications involving the combination of SEC and gradient HPLC was published by Glöckner [23].

At present, standard HPLC methods related to polymers, e.g. gradient chromatography or chromatography at critical conditions, are limited to ambient temperatures [24,31,32]. Therefore, they cannot be applied to the separation of polyolefins and, indeed, high-temperature gradient HPLC work on polyolefins has never been published. In a previous work, the isocratic separation of polyethylene–polypropylene blends was published by our group [33]. For this type of separation, limiting conditions for PE were used [34]. The separation at limiting conditions is based on the fact that the thermodynamically good sample solvent builds a stable plug in the column, when injected into a non-solvent that is used as an eluent. The PE excludes from the solvent plug and encounters a mobile phase under which conditions it is not soluble and precipitates. The polymer is redissolved when the solvent plug reaches the precipitate. These exclusion–precipitation–redissolution steps repeat until the polymer elutes with the solvent peak of the column. For the separation of PE and PP 1,2,4-trichlorobenzene (TCB) was used as thermodynamically good solvent for both components and ethylene glycol monobutylether (EGMBE) as eluent. A column packed with dimethylsiloxane modified silicagel was used as stationary phase.

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EGMBE is a non-solvent for PE but a solvent for PP [19]. As a result, PE eluted almost irrespective of its molar mass under limiting conditions, while PP eluted in the SEC mode before the PE components.

The majority of published HPLC separations are conducted at operating temperatures of up to 60 °C [23,24]. These temperatures are too low for the dissolution of polyolefins, which require at least 120 °C for dissolution. The stability of column packings under high-temperature conditions has been investigated for normal phase [35,36], as well as for reversed phase materials in HPLC of small molecules [37]. Most of the solvent combinations were aqueous with either acetonitrile or methanol as organic component. Results about the stability of column packing materials at high-temperature gradient HPLC in solvents for PE and PP have not been published yet.

In the present paper, we report for the first time the separation of PE–PP blends by high-temperature gradient HPLC.

2. Experimental

2.1. Equipment

A prototype of a high-temperature gradient HPLC system PL XT-220 (Polymer Laboratories, Church Stretton, England) was used [38]. The stationary phase was Nucleosil 500, column size 25×0.46 cm I.D., average particle diameter 5 μm (Macherey Nagel, Düren, Germany). The column outlet was connected to a customized evaporative light scattering detector (ELSD, model PL-ELS 1000 of Polymer Laboratories) working at a nebulization temperature of 160 °C, an evaporation temperature of 270 °C and with an air velocity of 1.5 L/min. The eluent flow rate was 1 mL/min. A robotic sample handling system PL-XTR (Polymer Laboratories) was applied for sample preparation and injection. The column compartment was set to 140 °C, the injection port and transfer line between the chromatograph and the auto sampler was set to 150 °C, while the temperature of the sample block and the tip of the robotic arm was 160 °C. The software package 'WinGPC-Software' (Polymer Standards Service GmbH, Mainz, Germany) was used for data collection and processing.

2.2. Solvents

1,2-Dichlorobenzene, 1,3-dichlorobenzene, 1,2,4-trichlorobenzene (TCB), decalin, 2-ethyl-hexyl acetate, 2-ethyl-1-hexanol, cyclohexyl acetate, *n*-decanol, cyclohexanol, cyclohexanone and ethylene glycol monobutylether (EGMBE), all of synthesis quality (Merck, Darmstadt, Germany) were used in this study.

2.3. Samples

Linear polyethylene standards ($M_p/M_n/M_w$: 1.1:1.1:1.23, 33.5:28.0:36.5, 77.5:60.0:91.5 and 126:114:183 kg/mol) were 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.

3. Results and discussion

3.1. Influence of the sample solvent on the elution behavior of PE

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 redissolved and separated by adsorptive or solubility effects. These adsorptive or solubility effects correlate with the chemical composition of the sample and a separation according to chemical composition can be achieved.

