



## High-temperature two-dimensional liquid chromatography of ethylene-vinylacetate copolymers

Anton Ginzburg<sup>a,b</sup>, Tibor Macko<sup>a,b</sup>, Volker Dolle<sup>c</sup>, Robert Brüll<sup>a,\*</sup>

<sup>a</sup> Deutsches Kunststoff-Institut (German Institute for Polymers), Schlossgartenstr. 6, 64289 Darmstadt, Germany

<sup>b</sup> Dutch Polymer Institute (DPI), PO Box 902, 5600 AX Eindhoven, The Netherlands

<sup>c</sup> LyondellBasell, Industriepark Hoechst, C 657, 65926 Frankfurt am Main, Germany

### ARTICLE INFO

#### Article history:

Received 28 May 2010

Received in revised form 5 August 2010

Accepted 16 August 2010

Available online 24 August 2010

#### Keywords:

Ethylene-vinyl acetate copolymers (EVA)  
High-temperature two-dimensional liquid chromatography (HT 2D-LC)  
TREF × SEC

### ABSTRACT

Temperature rising elution fractionation hyphenated to size exclusion chromatography (TREF × SEC) is a routine technique to determine the chemical heterogeneity of semicrystalline olefin copolymers. Its applicability is limited to well crystallizing samples. High-temperature two-dimensional liquid chromatography, HT 2D-LC, where the chromatographic separation by HPLC is hyphenated to SEC (HPLC × SEC) holds the promise to separate such materials irrespective of their crystallizability. A model blend consisting of ethylene-vinyl acetate (EVA) copolymers covering a broad range of chemical composition distribution including amorphous and semicrystalline copolymers and a polyethylene standard was separated by HT 2D-LC at 140 °C. Both axes of the contour plot, i.e. the compositional axis from the HPLC and the molar mass axis from the SEC separation were calibrated for the first time. Therefore, a new approach to determine the void and dwell volume of the developed HT 2D-LC instrument was applied. The results from the HT 2D-LC separation are compared to those from a cross-fractionation (TREF × SEC) experiment.

© 2010 Published by Elsevier B.V.

### 1. Introduction

Copolymers of ethylene and vinyl acetate (EVA) are commercially important products. Depending on their comonomer content, these materials are used in the production of films, foams or hot melt adhesives. Like in all other copolymers EVA may be distributed with regard to the molar mass, the chemical composition and the branch length. A comprehensive characterization of these polymers being distributed in more than one compositional feature is essential for understanding the catalyst performance [1], as well as for optimization of the synthesis and fundamental understanding of key structure-property relations, advancing the field considerably.

A number of techniques are commonly used to analyze the various distributions present in semicrystalline polyolefins. High-temperature size exclusion chromatography (HT-SEC) is the established method to determine the molar mass distribution, MMD [2,3]. SEC is based on the size of molecules in solution (hydrodynamic volume) and the extent to which they are excluded

from porous particles. Temperature rising elution fractionation (TREF) and crystallization analysis fractionation (CRYSTAF) [4–9] are non-chromatographic separation techniques, which fractionate polyolefins according to the differences in crystallizability. The separation of the macromolecules is driven by the crystallization from solution, which in turn mainly depends on the chemical composition and branching. Both techniques are routinely used to obtain information on the chemical composition distribution of olefin copolymers. However, as the distributions present in a polymer sample are interrelated, fractionation with regard to all parameters of interest, i.e. the chemical composition and the molar mass, is required. This means that a separation according to chemical composition has to be combined with a separation according to the molar mass.

The coupling of TREF and HT-SEC, where the sample is first fractionated by TREF with respect to chemical composition and the obtained TREF fractions are then analyzed either on-line or off-line by SEC, offers the required comprehensive characterization [10–12]. This approach was first introduced by Wild [4], who combined off-line a preparative fractionation by TREF with SEC analysis of the obtained fractions. The first attempt to introduce automation in cross-fractionation of polyolefins was reported by Nakano and Goto [10]. Ortin et al. have commercialized the automated cross-fractionation apparatus for a full characteriza-

\* Corresponding author. Tel.: +49 6151 162305; fax: +49 6151 292855.

E-mail addresses: [AGinzburg@dki.tu-darmstadt.de](mailto:AGinzburg@dki.tu-darmstadt.de) (A. Ginzburg), [TMacko@dki.tu-darmstadt.de](mailto:TMacko@dki.tu-darmstadt.de) (T. Macko), [RBruell@dki.tu-darmstadt.de](mailto:RBruell@dki.tu-darmstadt.de) (R. Brüll).

