Separation of Ethylene−Vinyl Acetate Copolymers by High-Temperature Gradient Liquid Chromatography

Andreas Albrecht, Robert Brüll, Tibor Macko, and Harald Pasch*

Deutsches Kunststoff-Institut (German Institute for Polymers), Schlossgartenstr. 6, 64289 Darmstadt, Germany

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ABSTRACT: Ethylene−vinyl acetate (EVA) copolymers can be semicrystalline or amorphous materials, depending on their chemical composition. A variety of different methods were used for the analysis of the chemical composition distribution of these copolymers, which in general were time- and labor-consuming and could be applied only for a limited range of compositions. In the present work a novel chromatographic method is presented that can be used for chemical composition analysis regardless of the composition of the copolymer. High-temperature gradient HPLC has been found to be suitable for chemical composition separation of semicrystalline and amorphous EVA copolymers. In addition, separation is achieved from the respective homopolymers. We have found that gradients of 1,2,4-trichlorobenzene/cyclohexanone, decalin/cyclohexanone, and decalin/1-decanol enable the selective elution of the copolymers from silica gel at 140 °C. The EVA copolymers elute in dependence of their content of the polar vinyl acetate comonomer. Full adsorption and desorption of the samples controlled by the gradient could be achieved for all compositions. Coupling of the gradient HPLC system with FTIR spectroscopy through a LC−transform interface confirmed the chemical composition separation and revealed the chemical heterogeneity of the copolymers. Conditions for liquid chromatography at critical conditions (LCCC) have been established for poly(vinyl acetate) at 140 °C.

Introduction

Copolymers of ethylene and vinyl acetate (EVA) are commercially important products. Depending on their comonomer content, these materials find application in the production of films (2−18% vinyl acetate content), foams (20−30% VA), or hot melt adhesives (above 50% VA).[1] The average chemical composition of EVA copolymers can be analyzed using vibrational spectroscopy, e.g., FTIR,[2,3] Raman,[4] or NMR spectroscopy.[3,5,6] Wild and Kelusky analyzed the chemical composition distribution (CCD) of EVA copolymers containing 9−42% VA using temperature rising elution fractionation (TREF),[7,8] but the long analysis times and the complexity of this method prevented an extensive use. Moreover, EVA copolymers with a higher content of vinyl acetate do not crystallize and, thus, cannot be separated by TREF.

When liquid chromatography shall be used to separate EVA copolymers, one has to take into account that the solubility is a function of the copolymer composition. Copolymers with high VA contents are soluble at ambient temperature in, e.g., tetrahydrofuran and can be analyzed by standard methodologies. At low VA content, however, the semicrystalline copolymers are soluble only at high temperatures in solvents like trichlorobenzene (TCB). Thus, depending on the copolymer composition, different chromatographic setups have to be used.

As for ethylene-rich EVA copolymers that are only soluble at temperatures of 130 °C or higher, only size exclusion chromatography (SEC) has been used up to now to analyze the molar mass distribution.[9] Only apparent molar masses are obtained for copolymers with a broad chemical composition distribution since components with different chemical compositions and molar masses may coelute. When coupling SEC and FTIR, average chemical compositions corresponding to each elution volume increment are determined.[10−12]

Copolymers that are soluble at ambient temperature may be separated according to chemical composition by gradient HPLC,[13] liquid adsorption chromatography (LAC),[14] precipitation liquid chromatography, or liquid chromatography at critical conditions (LCCC).[15−17] Such separations have been described for temperatures between 20 and 50 °C. Lyons et al. developed a gradient chromatographic system for the fractionation of ethylene−styrene copolymers according to composition in a temperature range between 30 and 80 °C.[18] Silica gel and modified silica gels were used as stationary phases. Mobile phases were different combinations of acetonitrile, tetrahydrofuran, *n*-hexane, chloroform, and cyclohexane.

The first chromatographic system operating above 100 °C at gradient conditions was recently reported by Heinz and Pasch et al. It was shown that ethylene−styrene copolymers[18,19] and ethylene−methyl methacrylate copolymers[20] can be separated according to chemical composition by high-temperature gradient HPLC. Silica gel was used as the column packing, and the mobile phases contained mixtures of decalin, cyclohexanone, and 1,2-dichlorobenzene. Isocratic (LCCC)[19,20] as well as gradient separation procedures[18] at temperatures of 140 °C were developed.

Although the adsorption of EVA copolymers with high VA content from trichloroethylene[21,22] and cyclohexane[23] on silica gel has been described, interaction chromatography of these copolymers for the chemical composition separation has never been attempted. In this work we like to present the first chromatographic system for the separation of commercial EVA copolymers according to their vinyl acetate content. It will be demonstrated that this system is suitable for all copolymer compositions irrespective of their crystallinity.

Experimental Section

High-Temperature Chromatograph PL XT-220. A prototype high-temperature gradient HPLC system PL XT-220 (Polymer Laboratories, Varian Inc, Church Stretton, England)[24] was used for

* Corresponding author. E-mail: hpasch@dki.tu-darmstadt.de.