As has been shown by Macko et al., [33] modified silica gel is a stable stationary phase for high-temperature isocratic HPLC experiments. In the present case, we used non-modified silica gel to make sure that the drastic conditions during gradient runs (high temperature, pressure fluctuations and solvent gradients) do not deteriorate the stationary phase.

For the separation of PE and PP, 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. After a number of experiments with stepwise gradients, a linear gradient of EGMBE–TCB was chosen. Starting at 100% EGMBE for 2 min, the volume fraction of TCB is increased linearly to 100% within the following 3 min and then kept constant for another 3 min. Finally, the initial chromatographic conditions are re-established. The corresponding gradient profile is shown in Fig. 1 (dotted line). The times given represent the gradient produced at the pump. The gradient reaches the detector with a shift of 5 min caused by the dead volume of the chromatographic system.

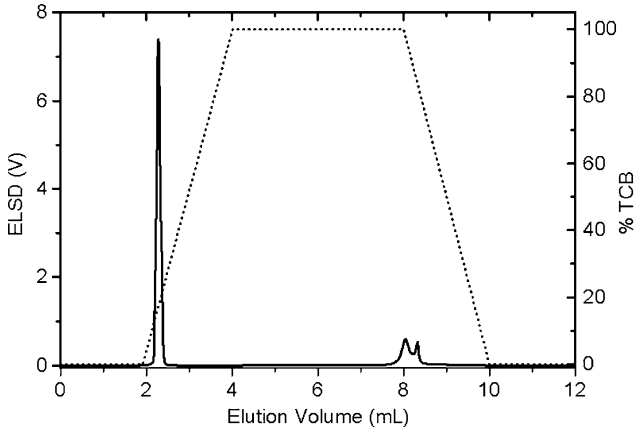

Fig. 1. Chromatogram of a PE standard (M_p: 126 kg/mol) and gradient profile (dotted line), stationary phase: Nucleosil 500, mobile phase: EGMBE–TCB, temperature: 140 °C, detector: ELSD, sample solvent: TCB, injection volume 50 μL (1 mg/mL).

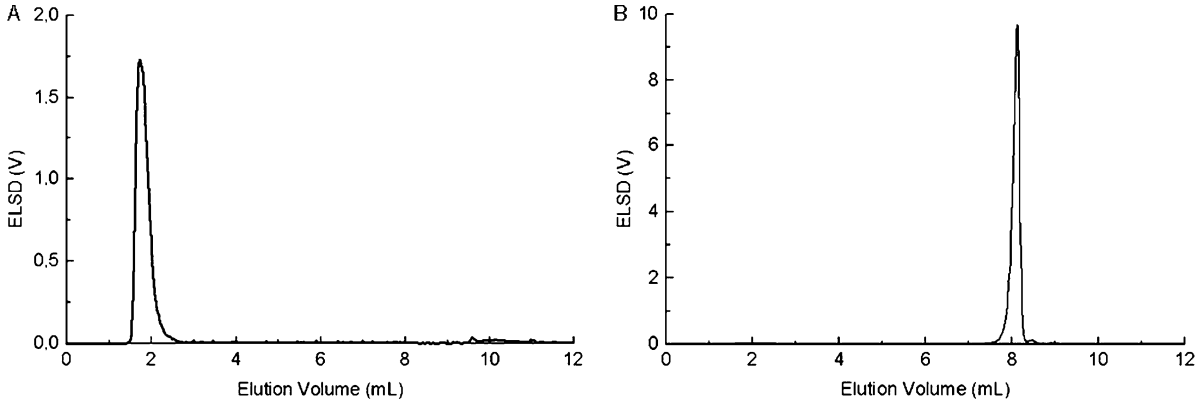

Fig. 2. Chromatogram of an isotactic PP sample (A) and a PE standard (126 kg/mol) (B), stationary phase: Nucleosil 500, mobile phase: EGMBE–TCB, temperature: 140 °C, detector: ELSD, sample solvent: *n*-decanol, injection volume 50 μL, sample concentration 1 mg/mL.