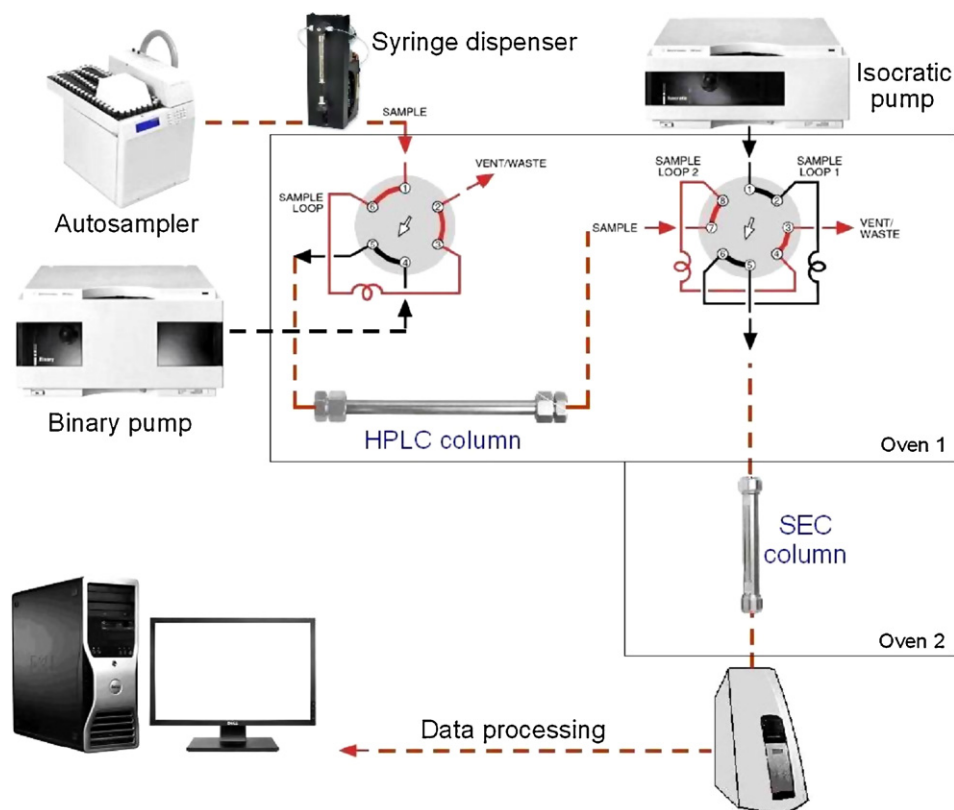


Fig. 1. Set-up for high-temperature 2D-LC.

tion of the bivariate distribution of polyolefins [12]. At the time being, this cross-fractionation apparatus is commercially available. However, as the separation according to composition is achieved by TREF, it is only applicable to well-crystallizable samples. Wild and Kelusky [4,5] analyzed the CCD of EVA copolymers containing 9–42 wt.% VA by TREF and found that copolymers with the content of polar comonomer higher than 20 wt.% are fully amorphous and thus cannot be separated by TREF or CRYSTAF.

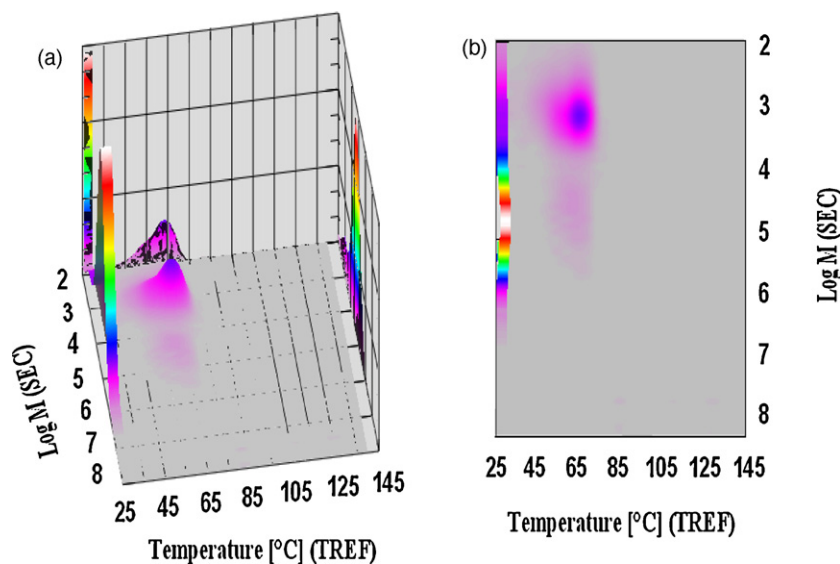
High-performance liquid chromatography (HPLC) is routinely used for the fast separation of complex polymers with regard to chemical composition or architecture. HPLC separations can be done via different mechanisms, including adsorption–desorption and precipitation–redissolution. The majority of published HPLC separations are realized at operating temperatures of up to 60 °C [13–18]. Dissolution and separation of semicrystalline samples, however, require in general the use of elevated temperatures up to 160 °C. Our group has recently developed first chromatographic systems for the separation of semicrystalline functionalized polyolefins. It was shown that ethylene-vinyl acetate (EVA) copolymers [19–21], ethylene-methyl acrylate copolymers [21,22], ethylene-methyl methacrylate block copolymers [23], ethylene-styrene block copolymers [24] as well as ethylene-butylacrylate copolymers [22] can be separated according to chemical composition by high-temperature HPLC.

The hyphenation of HT-HPLC with SEC offers a promising alternative to TREF  $\times$  SEC. The advantages and disadvantages of using either HPLC  $\times$  SEC or SEC  $\times$  HPLC sequences were discussed in detail by van der Host and Schoenmakers [25,26]. From the practical point of view, a preferred 2D-LC set-up is fractionation of a sample by HPLC and subsequent analysis of the fractions eluting from the HPLC column by SEC. Namely, HPLC was found to be less sen-

sitive towards molar mass effects and yielded uniform fractions with respect to chemical composition. SEC is in the majority of publications used for the second dimension, which allows the use of different detectors [27]. Comprehensive two-dimensional liquid chromatography implemented by coupling two separations exists in three schemes: on-line; stop-and-go; and off-line. Each approach has distinct features and drawbacks; particular approaches allow making the use of one of them more advantageous than that of the other ones for some specific applications, as it was demonstrated by Fairchild et al. [28]. The last but not least is that the comprehensive two-dimensional operation greatly increases the peak capacity of LC systems and, as a consequence, the information content of the resulting data is substantially enhanced [29–31].

2D-LC separations of synthetic polymers using the on-line concept have been reported [25–27,32–44]. However, at the time being, the published 2D-LC methods and available instruments related to polymers are limited to separation at ambient temperatures and can therefore not be applied to the characterization of functionalized polyolefins, which require 130–160 °C for their dissolution. And, indeed, the high-temperature two-dimensional liquid chromatography work on such polyolefins has never been published.