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Table 1. Weight-Average Molar Mass (M_w), Polydispersity (PD), and Vinyl Acetate Content (VA) of Ethylene−Vinyl Acetate Copolymers

sample code	producer	M_w [kg/mol][a] (polystyrene equivalent)	PD[a]	VA (wt %)[b]
EVA 1	Exxon-Mobil	330	8.8	5
EVA 2		270	4.8	12
EVA 3		330	5.8	13.9
EVA 4		260	4.3	19
EVA 5		144	3.1	28
EVA 6	Bayer	430	9.4	45
EVA 7		270	4.8	50
EVA 8		370	5.9	60
EVA 9		267	3.9	70
EVA 10		225	4.1	80
EVA 11	Innospec	256	5.9	7
EVA 12		223	6.5	9
EVA 13		194	5.3	14
EVA 14		14	2.6	15
EVA 15		201	4.0	18
EVA 16		161	4.6	18
EVA 17		169	3.8	20
EVA 18		74	2.6	24
EVA 19		86	2.6	30

[a] Data from our SEC measurements. [b] Data from the producers.

the separation of the samples according to their chemical composition. Dissolution and injection of the samples were performed using a robotic sample handling system PL-XTR (Polymer Laboratories). The temperature of the sample block, the injection needle, the injection port, and the transfer line between the autosampler and the column compartment was set to 140 °C. The flow rate of the mobile phase was 1 mL/min. The copolymers were dissolved for 2 h in TCB or decalin at a concentration of 1−1.2 mg/mL and a temperature of 140 °C. 50 μL of the polymer solutions was injected. The column outlet was connected either to an evaporative light scattering detector (ELSD, model PL-ELS 1000, Polymer Laboratories) or to a LC-transform FTIR interface (Series 300, Lab Connections, Carrboro, NC). The ELSD was run at a nebulization temperature of 160 °C and an evaporation temperature of 270 °C and with an air flow of 1.5 mL/min. At the LC-transform the stage temperature was 150 °C. For the gradient elution, a temperature gradient for the nozzle was applied. The rotation speed of the germanium disc was 10°/min. FTIR spectroscopy of the deposited eluate was performed using a Nicolet Protegè 460 (Thermo Electron, Waltham, MA). The WinGPC software (Polymer Standards Service GmbH, Mainz, Germany) was used for data collection and processing.

High-Temperature Chromatograph PL 220. A high-temperature chromatograph PL 220 (Polymer Laboratories, Varian Inc., Church Stretton, England) was used for determination of the molar mass distribution. The temperature of the injection sample block and the column compartment was set to 140 °C. The mobile phase flow rate was 1 mL/min. The copolymers were dissolved for 2 h in TCB at a concentration of 1 mg/mL and a temperature of 150 °C. 200 μL of the polymer solutions was injected. Polystyrene standards were used for calibration.

Stationary Phases. The following columns packed with bare silica gels were used: Perfectsil 300 Å (particle diameter 5 μm, pore volume 1.05 mL/g, void volume $V_0 = 3.21$ mL) and Polygosil 1000 Å (particle diameter 10 μm, $V_0 = 3.15$ mL) both from MZ Analysentechnik, Mainz, Germany; Nucleosil 500 Å (particle diameter 5 μm, pore volume 0.8 mL/g, $V_0 = 2.38$ mL, Macherey-Nagel, Düren, Germany); LiChrosorb 100 Å (irregular particles with an average diameter of 5 μm, pore volume 1.0 mL/g, Merck, Darmstadt, Germany). The column dimensions were in all cases 250 × 4.6 mm i.d.. Four PL mixed A columns, column size 250 × 8.0 mm i.d., containing particles with an average diameter of 20 μm (Polymer Laboratories, Varian Inc, Church Stretton, England), were chosen for SEC analysis. The specifications of all column packings were given by their producers. The void volume was determined in the manner described in the Results and Discussion section.

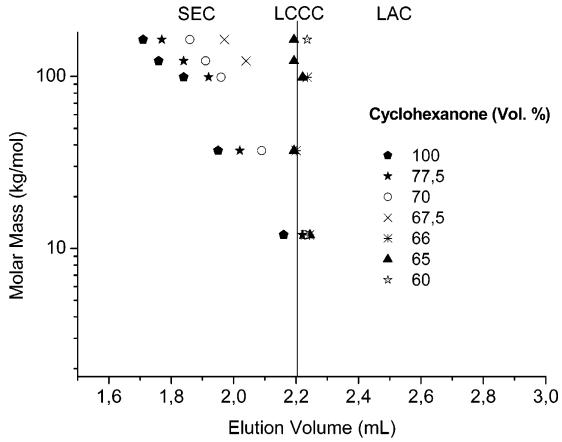

Figure 1. Dependence of the elution volumes of PVAc standards on the cyclohexanone content in the mobile phase (stationary phase: Nucleosil 500; mobile phase: TCB/cyclohexanone; temperature: 140 °C; sample solvent: mobile phase).