When a sample of PE is separated using the chromatographic system described above, a peak is detected at an elution volume of 2.2 mL. This peak appears at the elution volume of the solvent peak and is caused by the elution of a part of the sample at limiting conditions. As can be seen in Fig. 1, another portion of the PE sample is eluted with the gradient at a volume of 8 mL. This part is properly retained on the column and elutes in the precipitation–redissolution mode. The elution of polymer with the solvent peak in gradient HPLC experiments is called 'breakthrough peak'. The basic mechanism is analoguous to the elution of polymers at limiting conditions. The parameters that cause the 'breakthrough' of the polymer were investigated recently by Jiang [39]. It is caused by the fact that a polymer in a thermodynamically good solvent is injected into a weak or non-solvent.

For a baseline separation the elution of the injected polymer with the solvent peak must be prevented. There are several parameters that influence the breakthrough of the injected polymer: concentration of the injected sample, volume of the injected solvent, temperature, type of eluent and injected solvent. With the aim to minimize or to avoid the breakthrough peak, the influence of the injected volume (and thus the amount of sample) was investigated. The injection volume was decreased stepwise from 50 to 10 μL but no significant change on the breakthrough peak could be observed. As mentioned before it is possible to minimize the breakthrough peak by decreasing the strength of the sample solvent. Therefore, the PE sample was dissolved in several known solvents for both PE and PP, and injected into the chromatograph and the gradient was applied [40]. With 1,2-dichlorobenzene, 1,3-dichlorobenzene, decalin, 2-ethylhexyl acetate, 2-ethyl-1-hexanol, cyclohexyl acetate, cyclohexanol or cyclohexanone the breakthrough was still observed.

When the sample was dissolved in *n*-decanol no breakthrough peak has been detected (Fig. 2(B)). Apparently, PE is completely precipitated on the column and can only be eluted when a gradient is applied. It can be speculated that the reason for the absence of the breakthrough peak when *n*-decanol is used as sample solvent could be the fact, that the Θ-temperature of PE in *n*-decanol is 153 °C [41]. The column is operated at 140 °C and as a result the *n*-decanol solvent plug is not able to redissolve the precipitated PE.

As was assumed, under these conditions PP dissolves without problems and is eluted in the SEC mode, see Fig. 2(A).

3.2. Blend separation and quantification

Fig. 2(A) and (B) show the elution of PE and PP at distinctively different elution volumes. Therefore, the system should be suitable to separate PE–PP blends into the components. It is well known, that the response of the evaporative light scattering detector (ELSD) depends on the amount of the analyte and the mobile phase composition while it is considered to be independent of the chemical composition and molar mass of the analyte [42,43]. To prove if the amount of PE and PP in a given blend can be quantified using the ELSD, five blends of different compositions were prepared and analyzed. For the analysis about 3 mg of each blend were dissolved in 2 mL of *n*-decanol, see Table 1. The chromatograms of four blends with different PE–PP ratios are shown in Fig. 3.

As can be seen in Fig. 3, the PE–PP blends are perfectly separated into the components. There are no indications for the appearance of breakthrough peaks. For the quantification of the blend compositions from the ELSD peak areas, calibration curves with peak area vs. injected mass were constructed for PP and PE, see Fig. 4. For PP the normal exponential dependence of the ELSD response on sample amount is observed [44]. An asymptotic shape of the calibration curve is observed above an injected sample mass of 50 μg in the case of PE. One reason for

Table 1
Composition of the PE–PP blends

Sample	PP (mg)	PE (mg)	PE (wt%)
1	3.0	0	0
2	2.4	0.45	16
3	1.9	0.9	32
4	1.6	1.4	47
5	1.3	1.9	59
6	0.6	2.4	80
7	0	2.91	100

