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High-temperature gradient HPLC and LC-NMR for the analysis of complex polyolefins*

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Abstract: The synthesis and characterization of polyolefins continues to be one of the most important areas for academic and industrial polymer research. One consequence of the development of new "tailor-made" polyolefins is the need for new and improved analytical techniques for the analysis of polyolefins with respect to molar mass and chemical composition distribution. The present article briefly reviews different new and relevant techniques for polyolefin analysis. Crystallization analysis fractionation is a powerful new technique for the analysis of short-chain branching in linear low-density polyethylene (LLDPE) and the analysis of polyolefin blends and copolymers regarding chemical composition. For the fast analysis of the chemical composition distribution, a new high-temperature gradient high-performance liquid chromatography (HPLC) system has been developed. The efficiency of this system for the separation of various olefin copolymers is demonstrated. The correlation between molar mass and chemical composition can be accessed by on-line coupling of high-temperature size exclusion chromatography (HT-SEC) and ^{1}H NMR spectroscopy. It is shown that the on-line NMR analysis of chromatographic fractions yields information on microstructure and tacticity in addition to molar mass and copolymer composition.

Keywords: liquid chromatography; polyolefins; nuclear magnetic resonance; LC-NMR coupling; molecular structure.

INTRODUCTION

The polymerization of olefins to polymers with different microstructures and properties continues to be one of the most investigated areas for both industrial and academic laboratories in polymer science. The use of polyolefins as polymeric materials is rapidly growing due to the fact that polyolefins are made from simple and easily available monomers. In addition, they contain only carbon and hydrogen, and can be reused or degraded by thermal processes to oil and monomers [1]. New or improved properties are achieved by combining new monomers in copolymer systems, or by using new catalysts. Forty years after the discovery of the metallorganic catalyzed polymerization of olefins by Ziegler and the stereospecific polymerization of propene and α-olefins by Natta, the use of metallocene catalysts shows the way to expand the possibilities of olefin polymerization and the properties of the resulting polyolefin materials.

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One consequence of the development of new "tailor-made" polyolefins is the need for new and improved analytical techniques. In addition to monitoring the polymerization process, the molecular heterogeneity of the resulting products must be described by suitable methods. Irrespective of whether a Ziegler–Natta or a metallocene catalyst is used, information on molar mass distribution, chemical composition, tacticity, and branching is required to properly evaluate the polyolefin. Very frequently, polyolefins exhibit multiple distributions, e.g., long-chain branching and molar mass distribution in low-density polyethylene (LDPE) or chemical composition distribution and molar mass distribution in linear low-density polyethylene (LLDPE), copolymers, and polyolefin blends [2].

A number of fractionation techniques are used very sucessfully in polyolefin analysis. High-temperature size exclusion chromatography (HT-SEC) is the established method for molar mass analysis, while crystallization fractionation (CRYSTAF) [3–5] and temperature-rising elution fractionation (TREF) [6,7] are used for chemical composition or crystallinity analysis. For copolymers, CRYSTAF and TREF provide information about the chemical composition distribution. The drawbacks of these methods are that (1) they are very time-consuming and (2) they work only for crystallizable polyolefins.

High-performance liquid chromatography (HPLC) is an important tool for the fast separation of complex polymers with regard to chemical composition [8,9]. HPLC separations can be achieved via different mechanisms, including adsorption–desorption and precipitation–redissolution [10,11]. In gradient HPLC, frequently precipitation and adsorption processes are combined [12–15]. An overview of different techniques and applications involving the combination of SEC and gradient HPLC was published by Glöckner [8].

At present, standard HPLC methods for polymers, e.g., gradient chromatography or chromatography at critical conditions (LCCC), are limited to ambient temperatures [9,16,17]. The majority of published HPLC separations are conducted at operating temperatures of up to 60 °C [8,9]. These temperatures are too low for the dissolution of polyolefins, which require at least 120 °C for dissolution due to their mostly semicrystalline nature. It was, therefore, a challenge to develop HPLC methods for the separation of polyolefins that operate at temperatures of 120 °C and higher.

High-temperature gradient HPLC work on polyolefins has not been published until recently. In a previous work, the isocratic separation of polyethylene (PE)–polypropylene (PP) blends was published by our group [18,19]. For the separation of PE and PP, 1,2,4-trichlorobenzene (TCB) was used as a thermodynamically good solvent for both components and ethylene glycol monobutylether (EGMBE) as eluent. A column packed with dimethylsiloxane-modified silica gel was used as stationary phase. 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. Resolution of this method, however, was rather poor and additionally limited by the poor solubility of the polyolefins.

In addition to selective fractionation techniques, powerful detection methods (e.g., NMR spectroscopy) to be coupled to fractionation are highly relevant. The on-line coupling of HPLC and proton NMR is well established for the analysis of complex mixtures of organic compounds [20]. Coupled HPLC-NMR measurements are frequently conducted at ambient temperature with mobile phases comprising deuterated solvents, such as D_2O/acetonitrile or D_2O/methanol. For the analysis of synthetic polymers, this coupling has been used only in a few cases where single mobile phases and ambient temperature conditions could be applied. Hatada et al. used SEC-NMR for the analysis of polymethacrylates [21–23]. He studied isotactic poly(methyl methacrylate) (PMMA) with different molar masses [24] to analyze the end groups and the number-average molar mass as well as the chemical composition distribution of (methyl methacrylate)-co-(butyl methacrylate) copolymers [25]. These polymers were studied at slow flow rates in deuterated solvents. Further studies on coupled HPLC-NMR have shown the power of liquid adsorption chromatography for the analysis of polymers regarding the chemical composition [26–29].

One major drawback of all previous experimental set-ups is the fact that measurements could only be conducted at ambient temperature. Such conditions cannot be applied for polyolefins that dissolve only at temperatures above 100 °C.