Mobile Phases. TCB, 1-decanol, decalin, cyclohexanone, and cyclohexanol, all of synthesis quality (Merck, Darmstadt, Germany), were used as components of the mobile phases.

Polymer Samples. Linear polyethylene (PE) standards with weight-average molar masses (M_w) in the range of 2−126 kg/mol (M_w/M_n 1.12−1.59) and the following poly(vinyl acetate) (PVAc) standards were obtained from Polymer Standards Service (Mainz, Germany): $M_w = 17$ kg/mol (M_w/M_n 2.27), $M_w = 45.5$ kg/mol (M_w/M_n 2.43), $M_w = 124$ kg/mol (M_w/M_n 3.08), $M_w = 234.5$ kg/mol (M_w/M_n 3.17), and $M_w = 275$ kg/mol (M_w/M_n 4.19).

The polystyrene standard with $M_w = 0.761$ kg/mol was obtained from Sigma-Aldrich (Schnelldorf, Germany). Samples of the EVA copolymers were obtained from Exxon-Mobil Chemical (Meerhout, Belgium), Bayer (Leverkusen, Germany), and Innospec (Leuna, Germany). The compositional data given by the producer and the molar mass data of the copolymers are summarized in Table 1.

Results and Discussion

For the identification of suitable chromatographic conditions for the separation of EVA copolymers, interacting stationary phases and proper mobile phases have to be found. EVA copolymers are a combination of nonpolar ethylene units and polar vinyl acetate units. It can, therefore, be assumed that with a polar stationary phase the vinyl acetate units will selectively interact while the ethylene units will not contribute to retention. Thus, an elution of the copolymers can be expected in the direction of increasing vinyl acetate content. Accordingly, bare silica gel was selected as the polar stationary phase.

Trichlorobenzene (TCB), decalin, cyclohexanol, and cyclohexanone were tested with regard to their potential as components of the mobile phase. TCB, cyclohexanol, and cyclohexanone were identified as solvents for the homopolymers, PE and PVAc, while decalin is a good solvent for PE but a nonsolvent for PVAc. As a result, the EVA copolymers containing more than 80 wt % of VA were not soluble in decalin at 140 °C while all EVA copolymers were soluble in TCB. It was observed that PVAc was fully adsorbed from TCB on silica gel and fully desorbed by cyclohexanone. In order to identify the critical point of adsorption for PVAc on silica gel (Nucleosil Si 500 Å) at 140 °C, TCB as an adsorption promoting solvent was combined with cyclohexanone as a desorption promoting solvent. The critical point of adsorption was determined by measuring the elution volumes of PVAc with different molar masses in TCB/cyclohexanone of varying compositions. Figure 1 shows the dependence of the elution behavior of PVAc standards for different ratios of TCB/cyclohexanone.

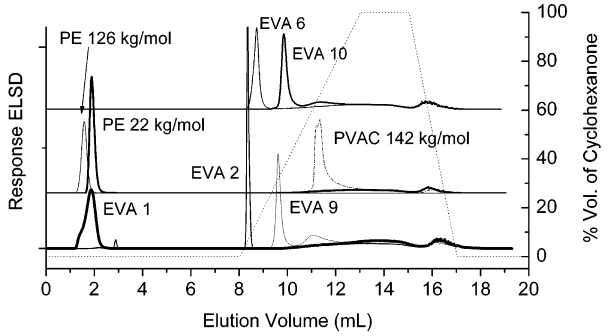

Figure 2. Overlay of chromatograms of PE, EVA, and PVAc (stationary phase: Nucleosil 500; mobile phase: gradient TCB/cyclohexanone (dotted line); temperature: 140 °C; sample solvent: TCB).

In the range of 100−66 vol % cyclohexanone in the mobile phase PVAc elutes in the SEC mode. At a mobile phase composition of TCB/cyclohexanone of 35:65 vol % all analyzed PVAc standards (17−275 kg/mol) elute at almost the same elution volume. This mobile phase composition corresponds to the critical conditions of adsorption. By using the critical conditions of adsorption for PVAc, it is possible to separate PE and PVAc in 2.4 min and to characterize the molar mass of PE in blends of PE and PVAc. For the separation of EVA copolymers with different VA contents and higher molar mass PVAc homopolymer the critical mobile phase composition gives a first hint for optimizing gradient elution conditions. For very high molar mass samples LCCC is not the best choice since irreversible adsorption can take place. For such samples gradient HPLC is preferred.

For the separation of the EVA copolymers a linear gradient TCB/cyclohexanone is applied (Figure 2). Starting with 100% TCB for 3 min, the volume fraction of cyclohexanone is linearly increased to 100% within 5 min and then held constant for 2 min. Finally, the initial chromatographic conditions are reestablished. Because of the column void volume and the dwell volume of the chromatographic system, the gradient reaches the detector with a delay of 5.03 min; i.e., the gradient reaches the detector at 8.03 min (Figure 2). The void volume of 2.38 mL was measured using a low molar mass PS standard (M_w = 0.761 kg/mol) which was injected in TCB. The dwell volume was determined on the basis of a linear gradient from pure TCB to TCB, containing 0.2 mg/mL of the PS standard (M_w = 0.761 kg/mol) according to the method described by Radke et al.[26] Figure 2 shows the elugrams of PE standards, EVA samples, and a PVAc standard.

