High Temperature Interaction Chromatography of Olefin Copolymers

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Summary: 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 chromatographic techniques for polyolefin analysis. For the fast analysis of the chemical composition distribution of polyolefins a new high-temperature gradient high-performance liquid chromatography (HPLC) system has been introduced. The efficiency of this system for the separation of various olefin copolymers is demonstrated. The correlation between elution volume and chemical composition can be accessed by on-line coupling of high temperature HPLC with FTIR spectroscopy. For the elucidation of the chemical composition as a function of molar mass high-temperature size exclusion chromatography and ^{1}H-NMR spectroscopy can be coupled. It is shown that the on-line NMR analysis of chromatographic fractions yields information on microstructure and chemical composition in addition to molar mass distribution.

Keywords: LC-FTIR coupling; LC-NMR coupling; liquid chromatography; molecular structure; polyolefins

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 is rapidly growing due to the fact that polyolefins are made from simple and easily available 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. 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. 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

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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. The latest development in this field, crystallization elution fractionation (CEF), is able to obtain similar results to TREF in less than one hour and is, therefore, a significant improvement.[8] High-performance liquid chromatography (HPLC) is an important tool for the fast separation of complex polymers with regard to chemical composition.[9,10] HPLC separations can be achieved via different mechanisms, including adsorption–desorption and precipitation–redissolution.[11,12] In gradient HPLC, frequently precipitation and adsorption processes are combined.[13–16]

At present, standard HPLC methods for polymers, e.g. gradient chromatography or chromatography at critical conditions (LCCC), are limited to ambient or slightly elevated temperatures.[10,17,18] The majority of published HPLC separations are conducted at operating temperatures of a maximum of 60 °C.[9,10] 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.[19,20] 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. 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. FTIR and NMR spectroscopy) to be coupled to fractionation are highly relevant. The present work will discuss the combination of highly selective fractionation techniques with FTIR and proton NMR. It will be shown that in a fraction of time that is required for TREF and CRYSTAF information on polyolefin blends and olefin copolymers can be obtained that covers not only the crystallizable but also the amorphous part of the samples.

Experimental Part

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 107 Å, 106 Å, 105 Å, 103 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.[21] 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 WinGPCSoftware (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. The 90 degree ^{1}H pulse was 6.7 μs. WET (water suppression enhanced through T1 effects) solvent suppression[22] 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.

Coupling of High-Temperature HPLC and FTIR

The column outlet of the chromatographic system was connected to the LC-Transform FTIR Interface (Series 300, Lab Connections, Carrboro, USA). At the LC-Transform the stage temperature was 150 °C. The temperature for the nozzle was set at 129 °C for the HPLC and 154 °C for the SEC experiments. The Germanium disc rotation speed was set at 10 degree/min. FTIR spectroscopy of the deposited eluate was performed using a Nicolet Protegè 460 (Thermo Electron, Waltham, USA).

Samples

All samples were industrial products. The EMA samples were products of Du Pont, while the EVA samples were products of Exxon Mobil, Bayer and Innospec. The calibration standards PE, PMMA, PVAc were products of Polymer Standards Service GmbH, Mainz, Germany.

Results and Discussion

High-Temperature HPLC

For the fast separation of polyolefins with regard to chemical composition, liquid chromatography is 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 (Figure 1). 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. Mobile-phase changes are accomplished via a multisolvent management system. The chromatograph is equipped with a robotic sample handling

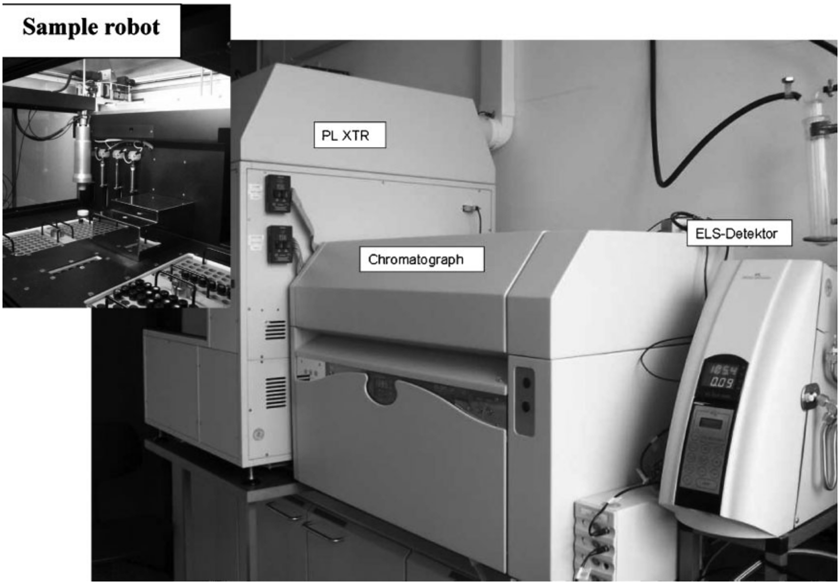


Figure 1.
View of high-temperature HPLC system (PL XT-220).

system, which enables sample preparation and injection at temperatures up to 220 °C.[21,23,24]

For fast column and mobile-phase screening, a column switching valve inside the column compartment (Figure 2) 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.