The present article briefly reviews different emerging techniques for polyolefin fractionation and analysis. Particular attention is paid to the analysis of polyolefins regarding chemical composition distribution and the correlation of molar mass and chemical composition. Novel HPLC methods for polyolefins will be highlighted. An on-line SEC-NMR set-up is presented that can be used at high operating temperatures necessary for polyolefin analysis. Olefin homopolymers and copolymers as well as polyolefin blends will be separated with regard to molar mass by HT-SEC and analyzed with regard to chemical composition by on-flow ^{1}H NMR.

EXPERIMENTAL

Crystallization fractionation

A commercial CRYSTAF instrument, model 200, manufactured by Polymer Char S.A. (Valencia, Spain) was used to perform the fractionations. In the CRYSTAF apparatus, a Hewlett Packard 6890 Series GC oven is used to perform the crystallization temperature program. The crystallization is carried out in stirred stainless steel reactors of 60 mL volume where dissolution and filtration takes place automatically. The detector is a dual wavelength optoelectronic unit with a heated flow-through microcell operating at 150 °C and using 3.5 μm as the measuring wavelength. About 20 mg of sample was dissolved in 30 mL of distilled TCB at 160 °C. After the samples were dissolved, the temperature was decreased according to a temperature program to perform the stepwise crystallization. The crystallization rate was 0.1 °C/min between 100 and 30 °C. Fractions were taken sequentially to determine the polymer concentration in the solution.

High-temperature SEC

A high-temperature chromatograph Waters 150C (Waters, Milford, USA) operating at a temperature of 130 °C was used. The pump of the Waters system was bypassed by an Agilent G1311A quarternary pump (Agilent, Waldbronn, Germany). Two sets of SEC columns were used: (1) SDV 10^7 Å, 10^6 Å, 10^5 Å, 10^3 Å, 100 Å, all of 10 μm average particle size, and column sizes of 300 × 8 mm I.D. (Polymer Standards Service GmbH, Mainz, Germany); (2) Styragel HT-2, HT-3, HT-4, HT-5, HT-6, all of 10 μm average particle size, and column sizes of 300 × 8 mm I.D. (Waters Inc., Eschborn, Germany). Operating temperature was 130 °C. TCB (Synthesis or HPLC grade, Merck, Darmstadt, Germany) was used as the mobile phase.

High-temperature gradient HPLC

A prototype of a high-temperature gradient HPLC system PL XT-220 (Polymer Laboratories, Church Stretton, England) was used [30]. 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.

High-temperature NMR and SEC-NMR

The NMR experiments were executed on a 400-MHz spectrometer AVANCE (Bruker BioSpin GmbH, Rheinstetten, Germany). The measurements were performed with a high-temperature flow probe containing a 120 μL flow cell. The probe was an inverse detection probe equipped with a pulsed field-gradient coil. The gradient strength was 53 G cm^{-1}. The 90 degree ^1H pulse was 6.7 μs. WET (water suppression enhanced through T_1 effects) solvent suppression [31] was applied to TCB. Three frequencies were suppressed.

The gel permeation chromatography (GPC)-NMR system (except chromatograph Waters 150C) was controlled by the Hystar software (Bruker BioSpin GmbH, Rheinstetten, Germany). The sample concentration was 2 mg/mL for each polymer component. The injection volume was 300 μL of the sample solution for all measurements.

RESULTS AND DISCUSSION

Crystallization fractionation

The principles of polymer fractionation by solubility or crystallization are based on the thermodynamic treatment of melting in polymers that was developed by Flory et al. and accounts for melting-point depression by the presence of a diluent. A solvent or a comonomer can act as the diluent. In both cases, the crystallization temperature decreases with increasing diluent concentration. Accordingly, for copolymers the separation by crystallizability can be regarded as a separation by chemical composition.

There are two experimental techniques which separate polyolefins by crystallizability: TREF and CRYSTAF. TREF is regarded as the most common technique for analysis of the chemical composition of olefin copolymers and short-chain branching distribution (SCBD) of LLDPE. A TREF experiment includes dissolution of the sample, loading of the TREF column with hot solution and the crystallization of the sample by slow temperature-programmed cooling. After crystallizing the sample, the elution of the sample fractions is conducted by slow temperature-programmed heating of the TREF column. The total analysis time per sample is in the magnitude of hours or days, hence TREF can be used only in selected cases.

Compared to TREF, CRYSTAF is a much more feasible technique for the analysis of large numbers of samples. This powerful method is based on the monitoring of the concentration of a polyolefin solution during the crystallization. A schematic presentation of the experimental set-up is given in Fig. 1A. The analysis of a mixture of atactic, syndiotactic, and isotactic PPs is shown in Fig. 1B. In brief, crystallization is conducted in stainless steel containers where dissolution and filtration take place automatically. In total, five containers are placed in the CRYSTAF apparatus, making it possible to run five samples simultaneously. The sample is introduced into the container and dissolved in TCB at 160 °C. When the sample is fully dissolved, the temperature is decreased and aliquots of the solution are taken, filtered, and analyzed by a concentration detector. As the result, a concentration profile of the solution vs. temperature is obtained, which can be related directly to the amount of crystallizing fractions. As is shown in Fig. 1B, CRYSTAF readily separates a PP mixture into the highly crystalline i-PP, the lower crystalline s-PP, and the amorphous a-PP. The advantage of CRYSTAF over TREF is that the analysis time per sample is significantly lower. A set of five samples can be analyzed within 6–10 h.

In similar ways, blends of different polyolefins and olefin copolymers can be analyzed [32–34]. One major application is the analysis of LLDPE with regard to chemical composition distribution. Over the last few years, CRYSTAF developed into a standard technique for polyolefin analysis despite the significant analysis times.