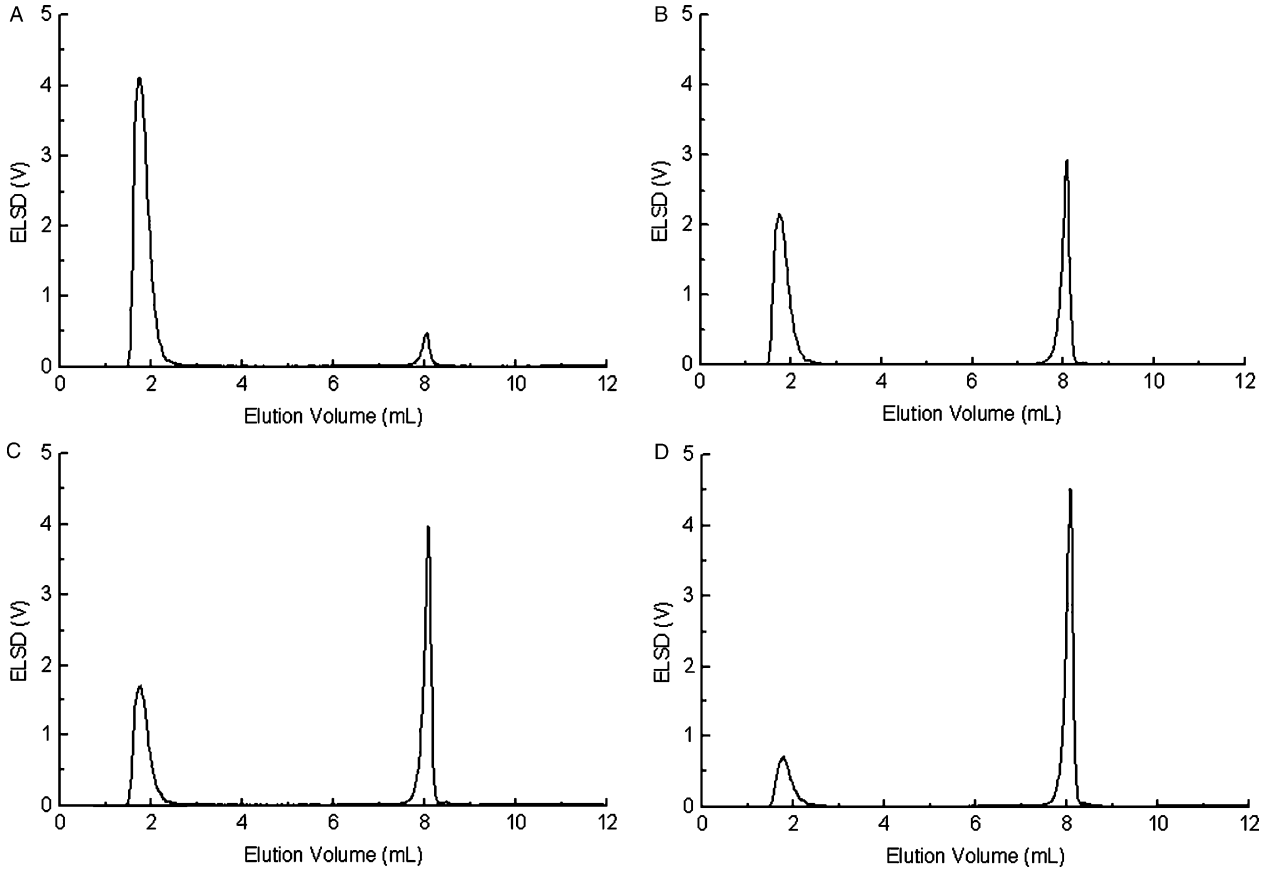

Fig. 3. High-temperature gradient HPLC separation of PE–PP blends of different compositions, sample concentration ~1.5 mg/mL, other experimental conditions see Fig. 2, (A) sample 2 (16% PE), (B) sample 4 (47% PE), (C) sample 5 (59% PE), (D) sample 6 (80% PE), see Table 1.

the different responses of PP and PE could be the different mobile phase compositions during detection. When the PP is detected the mobile phase contains 100% EGMBE whereas for the PE the mobile phase is a mixture of EGMBE and TCB. The peak intensities correspond to the relative concentration of each component in the blends.