The main objective of the present paper is to introduce a novel technique for the characterization of functionalized polyolefins and to show advantages of using it in comparison with the underlying one-dimensional chromatographic separations (as stand-alone). To do this, we have chosen the HPLC system developed in our laboratory that separates functionalized polyolefins according to the chemical composition and coupled it with SEC. It will be addressed that this system is suitable for all copolymers compositions regardless of their crystallinity.



**Fig. 2.** Diagrams obtained by TREF  $\times$  SEC of a blend of PE (1.18 kg mol<sup>-1</sup>), EVA (6.5 mol% of VA), EVA (20 mol% of VA), EVA (57 mol% of VA) and PVAc (37 kg mol<sup>-1</sup>) using conditions described in the text: (a) 3D plot; (b) 2D-contour plot.

## 2. Experimental

### 2.1. Chromatographic system

All chromatographic experiments were done using a prototype chromatographic system for high-temperature two-dimensional liquid chromatography constructed by PolymerChar (Valencia, Spain), comprising an autosampler, two separate ovens, valves and two pumps equipped with vacuum degassers (Agilent, Waldbronn, Germany). One oven was used for thermostating of the SEC column, while the second one, where the injector and a switching valve were located, was used for thermostating of the HPLC column. The autosampler is a separate unit with 70 vials of 10 mL hooked up to the injector through a heated interface. A high-pressure binary gradient pump was used for HPLC and an isocratic pump was used for SEC. The 2D-LC instrument is schematically shown in Fig. 1.

The coupling of HT-HPLC and HT-SEC was achieved by using an electronically controlled eight-port valve system EC8W (VICI Valco instruments, Houston, Texas, USA) equipped with two 200  $\mu$ L loops. From the moment of injection into the HPLC column (100  $\mu$ L injection loop), the 8-port valve was switched every 2 min in order to inject 200  $\mu$ L of effluent from the HPLC into the SEC column. This is in close agreement with the consequences of the M-S-F-(Murphy, Schure and Foley) quantitative approach, which has become the basis for a widely accepted sampling criterion [45–47], stating that the effluent must be sampled at least three times over the  $8\sigma$  base width of a first dimension peak to avoid serious loss of resolution between a pair of peaks when the first dimension contributes heavily to the overall resolution, which is our case. An evaporative light scattering detector (ELSD, model PL-ELS 1000, Polymer Laboratories, Church Stretton, England) was used as detector. The ELSD was operated at a nebulisation temperature of 140 °C, an evaporation temperature of 260 °C and an air flow of 1.5 L/min.

2D-LC system handling was done with software provided by Polymer Char (Valencia, Spain). WinGPC-Software v.7.0 (Polymer Standards Service, Mainz, Germany) was used for data acquisition and evaluation.

### 2.2. Chromatographic conditions

#### 2.2.1. High-temperature HPLC

First dimension separations were carried out on a silica gel Nucleosil 500 column with the following parameters: column size 250 mm  $\times$  4.6 mm i.d., average particle size diameter 5  $\mu$ m (MZ Analysentechnik, Mainz, Germany) and a silica gel Perfecsil 300 column with the following parameters: column size 250 mm  $\times$  4.6 mm i.d., average particle size diameter 5  $\mu$ m (MZ Analysentechnik, Mainz, Germany). 1,2,4-Trichlorobenzene (TCB) and cyclohexanone were used as the components of the mobile phase with a flow rate of 0.1 mL/min.

#### 2.2.2. High-temperature SEC

A column PL Rapide H, 150 mm  $\times$  7.5 mm (Polymer Laboratories, Church Stretton, England) was used in the second dimension (SEC). TCB was used as the mobile phase with a flow rate of 2.5 mL/min.

### 2.3. TREF $\times$ SEC

A TREF-300 (Polymer Char, Valencia, Spain) was used for cross-fractionation experiments (TREF  $\times$  SEC). The instrument comprises an oven used for sample preparation, a high precision TREF column oven equipped with a set of 5 stainless steel vessels with internal filters and magnetic stir bars, syringe pump, HPLC pump and a high-temperature isothermal oven, where the injection valve, multi-position switching valve and the set of GPC column are placed. A dual band IR4 infrared detector (Polymer Char, Valencia, Spain) was used as the concentration detector. The procedure described by Ortin et al. [12] was used to perform TREF  $\times$  SEC. A sample is first dissolved in the stainless steel vessel. Once the sample is dis-

**Table 1**

Weight average molar mass ( $M_w$ ), polydispersity index (PDI) and vinyl acetate content (VA) of the polymer samples.

Sample	Producer	$M_w$ (kg mol <sup>-1</sup> )	PDI	VA (mol%)
ESCORENE 0019	Exxon Mobil	197.5	3.08	6.5
LEVAPREN 450	BAYER	377.9	8.06	20
LEVAPREN 800 HV	BAYER	224.6	4.1	57