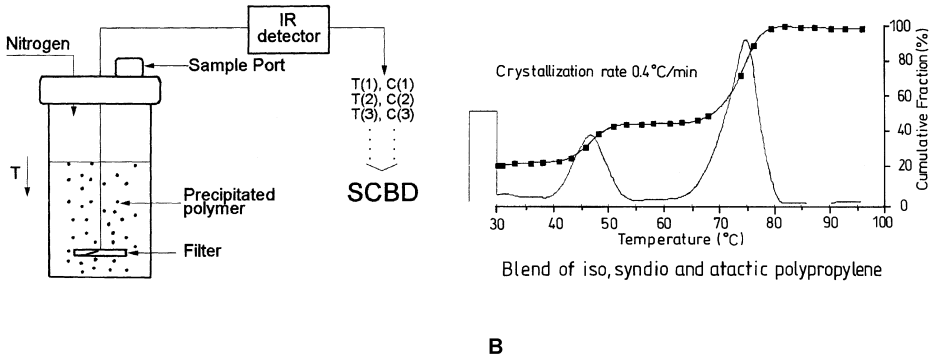


Fig. 1 Schematic representation of a CRYSTAF experiment (A) and analysis of a mixture of atactic, syndiotactic, and isotactic PPs (B) from ref. [2].

High-temperature HPLC

For the fast separation of polyolefins with regard to chemical composition, liquid chromatography would be a good candidate. However, firstly an instrument is required that is capable of handling solvent mixtures and gradients at high temperatures. Such an instrument has not been available until recently. As a joint development of Polymer Laboratories, Ltd. (Church Stretton, England) and our group, the first instrument that combines both high operation temperatures and the necessary requirements for gradient HPLC has been introduced (Fig. 2). The instrument set-up contains a high-pressure gradient pump for either running a binary solvent gradient or pumping of a single solvent (SEC) or a mixture of two solvents at constant composition (for HPLC). When two solvents are used, the mixing of the solvents requires high accuracy, especially, when using LCCC, due to the high sensitivity of the critical point to the mobile-phase composition [30,35,36].

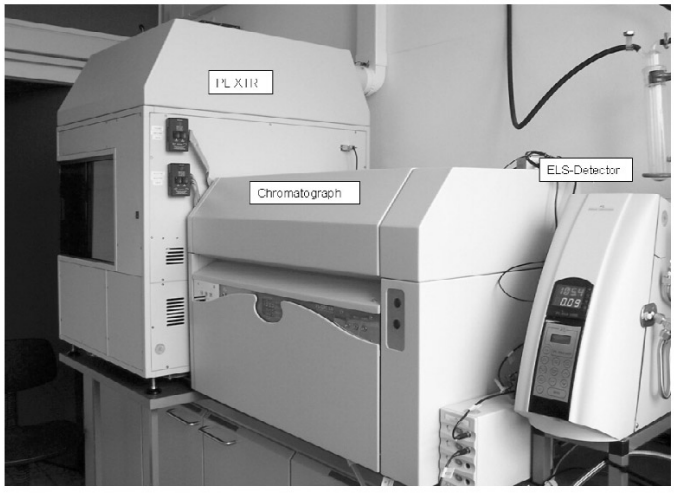


Fig. 2 View of high-temperature HPLC system (PL XT-220).

Mobile-phase changes are accomplished via a multisolvent management system. The chromatograph is equipped with a robotic sample handling system, which enables sample preparation and injection at temperatures up to 220 °C.

For fast column and mobile-phase screening, a column switching valve inside the column compartment (Fig. 3) enables the successive use of up to 6 different columns (or 5 columns and a reference capillary for direct injection into the detector). The choice of detectors for high-temperature HPLC of polyolefins and their copolymers is very limited. The present instrument contains a high-temperature differential refractive index (RI) detector for isocratic elution (e.g., SEC and LCCC) and an ELSD for gradient and isocratic elution modes. The ELSD is attached to the chromatograph via a heated transfer line.

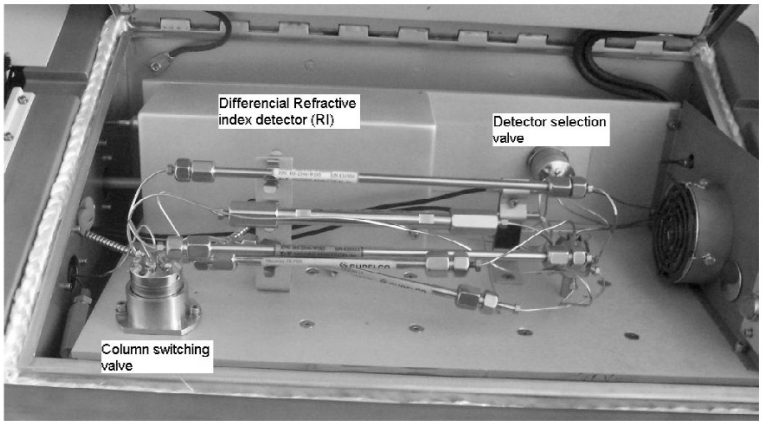


Fig. 3 View into the column compartment with 5 columns attached to the column switching valve and detector selecting valve.

Fast HT-SEC

For SEC measurements of polyolefins, columns with sizes of 300 × 8 mm I.D. are used routinely [37]. Typically, column sets of 3–5 columns are used to obtain optimum resolution. The time requirements per analysis are 40–60 min, respectively. Recently, it has been shown, however, that smaller SEC columns can be used for fast analysis [38]. These columns enable us to obtain molar mass data that are close to data that are obtained with conventional columns. Depending on the specific case, some loss in resolution may be encountered. Figure 4 shows chromatograms obtained with the PL XTR-220 and one high-resolution PL gel column. The separation was accomplished within 5 min in comparison with up to 60 min needed for analysis with 5 conventional columns.