3.3. Influence of the molar mass on the elution behavior of PE

As has been pointed out, the present separation procedure is based on the different solubility of PE and PP in EGMBE at 140 °C. The solubility of these polymers is, of course also influenced by the molar mass and the microstructure. The effect of the molar mass on the elution behavior of polyethylene is shown in Fig. 5.

Very low molar mass PE is soluble in EGMBE and, accordingly, elutes in the SEC mode at an elution volume of 2.2 mL, see Fig. 5(A) for a molar mass of 1.1 kg/mol. For such samples the precipitation–redissolution mechanism does not work. When the molar mass is sufficiently high, PE becomes insoluble in EGMBE and elutes with the solvent gradient, see Fig. 5(C) for a molar mass of 77 g/mol. PE with intermediate

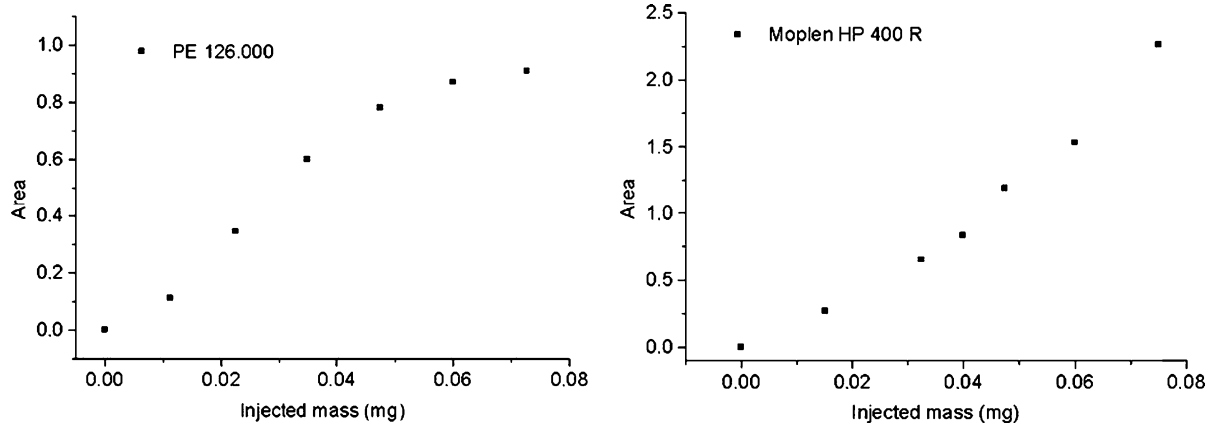

Fig. 4. ELSD calibration curves peak area vs. injected mass for PP and PE.