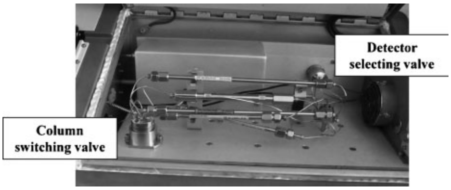


Figure 2.
View into the column compartment with 5 columns attached to the column switching valve and detector selecting valve.

High-Temperature Liquid Chromatography at 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.[25] 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 >120 °C to keep the complete samples dissolved.

In a recent application PE–polystyrene blends were separated by LCCC. On polar LiChrosorb as the stationary phase and decaline-cyclohexane as the mobile phase using at a column temperature of 140 °C, blend separations were accomplished. As has been shown, the elution behavior of polystyrene changes pronouncedly even with changes of the mobile-phase composition by only 0.1 vol %.[26] This demonstrates the importance of high accuracy and reproducibility of the mixing of desired mobile-phase compositions.

The critical mobile-phase composition corresponded to decaline-cyclohexane 95.9:4.1% by volume indicated by the molar mass independence of the elution volume. PE eluted in the size exclusion mode whereas polystyrene eluted irrespective of its molar mass. The full separation of the blend components was accomplished within only 4 min. In addition to the separation of blends, the critical conditions for polystyrene were 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. [23].

High-Temperature Precipitation–Redissolution Gradient Chromatography

Various combinations of solvents and non-solvents were tested for preparative separations of polyolefins according to their molar masses and/or chemical compositions. Lehtinen et al.[27] applied EGMBE for the preparative separation of polyolefins using the fact that EGMBE is a good solvent for PP but a non-solvent 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 was used.[19] 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 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 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 Figure 3A.[24]

With the present gradient system, PE is completely precipitated on the column with the initial mobile phase, while PP elutes in the size exclusion mode. When the content of TCB in the mobile phase is increased by performing a gradient, the precipitated PE elutes, 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 and molar masses by liquid chromatography at 140 °C. Applications of this chromatographic system for the separation of various polyolefins with regard to the chemical

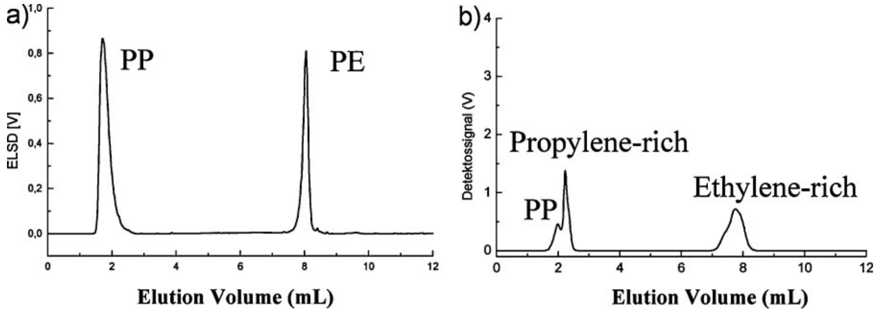


Figure 3.

Chromatogram of (A) a blend of isotactic PP (305 kg/mol) and linear PE (126 kg/mol) and (B) an ethylene-propylene copolymer. 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; from Ref. [24].

composition of the components are currently developed. One example is given in Figure 3B showing the separation of an ethylene-propylene copolymer regarding chemical composition. Clearly, the separation into PP homopolymer, a propylene-rich fraction and an ethylene-rich fraction is obtained. As this sample has been prepared by Ziegler-Natta catalysis in a two-step process, the formation of a multiphase copolymer could be assumed. A quantification of the chemical composition of the different fractions by FTIR spectroscopy using the LC Transform approach is in preparation.

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 Figure 4. 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 chromatographic system is available that separates olefin copolymers irrespective of crystallinity and solubility over the entire range of compositions.