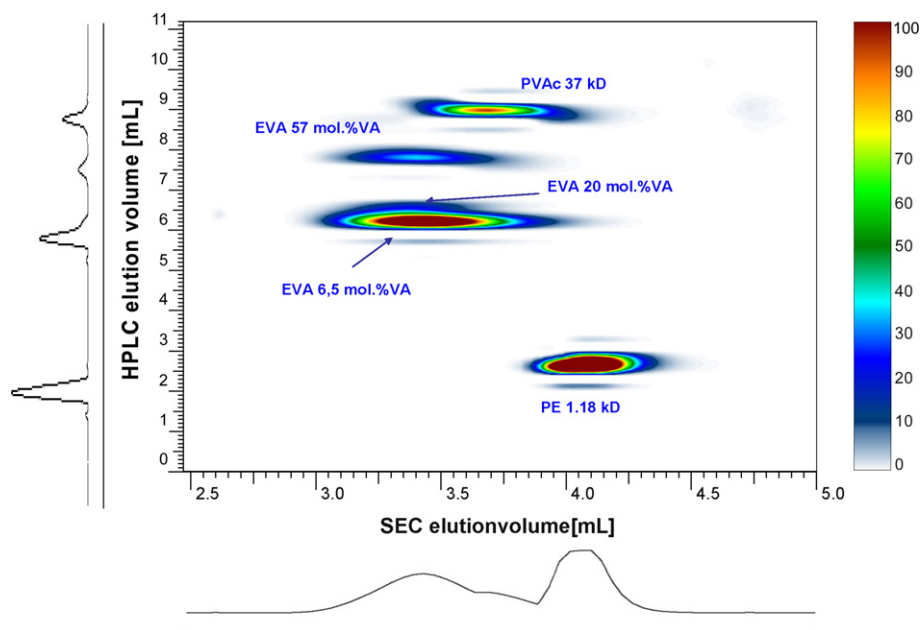


Fig. 3. Contour plot obtained by high-temperature 2D-LC of the same blend as described in Fig. 2; columns and flow rates: HPLC: Perfectsil 300, 0.1 mL/min; SEC: PL Rapide H, 2.5 mL/min.

solved, an aliquot is taken from the vessel through its filter and loaded into the TREF column heated up to 150 °C where the sample is then crystallized at 0.5 °C/min. Then a discontinuous elution process is followed by increasing the temperature in 5 °C-steps. TREF fractions with the increasing crystallinity are then injected into the SEC column. The SEC column was calibrated with PS standards.

#### 2.4. Polymer samples and solvents

The EVA copolymers were obtained from Exxon-Mobil Chemical (Meerhout, Belgium) and Bayer (Leverkusen, Germany). The compositional data given by the producers and the molar mass data of the copolymers are summarized in Table 1.

Linear polyethylene (PE) standards with peak molar masses ( $M_p$ ) in the range of 1.18–126 kg mol<sup>-1</sup> (PD=1.12–1.59), poly(vinyl acetate) (PVAc) with  $M_w$ =45.5 kg mol<sup>-1</sup> (PD=2.43) and polystyrene standards (PS) with  $M_p$  in the range of

1.62–2570 kg mol<sup>-1</sup> (PD=1.02–1.07) were obtained from Polymer Standard Service (Mainz, Germany). Linear PE with  $M_w$ =260 kg mol<sup>-1</sup> was obtained from PSD Polymers (Linz, Austria). PS with  $M_w$ =0.687 kg mol<sup>-1</sup> was purchased from Aldrich Chemical Company (Milwaukee, USA). All samples were dissolved in TCB at a concentration of 2 mg/mL and a temperature of 160 °C.

1,2,4-Trichlorobenzene (TCB) and cyclohexanone of synthesis quality were obtained from Merck (Merck, Darmstadt, Germany). TCB was freshly distilled.

### 3. Results and discussion

In order to investigate the chemical heterogeneity by a conventional method, a model mixture containing PE, several EVA copolymers and PVAc was cross-fractionated by TREF × SEC. The 3D plot is presented in Fig. 2. The figure shows the set of SEC elugrams measured at different TREF temperatures. Taking into account the principles of TREF × SEC, the less crystalline part (amorphous) of the blend elutes at a temperature of 30 °C. The SEC profile shows a very broad bimodal molar mass distribution. Considering the molar masses and the chemical composition of the components used in the model mixture, it can be supposed that the soluble TREF fraction contains PVAc 37 kg mol<sup>-1</sup>, EVA with 20 and 57 mol% of VA and to some extent EVA with 6.5 mol% of VA. However, no information about the chemical composition of this fraction can be obtained. The next TREF fractions with the increasing crystallinity exhibit molar mass distributions in the area of smaller molar masses. They can be assigned to both PE (1.18 kg mol<sup>-1</sup>) and EVA copolymers. Moreover, the fractions with crystallization temperatures at 60 and 70 °C show additional peaks in the area of higher molar mass, which is apparently EVA with 6.5 mol% of VA. We conclude that the major part of the mixture elutes as the soluble fraction and the rest elutes (cocrySTALLIZES) in a broad zone with respect to crystallinity, i.e. the cross-fractionation by TREF × SEC does not result in a selective separation of all components according to their chemical composition.