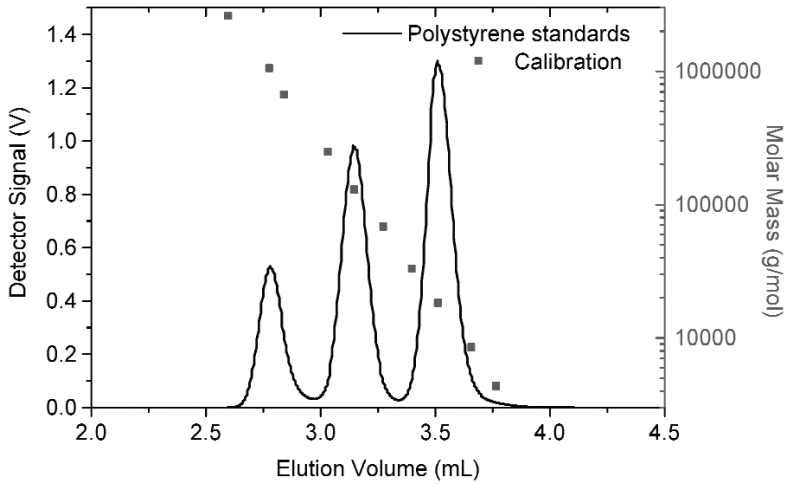


Fig. 4 SEC elugram of a mix of polystyrene standards with molar masses of 1.04, 18.1, and 128 kg/mol and polystyrene calibration curve; column: PLgel HTS-B, 150 × 7.5 mm I.D.; mobile phase: TCB; temperature: 140 °C; detector: PL-ELS 1000.

High-temperature liquid chromatography under critical conditions

At critical conditions, polymers of identical chemical composition elute at the same elution volume irrespective of their molar masses. Examples of such chromatographic behavior were recently published for more than 150 sorbent–eluent systems [39]. However, in the majority of cases, the critical conditions were obtained only for applications operating at room temperature. Chromatographic separations of polyolefin blends and copolymers, however, must be carried out at temperatures >100 °C to keep the complete samples dissolved.

The analysis of PE–polystyrene blends by LCCC is presented in Figs. 5 and 6. On polar Lichrosorb as the stationary phase and decaline-cyclohexane as the mobile phase using at a column temperature of 140 °C, blend separations can be accomplished. The adjustment of the critical mobile-phase

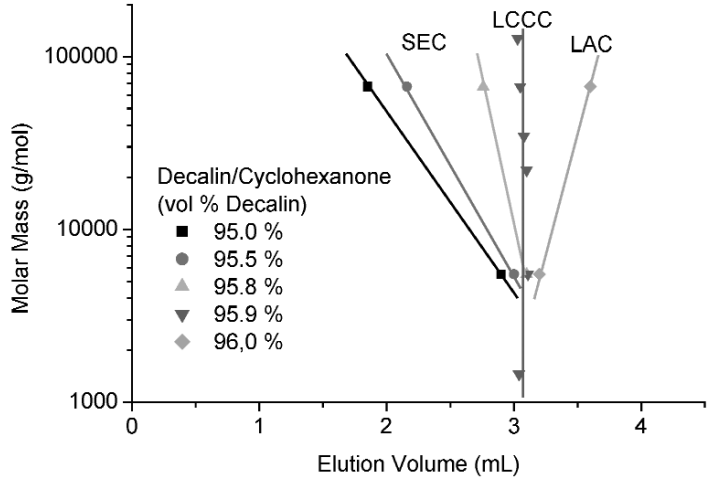


Fig. 5 Dependence of the elution volume of polystyrene standards on the composition of the mobile phase. Mobile phase: decalin-cyclohexanone (in vol %); column: Lichrosorb 100, 250 × 4.6 mm I.D.; temperature: 140 °C; detector: PL-ELS 1000; flow rate: 1 mL/min.

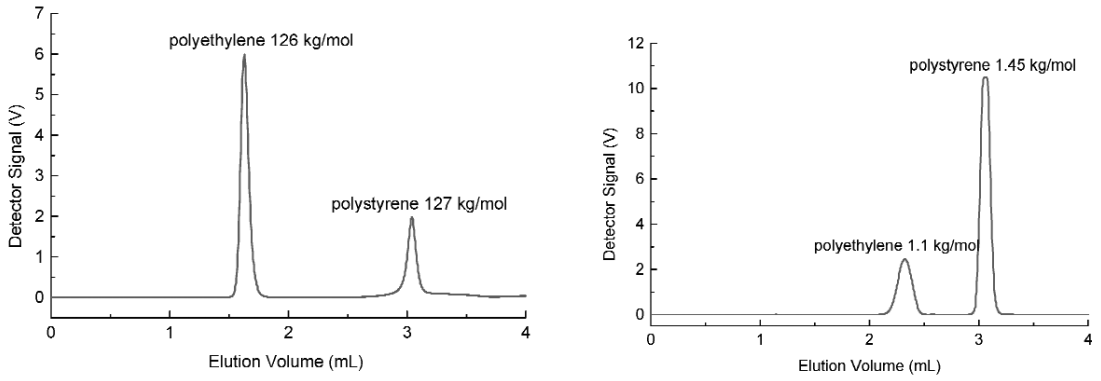


Fig. 6 Chromatograms of mixtures of PE and polystyrene with similar molar masses obtained at LCCC for polystyrene. Mobile phase and sample solvent: decalin-cyclohexanone 95.9:4.1 vol %. Other experimental conditions, see Fig. 5, from ref. [40].

composition is shown in Fig. 5. As can be seen, the elution behavior of polystyrene changes pronouncedly even with changes of the mobile-phase composition by only 0.1 vol % [40]. This demonstrates the importance of high accuracy and reproducibility of the mixing of desired mobile-phase compositions. The critical mobile-phase composition corresponds to decaline-cyclohexane 95.9:4.1 % by volume indicated by the molar mass independence of the elution volume.

Figure 6 illustrates the separation of polystyrene–PE blends by LCCC. As can be seen, PE is eluted in the size exclusion mode, whereas polystyrene is eluted irrespective of its molar mass. The full separation of the blend components is accomplished within only 4 min. In addition to the separation of blends, the critical conditions for polystyrene can be used for the separation of polystyrene–PE block copolymers.

Critical conditions for polymethyl methacrylate at a temperature of 140 °C have been also identified. The separation of ethylene-methyl methacrylate block copolymers with high-temperature LCCC is described in ref. [35].