As is shown in Figure 2, the different samples elute in the order of increasing polarity. First, the least polar PEs elute between 1.5 and 2.0 mL. The last eluting peak is PVAc, which is the most polar component. Between these the EVA copolymers elute in the order of increasing VA content beginning with the sample EVA 1 having a vinyl acetate content of 5 wt %. The last eluting copolymer is EVA 10 with a vinyl acetate content of 80 wt %.

Figure 2 indicates that the separation is not yet ideal. EVA 1 elutes between 1.2 and 2.3 mL and, therefore, may coelute with PE (1.6 mL for M_p = 126 kg/mol and 1.9 mL for M_p = 22 kg/mol). According to the elution behavior of the two PE standards, which elute in the SEC mode before the column void volume of 2.38 mL, it can be suggested that EVA 1 also elutes in the SEC mode; i.e., no adsorption takes place. For EVA copolymers with VA contents above 12 wt %, separation takes place with regard to chemical composition. For these samples, the separation mechanism is based on the adsorption of the copolymer on the silica surface. TCB promotes adsorption while the following desorption is promoted by the cyclohexanone gradient. EVA 9 eluted in a main peak at 9.6 mL and a smaller

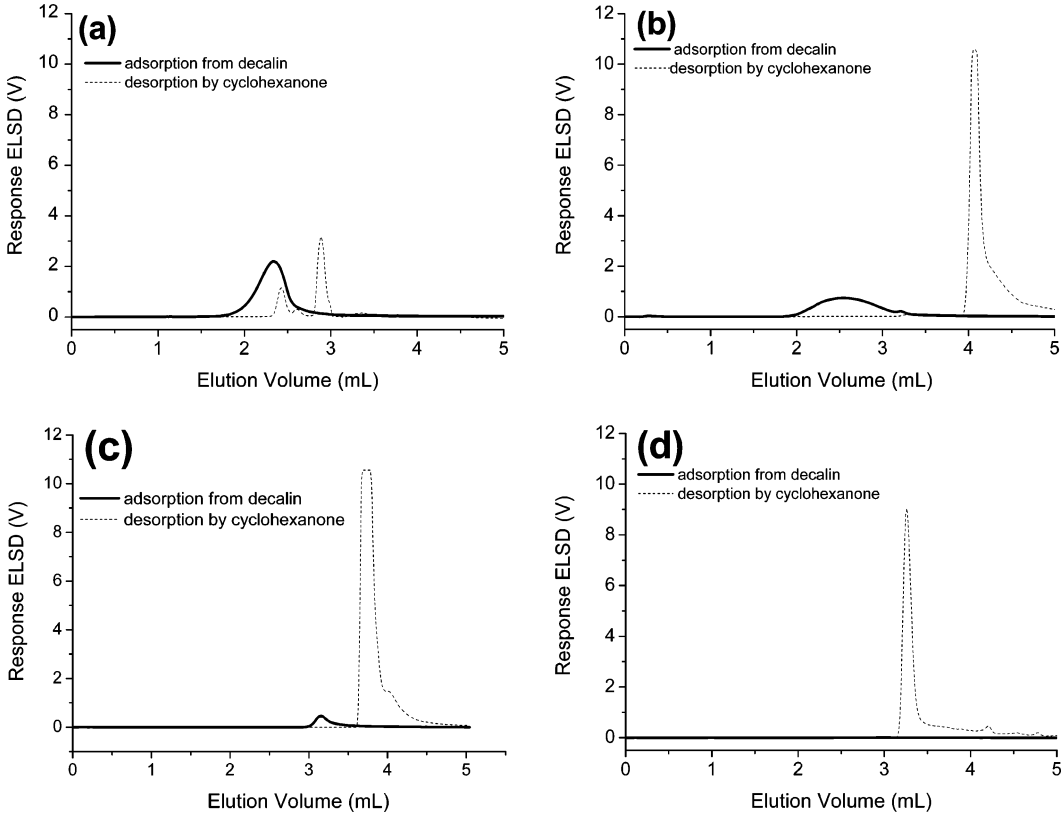

Figure 3. Chromatograms of sample EVA 1 at adsorption and desorption steps (stationary phase: LiChrosorb 100 (a); Nucleosil 500 (b); Polygosil 1000 (c); Perfectsil 300 (d); flow rate: 1 mL/min; sample solvent: decalin; temperature: 140 °C).