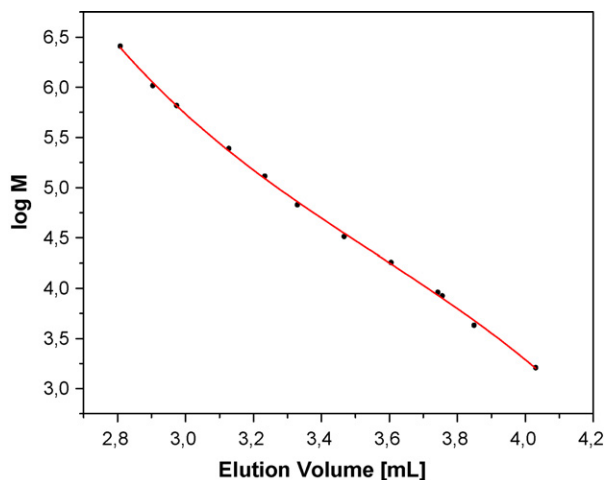
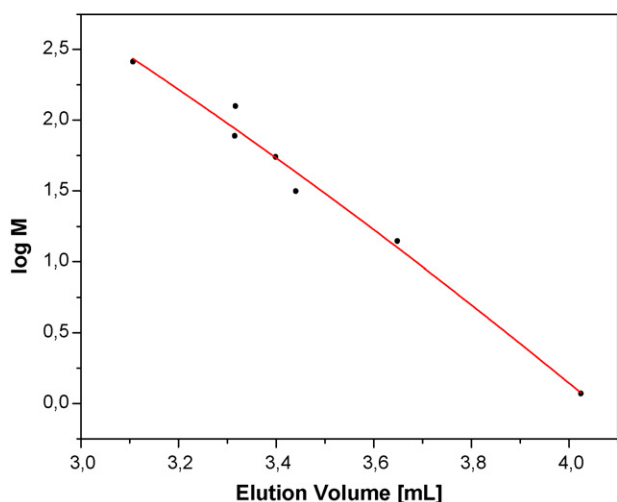
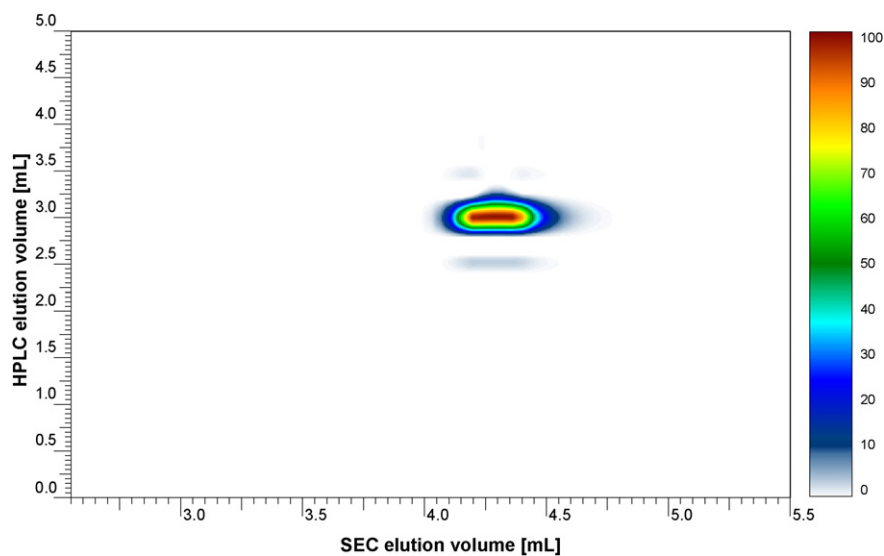


Fig. 4. PS calibration curve for PL Rapide H column (140 °C, TCB, 2.5 mL/min) obtained in 2D-LC system (1st dimension: Perfectsil 300, TCB, 0.1 mL/min).

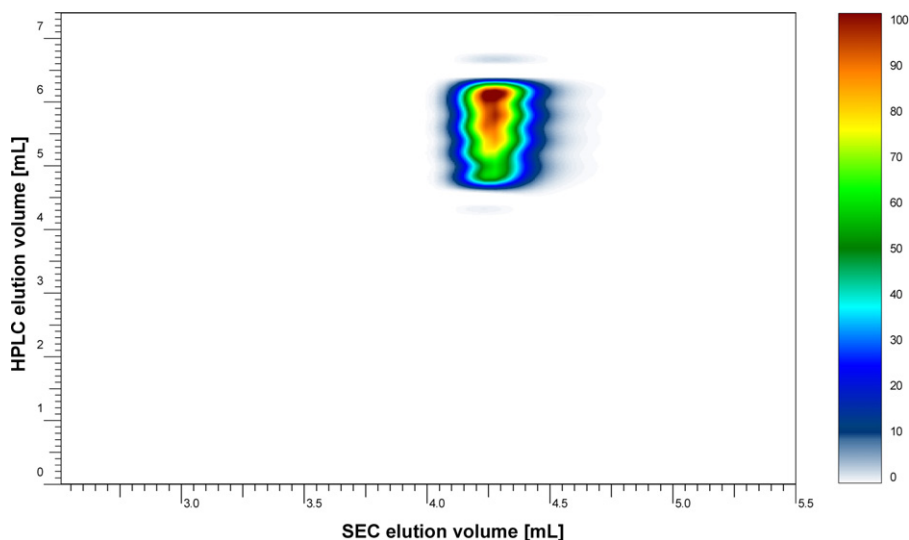


**Fig. 5.** PE calibration curve for PL Rapide H column (140°C, TCB, 2.5 mL/min) obtained in 2D-LC system (1st dimension: Perfectsil 300, TCB, 0.1 mL/min).

Having appropriate chromatographic systems is the main requisite for the realization of 2D-LC separation. As has been pointed out, EVA copolymers could be separated according to their VA-content on bare silica using TCB and cyclohexanone as components of the mobile phase. The separation is based on the full adsorption of EVA from TCB and a subsequent controlled desorption by a TCB → cyclohexanone solvent gradient. The contour plot in Fig. 3 shows the 2D-LC separation of the same polymer mixture as for the TREF × SEC experiment described above. The gradient separation is represented along the y-axis whereas the elution along the x-axis corresponds to the SEC separation. As can be seen, the individual samples elute in the order of their polarity. The first eluting spot can be assigned to the polyethylene and the last one is PVAc which are the least and most polar component, respectively. Between these three EVA copolymers elute. Only two EVA copolymers (6.5 and 20 mol% of VA) are not baseline separated, but the presence of two components with different chemical composition as well as with different average molar masses can be concluded. The TREF × SEC cross-fractionation by contrast did not separate the components of the mixture as clearly as 2D-LC. The small narrow part in the

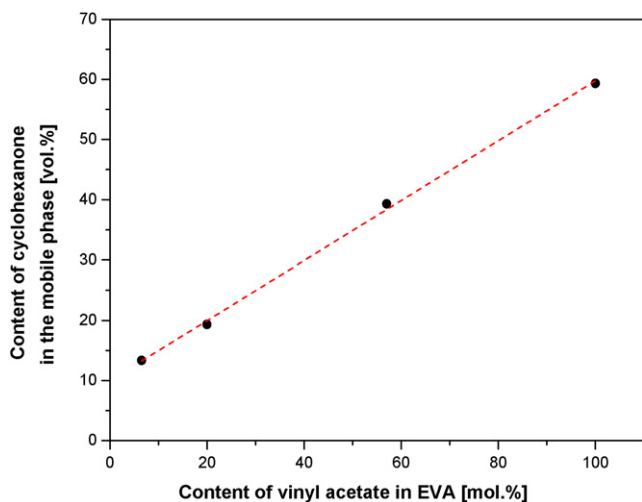


**Fig. 6.** 2D-LC contour plot of a PS 0.687 kg mol<sup>-1</sup> used for the determination of the void volume: columns and flow rates: HPLC: Perfectsil 300, TCB, 0.1 mL/min; SEC: PL Rapide H, TCB, 2.5 mL/min.