In a next step, this highly selective type of copolymer separation is coupled to FTIR spectroscopy to analyse the chemical composition distribution of the samples. For the HPLC-FTIR coupling the LC Transform interface system is used, see Figure 5. After the chromatographic separation the eluate that is leaving the column is sprayed at high temperature onto a rotating Germanium disc. The mobile phase evaporates and the polymer fractions are deposited as a thin film. After deposition of the chromatographic run, the Germanium disc is placed into a FTIR spectrometer and spectra are taken from all positions on the disc.[29,30]

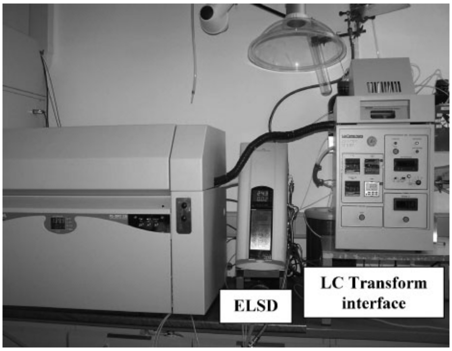


Figure 5.
Coupling of the HT-HPLC system to the ELSD for concentration detection and the LC Transform interface.

The results of the FTIR coupling are presented in Figure 6 for three EVA copolymer samples.

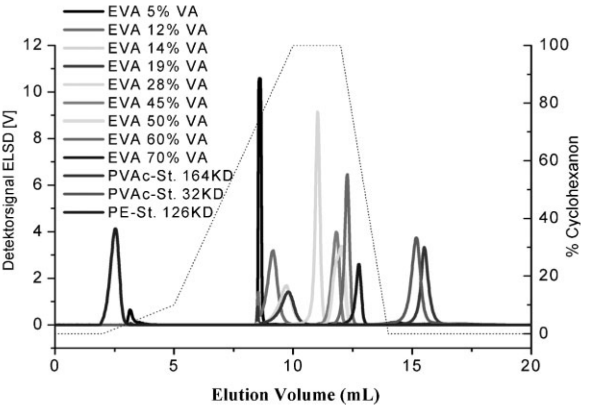


Figure 4.
Overlay of the chromatograms of ethylene-vinyl acetate (EVA) copolymers; stationary phase: Polygosil 1000; mobile phase: gradient decalin/cyclohexanone (dotted line); temperature: 140 °C; detector: ELSD; sample solvent: decalin (TCB for the PVAC standards), from ref. [28].

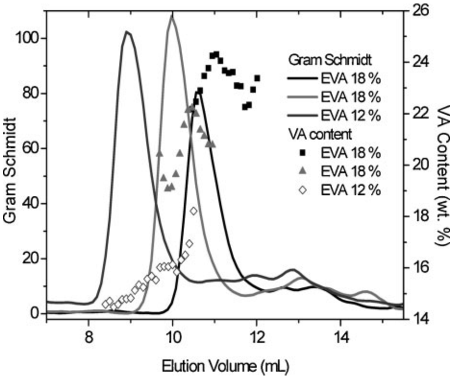


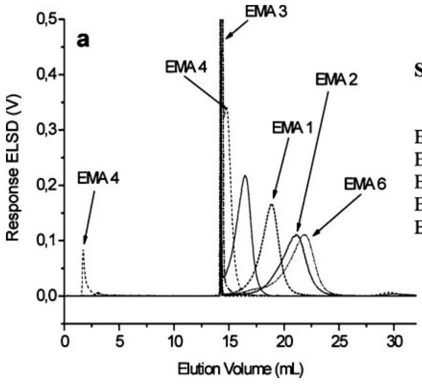
Figure 6.
Separation of three EVA samples with regard to chemical composition, the vinyl acetate contents across the elution curves are presented as dotted lines.

Figure 6 shows the elugrams of the samples presented as Gram-Schmidt plots. The Gram-Schmidt plots are obtained from FTIR measurements by summarizing all peak intensities at all frequencies and compare well with the total concentration profile. Across the Gram-Schmidt plots the vinyl acetate (VA) contents are given as obtained from the ratio of the peak for the carbonyl group (1736 cm^{-1}) to the peak of the CH_2 vibration (1463 cm^{-1}, presenting the total polymer concentration). This peak ratio is correlated with true copolymer compositions that were obtained by NMR. As can be seen there is a clear correlation between the VA content and the elution volume indicating that, indeed, separation takes place with regard to the chemical composition of the copolymer. It is interesting to see that the two samples with the same nominal VA content (18%, curves ▲ and ■) show distinctively different elution patterns.