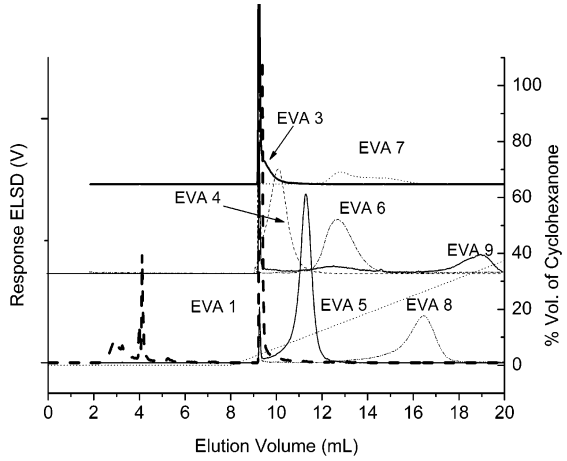

Figure 4. Overlay of the chromatograms of EVA copolymers (mobile phase: gradient decalin/cyclohexanone (dotted line); stationary phase: Perfectsil 300; for other experimental, conditions see Figure 3).

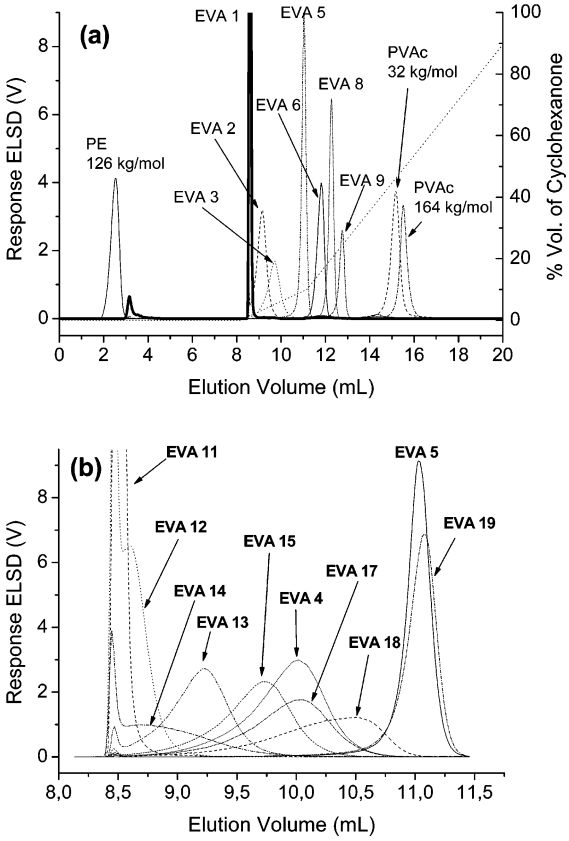

Figure 5. Overlay of the chromatograms of EVA copolymers (stationary phase: Polygosil 1000; mobile phase: gradient decalin/cyclohexanone (dotted line); temperature: 140 °C; detector: ELSD; sample solvent: decalin (TCB for the PVAc standards)): samples EVA 1−3, 8, 9 (a) and EVA 4,5,11−19 (b).

peak at 11.1 mL, indicating bimodality in the chemical composition distribution.

Two very broad elution peaks at around 14 and 16.5 mL appear in the chromatograms even when only pure TCB is injected. This indicates that the response of the ELSD changes with the gradient.

It is interesting to notice that the PVAc standard elutes at a mobile phase composition of TCB−cyclohexanone 32:68 vol %. This mobile phase composition is very close to the critical mobile phase composition (Figure 1), which is TCB−cyclohexanone 35:65 vol %. This is an excellent confirmation of the theoretical and experimental work of Brun et al.[27,28] and Radke et al.,[26] that polymers with high molar masses elute in a linear gradient mode close to their critical conditions.

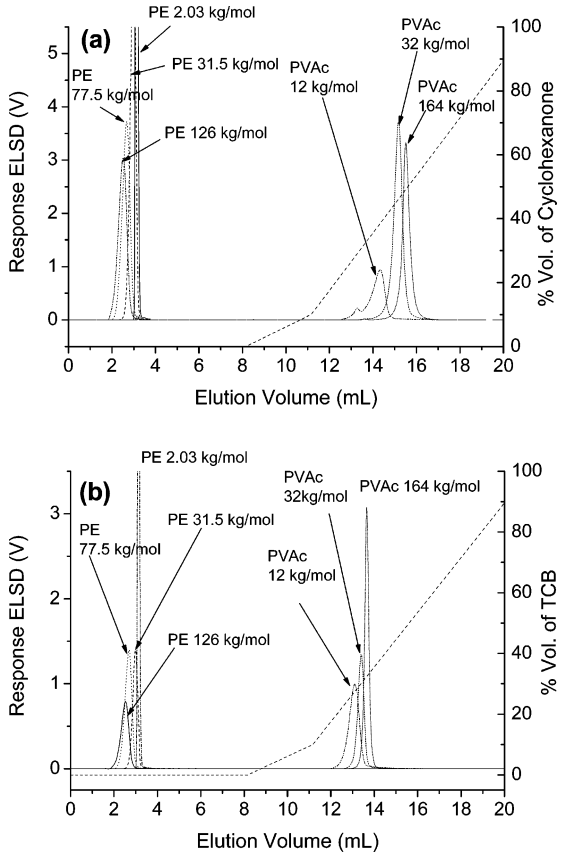

Figure 6. Overlay of chromatograms for PE and PVAc (stationary phase: Polygosil 1000; mobile phase: gradient decalin/cyclohexanone (a) or TCB/cyclohexanone (b); temperature: 140 °C; detector: ELSD; sample solvent: decalin (TCB for the PVAc standards) (a) or TCB (b)).