**Fig. 7.** 2D-LC contour plot of a solution of PS 0.687 kg mol<sup>-1</sup> in TCB (1 mg/mL) used for the determination of a dwell volume: columns and flow rates like in Fig. 6.





**Fig. 8.** Relationship between concentration of cyclohexanone in the mobile phase and the average chemical composition of EVA copolymers.

contour plot eluting between 5.6 and 6.0 mL, i.e., before the main spot (it looks like a narrow peak with very small intensity), is coming from the mathematical data treatment in the WinGPC software (Polymer Standards Service, Mainz, Germany). The cause for this effect will be eliminated from the software in the future.

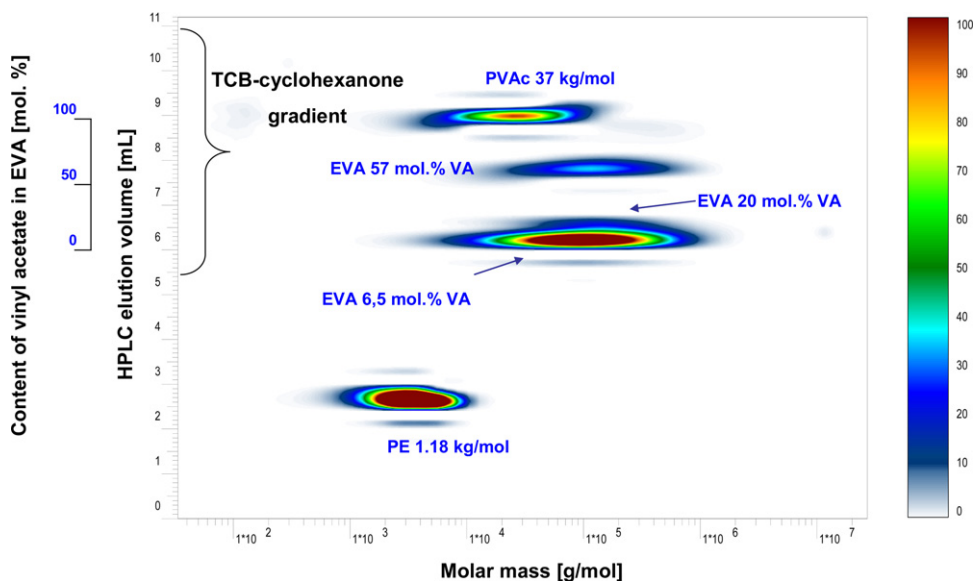
In the majority of publications describing 2D-LC separations at room temperature, only SEC is calibrated. Calibration of the first dimension (compositional axis) has never been reported. As the high-temperature two-dimensional liquid chromatography has not been studied, the calibration of both chromatographic modes is a challenging task. Therefore, a relationship between the molar mass and the elution volume in SEC as well as a relationship between the chemical composition and the elution volume in HPLC has to be established. The SEC calibration curve is valid as long as the chromatographic system and procedure are not changed. In a comprehensive 2D-LC set-up, two chromatographic modes (HPLC and SEC) are on-line hyphenated. It means, that, instead of an ordinary injection of a polymer sample into the SEC eluent, an injection of a polymer sample in a mixed solvent via an automated switching valve is made, which may cause a change of the hydrodynamic

volume and therefore the elution volume of the sample. In order to obtain reliable results, the SEC calibration standard should undergo the HPLC separation and enter the SEC system via an automated injection [13]. Thus, 11 PS and 7 PE standards were injected into the 2D system, so that each standard passed through the HPLC column and was analyzed by SEC. The obtained calibration curves are shown in Figs. 4 and 5.

As can be observed in Fig. 4, the data points could be fitted with a polynomial curve quite well, while the data points in Fig. 5 are rather scattered. It is known that the accuracy of the results strongly depends on the number of standards, the molar mass range covered by them, and the appropriate fit. One of the most important sources of error in establishing a calibration is the number of data points. Narrow disperse polystyrene standards are readily available on the market. Polyethylene standards with a well-defined molecular mass distribution are also available; however, their MMD is generally broader (see experimental part). Therefore, the PS calibration yields a much more accurate and reliable calibration curve in comparison with the PE calibration.

A calibration of the HPLC requires knowledge of the delay volume of the system, i.e. when a given gradient reaches the detector. The delay volume is the sum of a void volume and a dwell volume of the corresponding system. Taking into account controversial opinions regarding the meaning of these parameters as well as the methods of their determination [48,49], we note that in the present treatment we consider the void volume as the volume of the component that is not retained by the stationary phase while the dwell volume is the volume of liquid contained in the system between the point where the gradient is formed and the injector. The dwell and the void volume of the 2D-LC system were determined modifying a procedure proposed by Bashir et al. for HPLC [50]. The void volume was measured by injecting a low molar mass PS standard ( $M_w = 0.687 \text{ kg mol}^{-1}$ ) into the 2D-LC system, as it is not retained by the HPLC column and elutes with the initial mobile phase composition (i.e., in TCB). The elution volume of the PS standard corresponds then to the void volume of the chromatographic system which was determined to be 3.00 mL (Fig. 6).