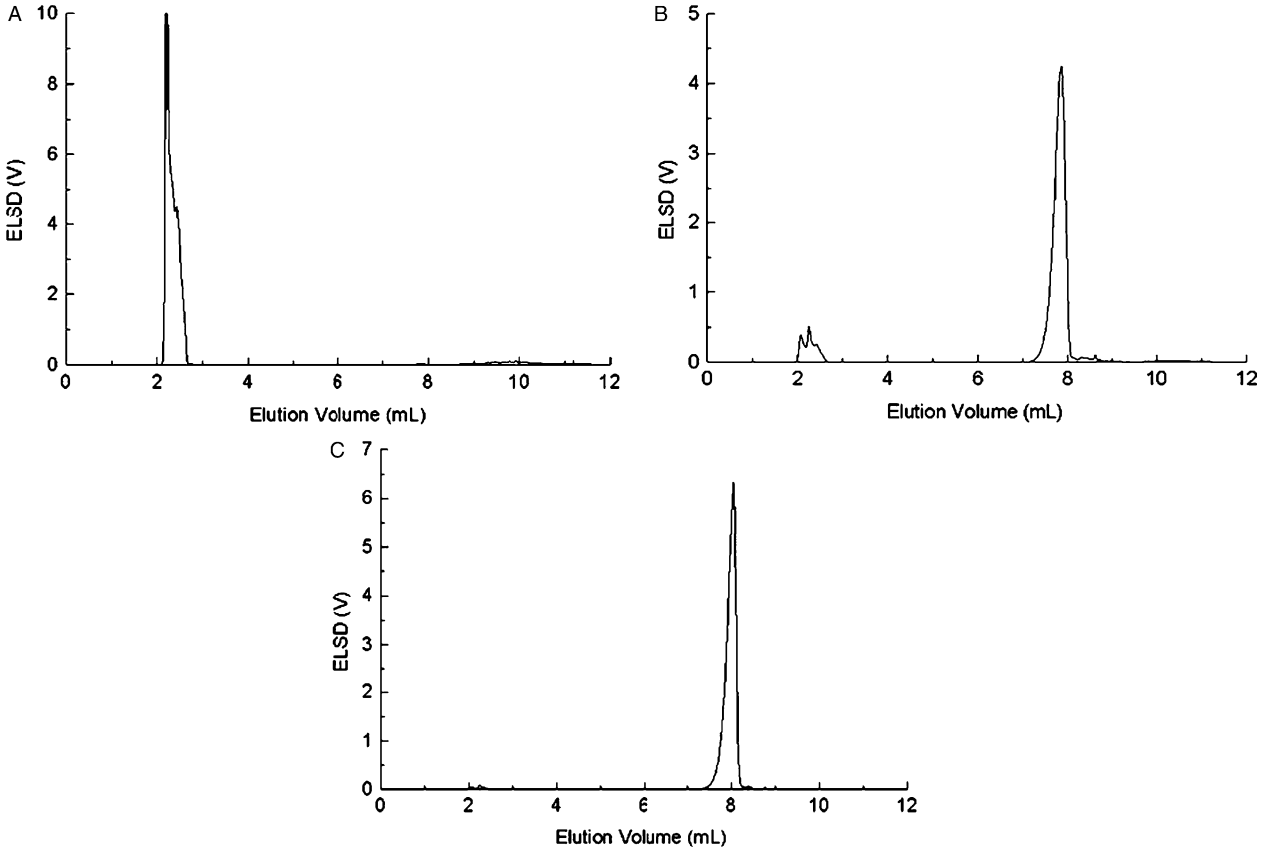

Fig. 5. High-temperature gradient HPLC separations of PE standards with different molar masses, samples: PE calibration standards with molar masses of 1.1 kg/mol (A), 33.5 kg/mol (B) and 77 kg/mol (C), experimental conditions see Fig. 2.

average molar masses, e.g. 33.5 kg/mol, may contain small fractions that are soluble in EGMBE and these fractions elute early while the major part of the sample elutes with the gradient, see Fig. 5(B). As can be concluded, for the present phase system a complete retention of PE is achieved above molar masses of about 40–50 kg/mol. This reasoning is based on samples with a rather low polydispersity. It is clear that with increasing polydispersity this retention limit shifts to higher molar masses. In particular, for Ziegler–Natta catalysed polyolefins with rather high polydispersities it can be suspected that certain amounts of low molar mass soluble species coelute with the solvent plug.

The aim of a number of ongoing experiments is the prevention of the co-elution of low molar mass PE and PP in PE–PP blends. To meet this requirement the pore size as well as the total pore volume of the stationary phase have to be adjusted. Another parameter that can be used to optimize the separation is the column temperature. In further experiments, the effect of branching on the chromatographic behaviour shall investigated.

4. Conclusion

A high-temperature gradient HPLC method has been developed which enables the analysis of PE–PP blends. For the first time it was possible to separate these blends by a chromatographic technique that is operating at 140 °C. The quantification of the amounts of PE and PP in PE–PP blends over a wide range of concentrations was accomplished. Furthermore, the elution behavior of PEs of different molar masses was studied and an influence of molar mass on the elution behavior of the PE was found.

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