It is known that silica gels differ in their adsorption capacity for polar substances depending on the concentration of silanol groups and the specific surface area.[29] To evaluate the adsorption properties of different silica gels, adsorption experiments were conducted. EVA 1 was adsorbed from decalin, and 15 min after the injection the mobile phase was changed to cyclohexanone and EVA 1 was desorbed. The response of the ELSD detector during the adsorption and desorption steps is shown in Figure 3.

The adsorption of EVA 1 from decalin increases in the following order: LiChrosorb 100 < Nucleosil 500 < Polygosil 1000 < Perfectsil 300 (Figure 3). The sample is fully retained from decalin on Perfectsil. In contrast, when the more polar TCB is used as the mobile phase, then elution of EVA 1 occurs in the size exclusion mode on all silica gels.

In a next set of experiments, the separation of the copolymers is conducted using a gradient of decalin/cyclohexanone. The elution behavior of EVA copolymers with different VA contents is shown in Figure 4.

Figure 4 clearly indicates that copolymers containing 5−70% comonomer are nicely separated with regard to their VA content. A further improvement of the separation, in particular at low VA contents, in the copolymers can be achieved when the Polygosil 1000 stationary phase is used (Figure 5a,b). With the aim to reduce the analysis time a step gradient was chosen in this case. With this gradient, shown in Figures 5a and 6, a better resolution of EVA copolymers with a VA content between 5 and 30% could be achieved.

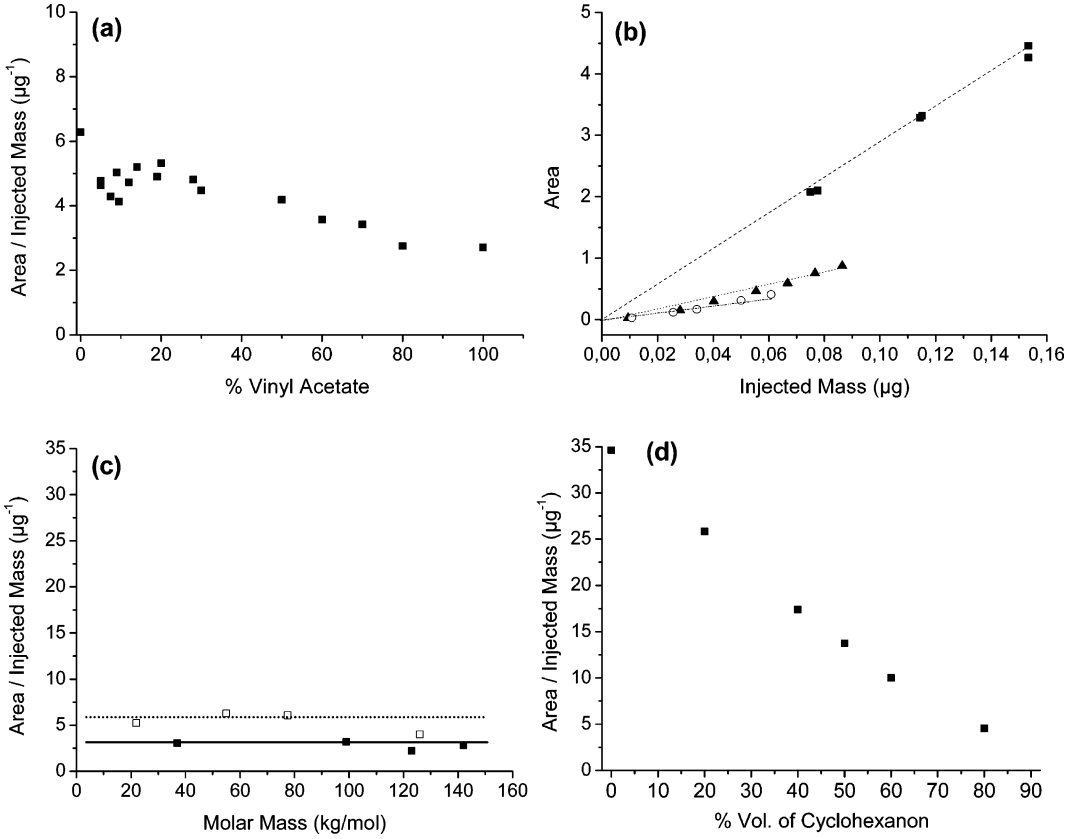

Figure 7. Influence of experimental parameters on the response of the ELSD detector (stationary phase: PL-gel HTSB, temperature: 140 °C): (a) specific ELSD response as a function of VA content of the EVA copolymers, mobile phase: TCB; (b) peak area vs injected mass of PE 60 kg/mol; mobile phase: decalin (■), cyclohexanone (□), TCB (▲); sample solvent: mobile phase; (c) detector response vs average molar mass; mobile phase and sample solvent: TCB; PE standards (□), PVAc standards (■); (d) specific response of PE 60 kg/mol as a function of mobile phase composition; mobile phase: decalin/cyclohexanone; sample solvent: mobile phase.