High-temperature precipitation–redissolution gradient chromatography

Various combinations of solvents and nonsolvents were tested for preparative separations of polyolefins according to their molar masses and/or chemical compositions. Lehtinen et al. [41] applied EGMBE for the preparative separation of polyolefins using the fact that EGMBE is a good solvent for PP but a nonsolvent for PE. We have shown recently that EGMBE as the mobile phase and a oligo(dimethyl)siloxane-modified silica gel as the stationary phase enable HPLC separation of PE from PP. As the injection solvent in this case TCB is used [42]. In this system, PP eluted in the size exclusion mode, whereas PE eluted with the solvent peak at limiting conditions. However, there was a serious problem with regard to full recovery of PEs with higher molar masses. In addition, the resolution of the separation method was limited.

With the PL XT-220 gradient system, we now have the tool to overcome these limitations. With a solvent gradient of a good solvent for both PE and PP, full recovery of the sample can be achieved. Using a weaker sample solvent, the elution of the PE with the sample solvent can be suppressed. If the sample is dissolved in *n*-decanol instead of TCB and a gradient EGMBE–TCB is applied with a silica gel column, a baseline separation of PE and PP can be achieved, as illustrated in Fig. 7 [36]. The dotted line represents the gradient produced at the pump. The gradient reaches the detector with a shift of 5 mL caused by the dead volume of the chromatographic system. With the present gradient system, PE is completely precipitated on the column with the initial mobile phase, while PP elutes in the size ex-

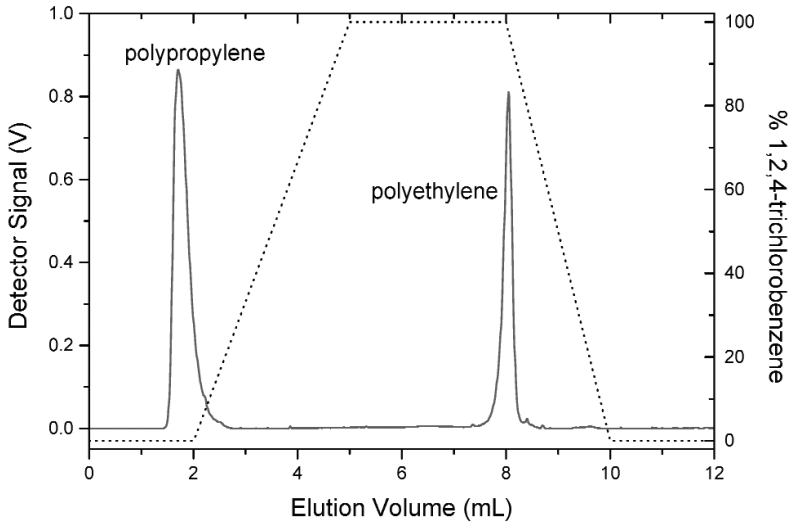
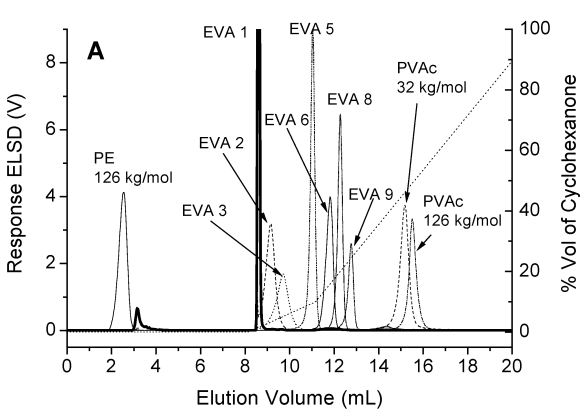


Fig. 7 Chromatogram of a blend of isotactic PP (305 kg/mol) and linear PE (126 kg/mol). Stationary phase: Nucleosil 500, 250 × 4.6 mm I.D.; mobile phase: Gradient of EGMBE and TCB (dotted line); temperature: 140 °C; detector: PL-ELS 1000; sample solvent: *n*-decanol; injection volume: 50 μL; concentration: 1 mg/mL, from ref. [36].

clusion mode. When the content of TCB in the mobile phase is increased by performing a gradient, the precipitated PE is eluted, thus confirming the expected precipitation–redissolution mechanism.

As is shown, for the first time blends of different polyolefins can be separated quantitatively over a wide range of concentrations by liquid chromatography at 140 °C. Applications of this chromatographic system for the separation of various polyolefins with regard to the chemical composition of the components are currently developed. As one very striking example for the capabilities of the high-temperature gradient HPLC system, the separation of random ethylene-vinyl acetate copolymers is presented in Fig. 8. On silica gel as the stationary phase and decaline-cyclohexanone as the eluent full separation of copolymers of different compositions is achieved. In addition, the homopolymers PE and poly(vinyl acetate) (PVAc) are well separated from the copolymers. This is the first time that a chro-



Sample	M_w [kg/mol]	VA [wt.%]
EVA 1	330	5
EVA 2	270	12
EVA 3	330	14
EVA 5	144	28
EVA 6	430	45
EVA 8	370	60
EVA 9	267	70

Fig. 8 Overlay of the chromatograms of ethylene vinyl acetate (EVA) copolymers; stationary phase: Polygosil 1000; mobile phase: gradient decalin/cyclohexanone (dotted line); temperature: 140 °C; detector: ELSD; sample solvent: decalin (TCB for the PVAC standards), from ref. [43].

matographic system is available that separates olefin copolymers irrespective of crystallinity and solubility over the entire range of compositions.

High-temperature LC-NMR

Another most fascinating new tool for the analysis of complex polyolefins is the direct coupling of high-temperature liquid chromatography and proton NMR. Such equipment became available only recently when a high-temperature flow-through NMR probe was introduced by Bruker. The construction and experimental set-up of the LC-NMR coupling is described in detail by Hiller et al. [44]. In brief, a new high-temperature NMR flow probe was designed which can operate at temperatures up to 150 °C. The probe has an active flow cell with a volume of 120 μL. It is a dual inverse $^{1}H/^{13}C$ probe with pulse field gradients. The temperature of the flow cell and the connecting capillaries can be regulated within an accuracy of ±0.1 °C. A stop-flow valve was developed as an interface for the SEC and the NMR. It physically connects the SEC with the flow probe. The valve is a two-position device and guides the flow either from the SEC to the NMR or directly to the waste, see Fig. 9. This set-up allows on-flow experiments, automatic stop-flow experiments, and time-slicing.