In [50] the dwell volume was determined by subtracting the void volume from the delay volume which was measured from the onset of the UV-signal when a linear gradient starting from



**Fig. 9.** Contour plot of a blend obtained from the original data (Fig. 2) with the calibrated axes.

pure methanol to methanol/acetone containing 0.3% acetone was applied. Analogously the dwell volume was determined by subtracting the void volume from the elution volume at the onset of the ELSD signal when a linear gradient from pure TCB to a solution of PS ( $0.687 \text{ kg mol}^{-1}$ ) in TCB ( $1 \text{ mg/mL}$ ) was started. This approach gave, however, an overestimated value for the dwell volume ( $3.54 \text{ mL}$ ). It was considered as overestimated, because if it was used to locate the exact position of the gradient on the  $y$ -axis, some EVA copolymers would elute before the gradient which is impossible. It is supposed that at the moment when the gradient reaches the detector the concentration of PS is not sufficient to be detected by the ELSD because the ELSD is less sensitive than a UV-detector. Moreover, in 2D-LC the sample concentration after the second dimension is significantly lower than after the first dimension only which means that a larger sample concentration has to be used as compared to the one-dimensional separation. Consequently, the procedure to determine the dwell volume was modified: In the first step pure TCB was pumped into the 2D system. Thereafter, the concentration of PS ( $0.687 \text{ kg mol}^{-1}$ ) in TCB ( $1 \text{ mg/mL}$ ) was abruptly changed to 100 vol.% and the data acquisition started. The contour plot resulting from the sudden change of the composition of the mobile phase is illustrated in Fig. 7.

The dwell volume obtained by using this procedure was  $1.44 \text{ mL}$  and the system delay volume could be explicitly estimated using the following equation:

$$V_{\text{system,2D}} = V_{\text{dwell}} + V_{\text{void,2D}}$$

As a consequence, the gradient reaches the detector with a delay of  $4.44 \text{ mL}$ . The knowledge of these chromatographic parameters allows to locate the exact position of the gradient on the  $y$ -axis of the contour plot. We have found previously that the dependence between the elution volume and the average chemical composition of EVA copolymers in gradient HPLC is linear. The obtained relationship is depicted in Fig. 8. As we have determined the delay volume of the system, the content of cyclohexanone in the mobile phase can be related to the elution volume and the dependence between the VA-content and the elution volume applied to the 2D-contour plot. Consequently, the  $x$ - and  $y$ -axis of the contour plot were converted and thus a new contour plot was obtained (Fig. 9).

Each axis in Fig. 9 represents one property of the analyzed polymer sample—either molar mass or the chemical composition of the analyzed polymer and information that could be extracted from the contour plot is greatly enhanced.

#### 4. Conclusion

High-temperature 2D-LC of EVA copolymers has been realized for the first time by coupling of interactive high-performance liquid chromatography (HPLC) with SEC at  $140^\circ\text{C}$ . This was successfully demonstrated by the analysis of a blend of PE, PVAc and EVA copolymers with varying vinyl acetate content. In the first step, the components were separated with regard to the content of the polar comonomer, while in the second step the obtained fractions were distinguished according to the molar mass distribution. Both distributions were obtained simultaneously in a relatively short period of time – 5 h for a complete 2D-LC analysis – including sample preparation. For the first time a calibration of both dimensions, HPLC and SEC, was achieved. Therefore a method to correctly determine the void and dwell volume in a 2D-LC system was developed. TREF  $\times$  SEC on the contrary was not able to separate the same mixture into the individual components. Although HT 2D-LC is experimentally not less demanding than TREF  $\times$  SEC, a great advantage is that it can be applied to samples regardless of their crystallinity. Thus effects of cocrystallization can be avoided which

might play a role in TREF-fractionation. The results can be presented in an impressively simple way.

#### Acknowledgements

This research is part of the Research Programme of the Dutch Polymer Institute (DPI) under the Project # 642/643. The authors thank Dipl. Ing. A. Ortin, J. Sancho-Tello and Dr. B. Monrabal (PolymerChar, Valencia, Spain) for technical help and appreciate very much their continuous effort to improve both the 2D-LC instrument and the corresponding software. Financial support from the Federal Ministry of Economics and Technology (Bundesministerium für Wirtschaft und Technologie (BMWi)) through the Federation of Industrial Cooperative Research Associations “Otto von Guericke” (Arbeitsgemeinschaft industrieller Forschungsvereinigungen “Otto von Guericke” e.V., AiF, AiF research project 14725N) is gratefully acknowledged.