In a similar way, ethylene-acrylate copolymers can be analyzed. Figure 7 shows the separation of ethylene-methyl acrylate copolymers by high-temperature gradient HPLC. In this case a silica gel Perfectsil 300 is used as the stationary phase. The mobile phase is a gradient of decaline-cyclohexanone.[31]

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. [32] 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



Sample	MA content (wt.-%)
EMA 3	9
EMA 4	14
EMA 1	23
EMA 2	27
EMA 6	28

Figure 7.
Overlay of the chromatograms of ethylene-methyl acrylate (EMA) copolymers; stationary phase: Perfectsil 300; mobile phase: gradient decalin/cyclohexanone; temperature: 140 °C; detector: ELSD; sample solvent: decalin, from Ref. [31].

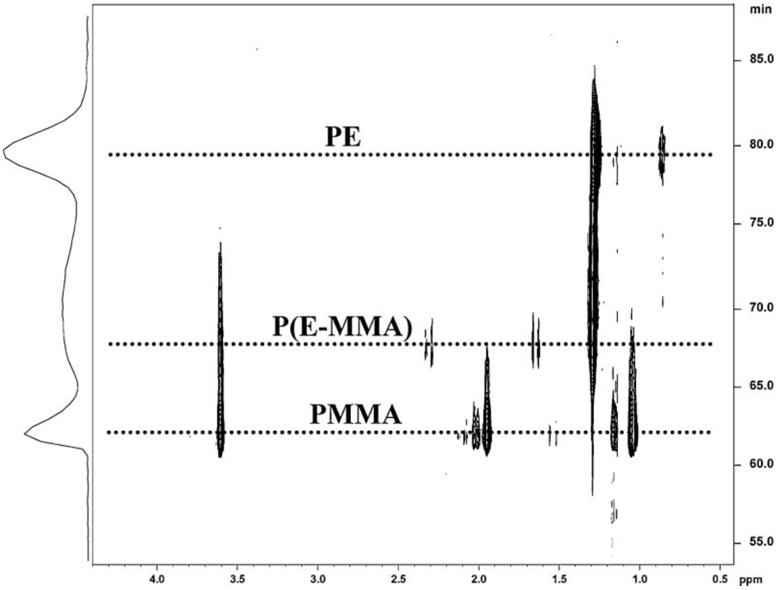


Figure 8.
SEC-NMR (400 MHz) on-flow run (corrected) of a blend of PE, PMMA and a P(E-MMA) copolymer at 130 °C in TCB; flow rate 0.5 mL/min, concentration 2 mg/mL of each polymer, 300 μL injection volume, 5 Waters columns, 24 scans per FID, 1.24 s repetition delay, from Ref. [32].

with a volume of 120 μL. It is a dual inverse $^1H/^{13}C$ 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. This set-up allows for on-flow experiments, automatic stop-flow experiments, and time-slicing.

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 8 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 chromatographic system, the elution of the blend components is in the order of decreasing molar masses. Accordingly, the highest molar mass PMMA elutes first, followed by the P(E-MMA) 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

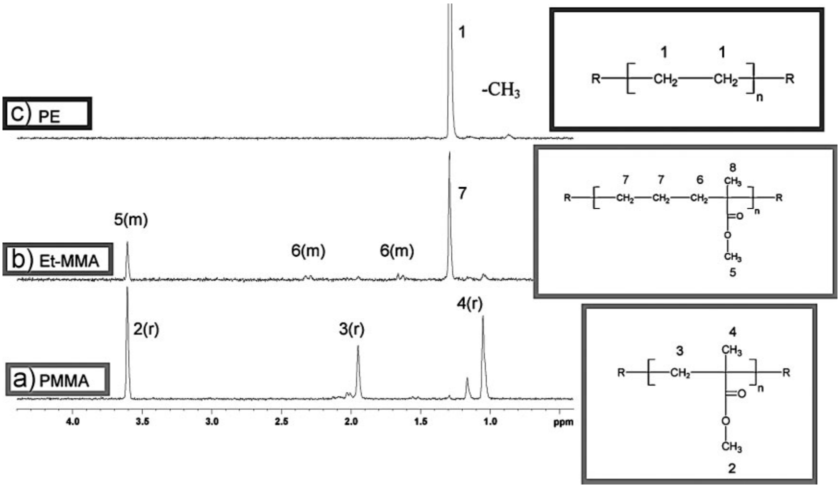


Figure 9.
^{1}H traces of the on-flow run of Figure 8, (a) PMMA (retention time, RT = 60.5 min); (b) P(E-MMA) copolymer (RT = 66.0 min); (c) PE (RT = 79.4 min).

elution of the copolymer can be measured by detecting signals for both MMA and ethylene. Figure 9 shows the different traces of the on-flow experiment. These traces clearly indicate the different components of the blend. The signals of 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 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.