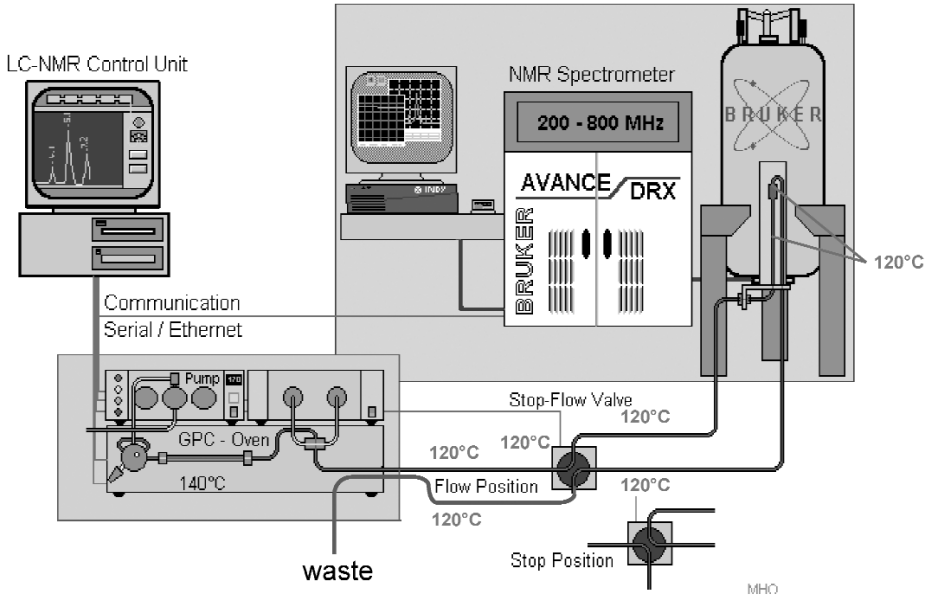


Fig. 9 Experimental set-up of the HT-SEC-NMR (SEC: 130 °C; LC probe, stop-flow valve and transfer lines: 120 °C), from ref. [44].

To evaluate the capabilities of the novel HT-SEC-NMR system, a polymer blend comprising PE and PMMA homopolymers and a PE-PMMA copolymer was prepared and analyzed. The molar masses of PE, PMMA, and the copolymer were M_n = 1100 g/mol, M_n = 263 000 g/mol, and M_n = 10 600 g/mol, respectively. On- and stop-flow experiments of both blends and the copolymer were carried out. All experiments were performed with TCB as the mobile phase. WET suppression was applied to the intrinsic solvent signals, i.e., three aromatic proton signals were suppressed. No lock solvent was added. The SEC column set was chosen to cover a wide range of molar masses (100–1 000 000 g/mol).

Figure 10 shows the on-flow run of the blend as a corrected contour plot by subtracting signals, which correspond to impurities of the solvent. The signals of these impurities were found in "TCB for synthesis", in redestilled TCB as well as in the most expensive "TCB for HPLC". In the present chro-

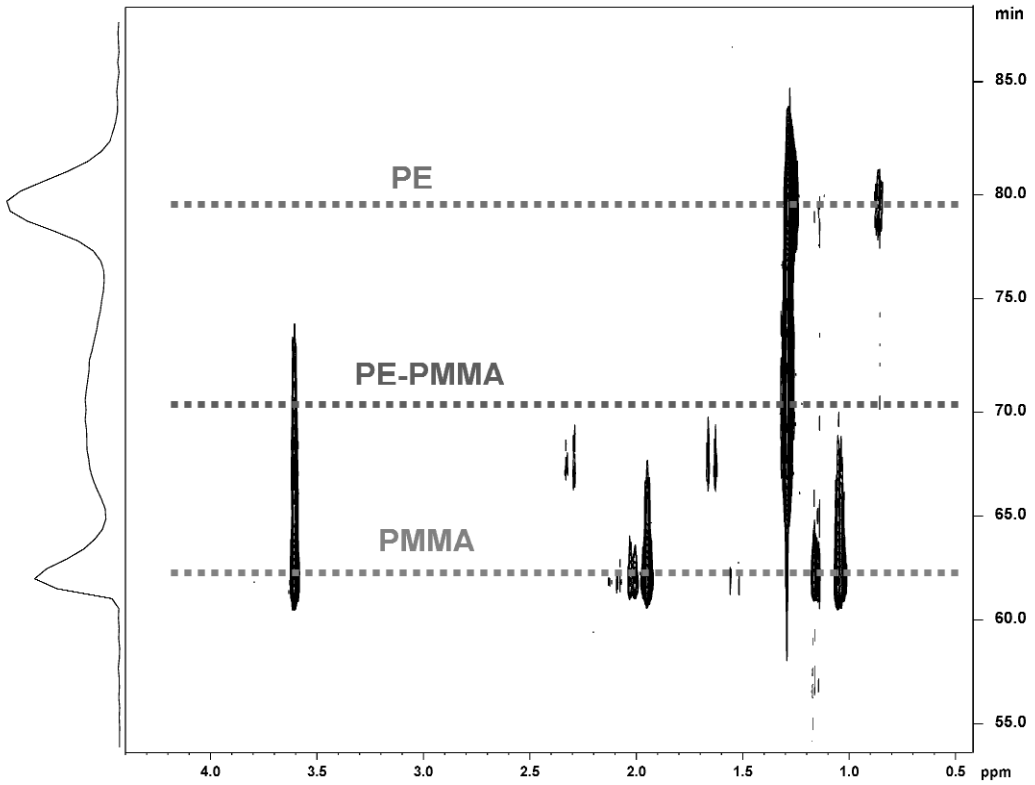


Fig. 10 SEC-NMR (400 MHz) on-flow run (corrected) of a PE-PMMA-copolymer blend at 130 °C in TCB; (flow rate 0.5 mL/min, concentration 2 mg/mL of each polymer, 300 µL injection volume, 5 Waters columns, 24 scans per FID, 1.24 s repetition delay), from ref. [44].