#### References

- [1] M.J. Yanjarappa, S. Sivaram, *Progress Polym. Sci.* 27 (2002) 1347.
- [2] S. Mori, H.G. Barth, *Size Exclusion Chromatography*, 1st ed., Springer, Berlin, 1999.
- [3] A. Striegel, W.W. Yau, J.J. Kirkland, D.D. Bly, *Modern Size-exclusion Liquid Chromatography*, Wiley, NY, 2009.
- [4] L. Wild, T.R. Ryle, D.C. Knobloch, I.R. Peat, *J. Polym. Sci. Polym. Phys.* 20 (1982) 441.
- [5] E.C. Kelusky, C.T. Elston, R.E. Murray, *Polym. Eng. Sci.* 27 (1987) 1562.
- [6] B. Monrabal, in: S. Hosoda (Ed.), *New Trends in Polyolefin Science and Technology*, Research Signpost, 1996, p. 119.
- [7] B. Monrabal, in: R.A. Meyers (Ed.), *Encyclopedia of Analytical Chemistry*, Wiley, New York, 2000.
- [8] S. Anantawaraskul, J.B.P. Soares, P.M. Wood Adams, *Adv. Polym. Sci.* 182 (2005) 1.
- [9] B. Monrabal, J. Blanco, J. Nieto, J.B.P. Soares, *J. Polym. Sci. Part A: Polym. Chem.* 37 (1999) 89.
- [10] S. Nakano, Y. Goto, *J. Appl. Polym. Sci.* 26 (1981) 4217.
- [11] W.W. Yau, D. Gillespie, *Polymer* 42 (2001) 8947.
- [12] A. Ortin, B. Monrabal, J. Sancho-Tello, *Macromol. Symp.* 257 (2007) 13.
- [13] H. Pasch, B. Trathnigg, *HPLC of Polymers*, Springer, Berlin/Heidelberg/New York, 1998.
- [14] G. Glöckner, *Gradient HPLC of Copolymers and Chromatographic Cross Fractionation*, Springer, Berlin/Heidelberg/New York, 1991.
- [15] W. Radke, in: K. Matyjaszewski, Y. Gnanou, L. Leibler (Eds.), *Structure–Property Correlation and Characterization Techniques*, *Macromolecular Engineering*, vol. 3, Wiley, Weinheim, 2007, p. 1881.
- [16] T. Macko, D. Hunkeler, *Adv. Polym. Sci.* 163 (2003) 61.
- [17] P. Kilz, H. Pasch, in: R.A. Meyers (Ed.), *Encyclopedia of Analytical Chemistry*, Wiley, New York, 2000.
- [18] T. Chang, *Adv. Polym. Sci.* 163 (2002) 1.
- [19] A. Albrecht, R. Brüll, T. Macko, H. Pasch, *Macromolecules* 40 (2007) 5545.
- [20] A. Albrecht, R. Brüll, T. Macko, F. Malz, H. Pasch, *Macromol. Chem. Phys.* 210 (2009) 1319.
- [21] H. Pasch, A. Albrecht, R. Brüll, T. Macko, W. Hiller, *Macromol. Symp.* 282 (2009) 71.
- [22] A. Albrecht, R. Brüll, T. Macko, P. Sinha, H. Pasch, *Macromol. Chem. Phys.* 209 (2008) 1909.
- [23] L.C. Heinz, S. Graf, T. Macko, R. Brüll, S. Balk, H. Keul, H. Pasch, *e-Polymers* (2005) 054.
- [24] L.C. Heinz, T. Macko, H. Pasch, M.S. Weiser, R. Mülhaupt, *Int. J. Polym. Anal. Charact.* 11 (2006) 47.
- [25] A. van der Horst, P.J. Schoenmakers, *J. Chromatogr. A* 1000 (2003) 693.
- [26] P.J. Schoenmakers, G. Vivo-Truyols, W.M.C. Decrop, *J. Chromatogr. A* 1120 (2006) 282.
- [27] F. Rittig, H. Pasch, in: A. Cohen, M.R. Schure (Eds.), *Multidimensional Liquid Chromatography Theory and Applications in Industrial Chemistry and the Life Sciences*, John Wiley & Sons, Inc., Hoboken, New Jersey, 2008, p. 385.
- [28] J.N. Fairchild, K. Horvath, G.J. Guiochon, *J. Chromatogr. A* 1216 (2009) 1316.
- [29] X. Li, D.S. Stoll, P.W. Carr, *Anal. Chem.* 81 (2009) 845.
- [30] J.M. Davis, D.R. Stoll, P.W. Carr, *Anal. Chem.* 80 (2008) 8122.
- [31] D. Berek, *Anal. Bioanal. Biochem.* 396 (2010) 421.
- [32] H. Gao, K. Min, K. Matyjaszewski, *Macromol. Chem. Phys.* 207 (2006) 1709.
- [33] S.J. Kok, Th. Hankenmeier, P.J. Schoenmakers, *J. Chromatogr. A* 1098 (2005) 104.
- [34] K. Im, H. Park, S. Lee, T. Chang, *J. Chromatogr. A* 1216 (2009) 4606.
- [35] J.-A. Raust, A. Brüll, P. Sinha, W. Hiller, H. Pasch, *J. Sep. Sci.* 33 (2010) 1.
- [36] J.-A. Raust, A. Brüll, C. Moire, C. Farcet, H. Pasch, *J. Chromatogr. A* 1203 (2008) 207.
- [37] M.I. Malik, B. Trathnigg, R. Saf, *J. Chromatogr. A* 1216 (2009) 6627.
- [38] R. Edam, D.M. Meunier, E.P.C. Mes, F.A. Van Damme, P.J. Schoenmakers, *J. Chromatogr. A* 1201 (2008) 208.

- [39] J. Adrian, D. Braun, H. Pasch, *LC–GC Int.* 11 (1998) 32.
- [40] J. Adrian, K. Mequanint, H. Pasch, *e-Polymers* (2002) 005.
- [41] J. Adrian, E. Esser, G.P. Hellmann, H. Pasch, *Polymer* 41 (2000) 2439.
- [42] J. Gerber, W. Radke, *e-Polymers* (2005) 045.
- [43] J. Gerber, W. Radke, *Polymer* 46 (2005) 9224.
- [44] A. Siewing, J. Schierholz, D. Braun, G.P. Hellmann, H. Pasch, *Macromol. Chem. Phys* 202 (2001) 2890.
- [45] R.E. Murphy, M.R. Schure, J.P. Foley, *Anal. Chem.* 70 (1998) 1585.
- [46] J.M. Davis, D.R. Stoll, P.W. Carr, *Anal. Chem.* 80 (2007) 461.
- [47] K. Horie, H. Kimura, T. Ikegami, A. Iwatsuka, N. Saad, O. Fiehn, N. Tanaka, *Anal. Chem.* 79 (2007) 3764.
- [48] A. Malik, K. Jinno, *Chromatographia* 30 (1990) 135.
- [49] C.A. Rimmer, C.R. Simmons, J.G. Dorse, *J. Chromatogr. A* 965 (2002) 219–232.
- [50] M.A. Bashir, A. Brüll, W. Radke, *Polymer* 46 (2005) 3223.