Conclusion

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. Much more rapidly than a conventional CRYSTAF or TREF experiment, 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.

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[1] W. Kaminsky, M. Arndt, *Adv. Polym. Sci.* **1997**, *127*, 143.
[2] H. Pasch, *Macromol. Symp.* **2001**, *165*, 91.
[3] B. Monrabal, *J. Appl. Polym. Sci.* **1994**, *52*, 491.
[4] B. Monrabal, *Macromol. Symp.* **1996**, *110*, 81.
[5] B. Monrabal, J. Blanco, J. Nieto, J. B. P. Soares, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 89.
[6] L. Wild, T. Ryle, D. Knobeloch, I. R. Peat, *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 441.
[7] L. Wild, *Adv. Polym. Sci.* **1991**, *98*, 1.
[8] B. Monrabal, J. Sancho-Tello, N. Mayo, L. Romero, *Macromol. Symp.* **2007**, *257*, 71.
[9] G. Glöckner, *Gradient HPLC of Copolymers and Chromatographic Cross-Fractionation*, Springer, Berlin 1991.
[10] H. Pasch, B. Trathnigg, *HPLC of Polymers*, Springer, Berlin 1997.
[11] M. A. Quarry, M. A. Stadalius, T. H. Mourey, L. R. Snyder, *J. Chromatogr., A* **1986**, *358*, 1.
[12] M. A. Stadalius, M. A. Quarry, T. H. Mourey, L. R. Snyder, *J. Chromatogr., A* **1986**, *358*, 17.
[13] S. Mori, H. Taziri, *J. Liq. Chromatogr.* **1994**, *17*, 305.
[14] P. J. C. H. Cools, A. M. van Herk, W. Staal, A. L. German, *J. Liq. Chromatogr.* **1994**, *17*, 3133.
[15] H. J. A. Philipsen, B. Klumperman, A. L. German, *J. Chromatogr., A* **1996**, *27*, 13.
[16] P. J. C. H. Cools, F. Maesen, B. Klumperman, A. M. van Herk, A. L. German, *J. Chromatogr., A* **1996**, *736*, 125.
[17] D. Berek, *Prog. Polym. Sci.* **2000**, *25*, 873.
[18] T. Chang, *Adv. Polym. Sci.* **2003**, *163*, 1.
[19] T. Macko, H. Pasch, Y. V. Kazakevich, A. Y. Fadeev, *J. Chromatogr. A* **2003**, *988*, 69.
[20] T. Macko, H. Pasch, J. F. Denayer, *J. Chromatogr. A* **2003**, *1002*, 55.
[21] L.-C. Heinz, T. Macko, A. Williams, S. O'Donohue, H. Pasch, *The Column, Feb.* 13–19. **2006**.
[22] S. H. Smallcombe, S. L. Patt, P. A. Keifer, *J. Magn. Res. A* **1995**, *117*, 295.
[23] L.-C. Heinz, S. Graef, T. Macko, R. Brüll, S. Balk, H. Keul, H. Pasch, *e-polymers* **2005**, *054*.
[24] L.-C. Heinz, H. Pasch, *Polymer* **2005**, *46*, 12040.
[25] T. Macko, D. Hunkeler, *Adv. Polym. Sci.* **2003**, *163*, 61.
[26] L.-C. Heinz, T. Macko, H. Pasch, M.-S. Weiser, R. Mülhaupt, *Int. J. Polym. Anal. Charact.* **2006**, *11*, 47.
[27] A. Lehtinen, R. Paukkeri, *Macromol. Chem. Phys.* **1994**, *195*, 1539.
[28] A. Albrecht, R. Brüll, T. Macko, H. Pasch, *Macromolecules* **2007**, *40*, 5545.
[29] S. M. Graef, R. Brüll, H. Pasch, U. M. Wahner, *e-polymers* **2003**, *005*.
[30] N. Luruli, T. Pipers, R. Brüll, V. Grumel, H. Pasch, V. B. F. Mathot, *J. Polym. Sci., Polym. Phys.* **2007**, *45*, 2956.
[31] A. Albrecht, R. Bruell, T. Macko, P. Sinha, H. Pasch, *Macromol. Chem. Phys.* **2008**, *209*, 1909.
[32] W. Hiller, H. Pasch, T. Macko, M. Hoffmann, J. Glanz, M. Spraul, U. Braumann, R. Streck, J. Mason, F. van Damme, *J. Magn. Reson.* **2006**, *183*, 309.