matographic system, the elution of the blend components is in the order of decreasing molar mass. Accordingly, the highest molar mass PMMA elutes first, followed by the PE-PMMA copolymer. The very low molar mass PE elutes last. This elution order can be clearly seen in the SEC-NMR contour plot. The spectra of the early eluting fractions show signals for PMMA but not for ethylene. In contrast, the late eluting fractions exhibit signals for ethylene but not for MMA and can be assigned to PE. Between the two homopolymers, the elution of the copolymer can be measured by detecting signals for both MMA and ethylene. Figure 10 also shows the vertical projections taken from the sum of the NMR signals. It can be used as the chromatogram which also indicates three separated peaks.

Figure 11 shows the different traces of the on-flow experiment. These traces clearly indicate the different components of the blend. The signals of the PMMA (a) correspond to syndiotactic species of this homopolymer. The second trace (b) contains the copolymer. It is a block copolymer where MMA is mainly isotactic. The tacticity of the corresponding PMMA homopolymers was already reported by Hatada et al. [23]. The third trace contains only the PE component. It even shows the CH_3 end group at 0.86 ppm. However, the signal-to-noise ratio of the CH_3 group is not sufficient for a precise molecular mass calculation.

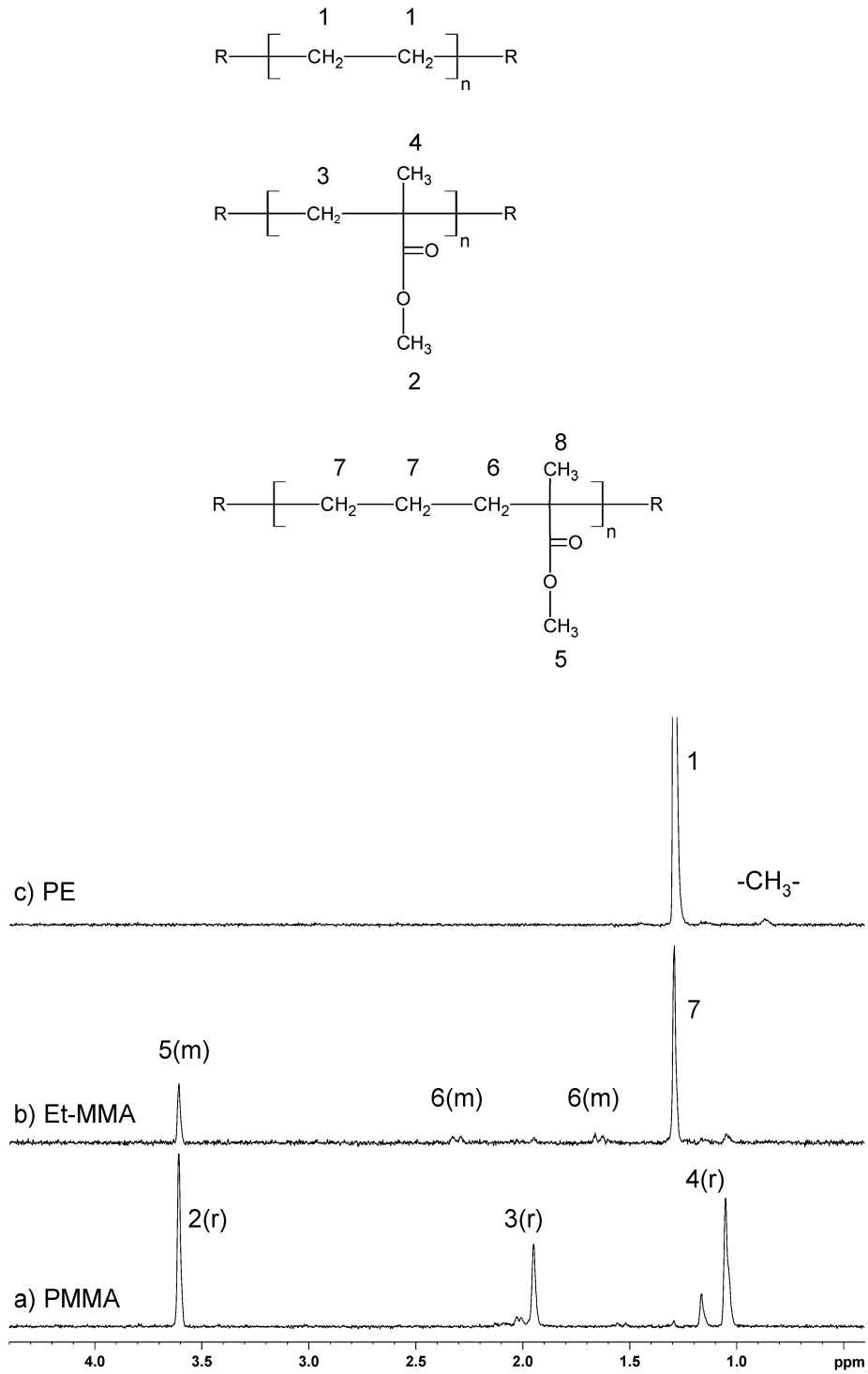


Fig. 11 ^{1}H traces of the on-flow run of Fig. 10, (a) PMMA (retention time, RT = 60.5 min); (b) PE-PMMA copolymer (RT = 66.0 min); (c) PE 1100 g/mol (RT = 79.4 min).

In the second experiment, the chemical composition distribution of the PE-PMMA copolymer was investigated by using on- and stop-flow experiments. To achieve an excellent separation, the first measurement was done by using column set 2 (Waters). This separation is presented as an on-flow run in Fig. 12. In this case, 24 scans per free induction decay (FID) were recorded.