An important parameter of most statistical copolymers is their blockiness that is the length of the microblocks of the same composition. In the case of EVA copolymers, however, according to the copolymerization parameters ($r_1 = 1.07$ and $r_2 = 1.09$) for ethylene and vinyl acetate an uniform copolymer composition could be expected.[29] In one of the forthcoming publications the influence of the blockiness on the described chromatographic systems will be addressed. The EVA copolymers eluted, as shown in Figures 2, 4, and 5, in order of their average chemical compositions, thereby supporting the conclusion that these samples are relatively homogeneous.

In order to compare the molar mass dependence of the elution volume for PE and PVAc, separations were carried out on Polygosil 1000 using the two different gradients, i.e., decalin/cyclohexanone and TCB/cyclohexanone. As can be seen in Figure 6, there is not much difference in the elution behavior. In decalin/cyclohexanone, PVAc elutes at 14.4 mL ($M_p = 12$ kg/mol), 15.2 mL, and 15.5 mL ($M_p = 32$ kg/mol and $M_p = 164$ kg/mol, respectively) while in TCB/cyclohexanone the elution volumes are 13.1 mL, 13.4 mL, and 13.7 mL, respectively. As expected, PE elutes in both gradient systems in the size exclusion mode. The elution volume of PVAc is a function of molar mass for low molar mass samples, while for higher molar masses it becomes less dependent on the molar mass.

Decalin is a less polar solvent than TCB, hence leading to larger retention of the copolymers in the decalin/cyclohexanone gradient than in the corresponding TCB/cyclohexanone gradient.

It is known that the response of the ELSD depends, at constant instrumental parameters (flow rate, temperature, sample loop volume, etc.), on the concentration of the analyte and the composition of the mobile phase and is not strictly independent of the structure of the analyte.[30−33] For this reason the influence of parameters such as concentration, molar mass, and chemical composition of the analyte as well as the composition of the mobile phase on the response of the detector were investigated. The results are shown in Figure 7a−d. For these investigations, a typical SEC stationary phase is used in order to make sure that adsorption on the column does not affect the results.

In agreement with refs 31−34, the detector response increases with the concentration of the analyte; i.e., an exponential response curve with a linear range[31] is obtained (Figure 7b), and it depends pronouncedly on the nature of the mobile phase (Figure 7d). The specific response (peak area per injected mass) is a function of the VA content of the sample, but not of its molar mass[32,33] (Figure 7a,c). While authors[32] have found an independence of the specific response on the chemical composition for styrene−acrylonitrile copolymers, for the EVA copolymers the response is a function of their chemical composition in isocratic elution (Figure 7a). In gradient elution the response additionally depends on the composition of the mobile phase (Figure 7d). Here a specific response depend on the cyclohexanone content in the mobile phase is found. Accordingly, a quantification of the ELSD response for the EVA copolymers will require to take all these parameters into account and to elaborate corresponding calibration procedures.

With the aim to analyze the chemical composition of the chromatographic fractions, the high-temperature gradient HPLC was coupled with FTIR spectroscopy using a LC-transform interface. In the LC-transform approach the eluate from the chromatograph is deposited on a rotating germanium disc, and the mobile phase is removed in vacuum. The trace of material that is formed is then analyzed off-line by infrared spectroscopy.