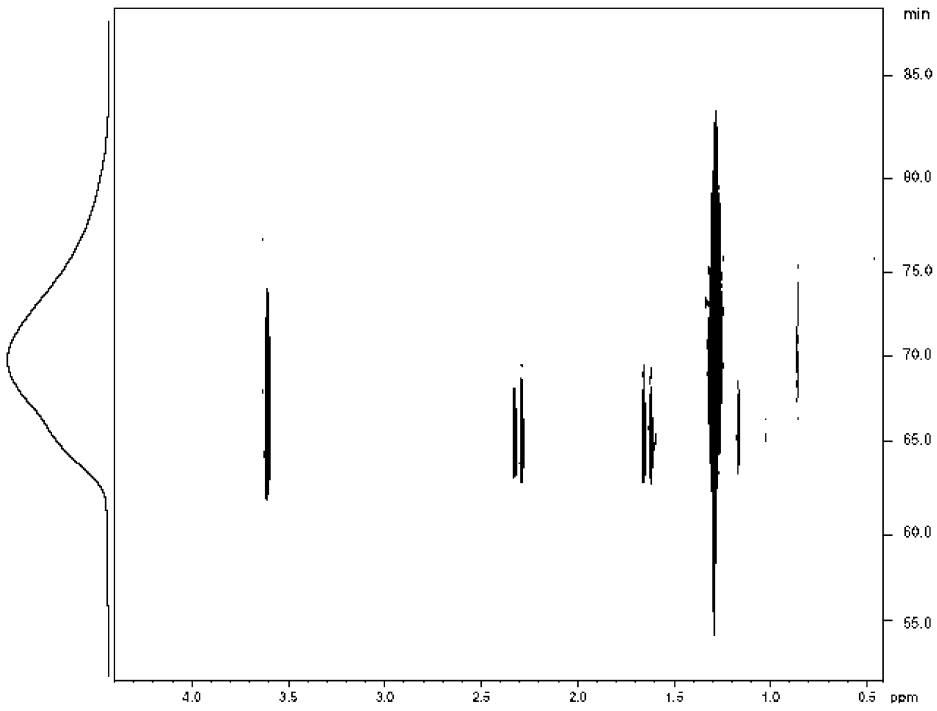


Fig. 12 SEC-NMR (400 MHz) on-flow run of PE-PMMA copolymer at 120 °C in TCB (flow rate 0.5 ml/min, concentration 3 mg/ml, 300 µl injection volume, 5 Waters columns, 24 scans per FID, 1.24 s repetition delay) corrected by subtraction of the impurities of TCB.

The distributions of the different structural moieties corresponding to MMA and ethylene can be seen and correlated with the corresponding molar masses. The quantification of the chemical composition based on the on-flow data is presented in Fig. 13. It shows that the MMA monomer units are mainly distributed at higher molar masses. A maximum of MMA (46.2 mol %) could be observed at RT = 63.5 min. On the other hand, the chemical composition distribution starts with a higher ethylene content at the very beginning (corresponding to high molar masses), passes a minimum of ethylene (RT = 63.5 min) and finally results in almost pure ethylene (low molar masses). Therefore, it can be concluded that the sample is very heterogeneous. It might be that it even contains PE as the homopolymer.

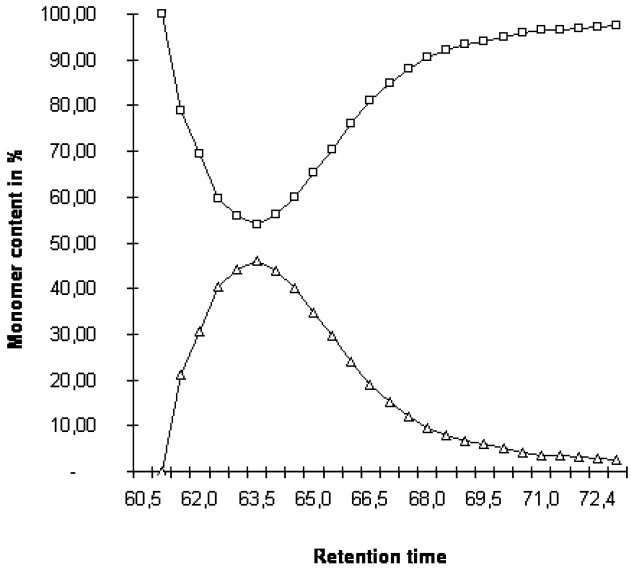


Fig. 13 Monomer composition of PE-PMMA copolymer vs. RT calculated from Fig. 12 (□ = mol % ethylene, △ = mol % MMA).

CONCLUSIONS AND OUTLOOK

New powerful analytical techniques have been developed that complement the rapid design of complex polyolefins with new microstructures. These techniques address molar mass and chemical composition distribution and correlate them to each other. CRYSTAF as a rather slow method is a useful tool for the analysis of the crystallizability and chemical composition distribution of olefin copolymers. Much more rapidly, high-temperature HPLC can separate olefin copolymers and blends with regard to chemical composition. Such analyses can be accomplished within 10–20 min per sample. The newly developed PL XT-220 rapid screening HPLC system enables one to perform isocratic and gradient separations in the temperature range between 30 and 220 °C. With the possibility to switch quickly between up to 6 different columns and to select easily one of 6 different solvents plus with the possibility to use either RI or ELS detection the apparatus has all features needed for fast screening and developing of new chromatographic systems as well as for fast switching between different chromatographic systems in the course of routine measurements.

The on-line coupling of HT-SEC and ^{1}H NMR opened the door to the analysis of complex polyolefins regarding both molar mass and chemical composition. This hyphenated technique holds much promise for the further advancement of polyolefin analysis because it can be adapted to a whole variety of analytical problems including the analysis of branched polyolefins such as graft and comb-like copolymers. Further selective detection methods like Fourier transform infrared (FTIR) spectroscopy and light scattering can be added to the system and, finally, other than SEC separation techniques can be used. These topics will be addressed in future investigations.

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