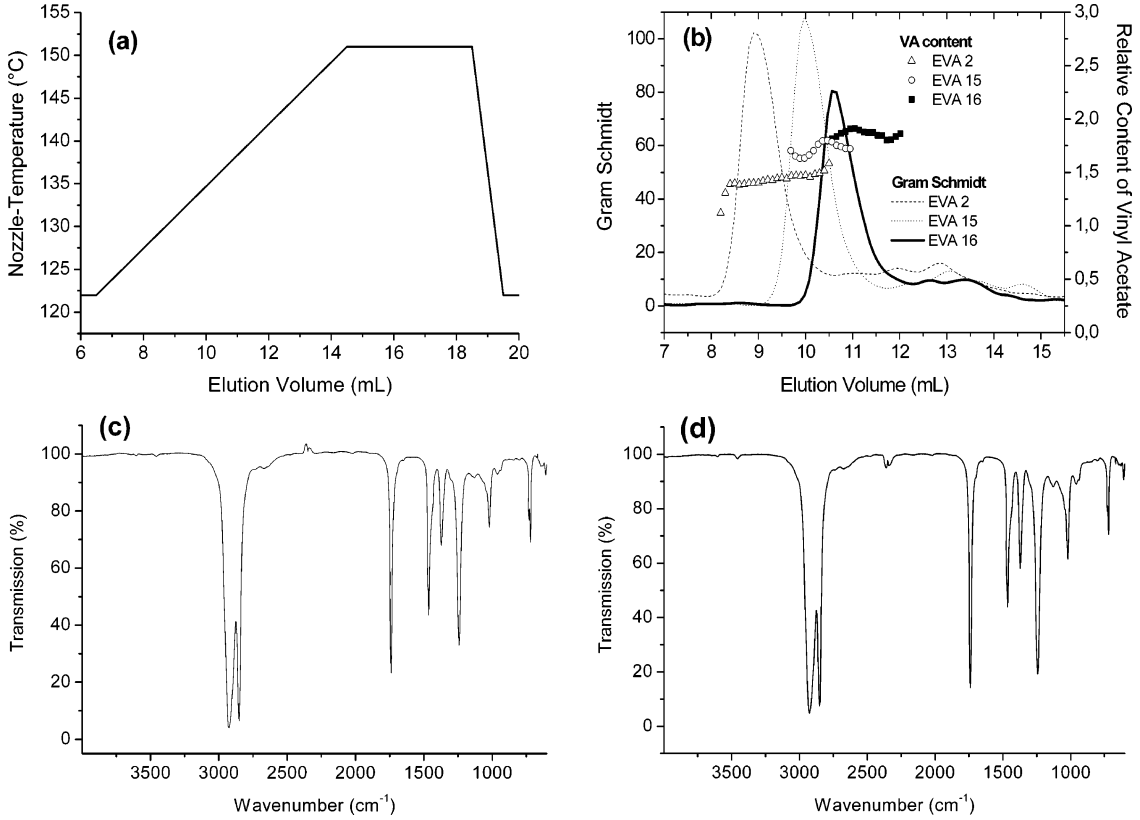

Figure 8. Temperature gradient for the nozzle of the LC-transform FTIR interface for the gradient decalin/1-decanol (a), HPLC−FTIR analysis of samples EVA 2, EVA 15, and EVA 16 using this gradient (b), and FTIR spectra of the sample EVA 2 (c) and EVA 15 (d) at the peak maximum at 8.8 and 10.0 mL.

Details of this method have been reported in the literature.[10−12] In order to obtain a homogeneous deposition of the polymer, the evaporation rate of the solvent has to be adjusted by tuning the spray temperature.[10] With decalin/cyclohexanone as mobile phase, a black residue was observed on the germanium disc under the conditions of deposition, indicating a degradation reaction. To overcome this problem, alternative mobile phases were tested. Good results were achieved with decalin/1-decanol. Because of the different boiling points of these solvents (decalin, bp 190 °C, and 1-decanol, bp 230 °C), a temperature gradient (Figure 8a) for the nozzle of the LC-transform interface had to be applied. The temperature gradient in Figure 8a has been found optimal. Using other temperatures and gradients, the nozzle has been blocked by the solid polymer or the quality of spraying of the mobile phase in the LC-transform (and subsequently the quality of the IR spectra) was poor. Figure 8b shows the Gram−Schmidt plot, which corresponds to the sample concentration, and the chemigrams for the peak area ratio of the carbonyl/CH_2 vibration band for the sample EVA 2 (12 wt % VA content) and EVA 15 and EVA 16 both having an average VA content of 18 wt % according to the producer.

An increase of the peak area ratio of the carbonyl group (1730 cm^{-1}) to the CH_2 group (1450 cm^{-1}) with the elution volume could be found for all three samples (Figure 8b). This means that the amount of VA in the copolymer increases with the elution volume; i.e., separation according to the chemical composition takes place and the analyzed samples are chemically inhomogeneous. Namely, a constant ratio between the signals of the carbonyl group and the CH_2 group would be obtained for a chemically homogeneous sample. The corresponding FTIR spectra at the peak maximum verify the chemical composition of the first peak as EVA copolymer with a lower VA content to the second one (Figure 8c,d).

Moreover, the elution volumes of copolymer samples with the same average VA content would be identical. The differences in the elution volume and in the relative content of vinyl acetate show that the sample EVA 16 has a higher amount of VA compared to EVA 15. These results demonstrate the sensitivity of the HPLC system to small differences in the chemical composition distribution of the EVA samples.

Conclusion

Three gradient HPLC methods have been developed for the analysis of EVA copolymers at a temperature of 140 °C, and critical conditions for PVAc have been established. The copolymer samples were separated with regard to the concentration of the polar comonomer in the samples. The separation in the system silica gel/TCB/cyclohexanone is based on full adsorption and the following controlled desorption of the polymers by a solvent gradient. Similar separations were also possible using decalin/cyclohexanone or decalin/1-decanol as mobile phases and silica gel as the stationary phase. The separation of the copolymers according to the chemical composition was confirmed by coupling the HPLC with the LC-transform FTIR interface. As a result, a gradient in the VA content along the elution volume was identified, revealing heterogeneity in the chemical composition of the copolymer samples.

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