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Comparison of on-line flow-cell and off-line solvent-elimination interfaces for size-exclusion chromatography and Fourier-transform infrared spectroscopy in polymer analysis

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Abstract

Two commercial liquid chromatography–Fourier-transform infrared spectroscopy interfaces (LC–FTIR), viz. a flow cell and a solvent-elimination interface have been assessed for use in size-exclusion chromatography (SEC) with respect to their chromatographic integrity (i.e. peak asymmetry, chromatographic resolution), quantitative and qualitative aspects. A polycarbonate/aliphatic polyester (PC/APE) blend and a polycarbonate-*co*-polydimethylsiloxane (PC-*co*-PDMS) copolymer were selected for the assessment. Both samples were successfully and selectively analyzed. The relatively large volume of the flow cell and the inherent deposition characteristics of the solvent-elimination interface led to a comparable decrease in the chromatographic resolution. The separation of oligomers was diminished in comparison with SEC-ultra-violet (UV). However, the peak asymmetry was not significantly affected by either interface. For both interfaces, a linear relationship was obtained for the FTIR response versus the injected concentration. The sensitivity was found to be higher for the solvent-elimination interface. For the current model compounds, the flow-cell interface detection limits are worse. However, the repeatability of flow-cell SEC–FTIR, evaluated by means of four SEC–FTIR analyses of polycarbonate, was considerably better than for solvent-elimination SEC–FTIR. This is probably due to the well-defined optical path length of the sample in the flow cell. By spectral subtraction, it was very well possible to obtain qualitative (functional group) information for compound identification also with flow-cell SEC–FTIR.

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1. Introduction

Characterization of chromatographic peaks in polymer analysis is nowadays performed mainly by mass

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spectrometric (MS) techniques [1–5]. MS is very useful in obtaining information on polymer molecular mass and end-group distributions. MS has great strengths, including high sensitivity, fast scan speed and the uniqueness of mass spectra, but also significant weaknesses. Quantitative (distribution) data are still hard to obtain due to mass-discrimination. Chemical composition information for copolymers is obscured by the extreme complexity of the spectra and MS cannot differentiate between structural isomers. Especially on-line liquid chromatography (LC)–MS (with electrospray ionization, ESI, or atmospheric pressure chemical ionization, APCI, interfaces) is limited to rather polar and relatively small polymers. Finally, it is difficult to obtain functional-group contribution with MS.

Fourier-transform infrared spectroscopy (FTIR) is therefore still an important complementary technique for coupling with size-exclusion chromatography (SEC). Using SEC–FTIR, variations in structural detail between molecules can be characterized as a function of the molecular mass, which is related to the molecular mass [6,7]. In this respect, FTIR is much superior to the conventional SEC detectors, differential refractive index (dRI), ultra-violet (UV), and evaporative light scattering (ELS) detection, neither of which provides significant information on molecular structure.

In interfacing LC and FTIR spectroscopy, two main approaches can be distinguished. In the first (on-line) approach, the effluent of the liquid chromatograph is passed through a flow cell and IR spectra are acquired on-the-fly. The second approach is based on solvent elimination, with the eluent being removed from the analyte prior to off-line detection. Typical character-

istics of these types of interfaces are summarized in Table 1 and will be discussed below.

On-line couplings via a flow-cell are based either on transmission, attenuated total reflection (ATR) [8,9], or reflection measurements [10]. In this paper, we will focus on the transmission flow-cell interfaces. In this, the spectral window (i.e. detection wavenumber range) is determined by the infrared characteristics of the cell window material and by the absorbance of the solvent used. Cell windows must be chemically resistant to the eluent used in the chromatographic method, withstand high pressures and offer sufficient transmittance to maintain a reasonable IR-energy throughput. Preferably, the eluents used in flow-cell LC–FTIR do not exhibit an excessive absorbance, which may obscure analyte absorption bands. However, it is almost impossible to find IR-inactive solvents. Highly chlorinated (or fluorinated) solvents with strong symmetry, such as carbon tetrachloride are most attractive due to the relatively small number of absorption bands and the broad transparent windows. However, these solvents are very unattractive from a health perspective. This leads to severe limitations, with all good LC eluents being strong IR absorbers. In supercritical-fluid chromatography, carbon dioxide can be used as eluent, but the applicability of this technique is limited. Obtaining qualitative, molecular information is limited by the transmission window provided by the mobile phase. This can partly be overcome by post-column extraction of the effluent with less strong IR absorbers [11], by the use of ATR flow cells [8,9], or by the use of (expensive) deuterated solvents, in which eluent absorption bands are shifted to lower wavenumbers, so that analyte absorption bands may be revealed [12]. The eluent absorbance can be reduced by reducing the

Table 1
Typical characteristics of flow-cell and solvent-elimination interfaces for HPLC

Condition	Flow cell	Solvent elimination
Gradient separations	No	Yes
Qualitative information	Limited, depends on eluent	Yes
Quantitative information	Excellent	Limited
Sensitivity	Moderate	Excellent
LOD	Low, eluent dependent	High
Spectral signal-to-noise ratio	Moderate, spectra collection on-the-fly	High, extended post-run scanning possible
Ease of operation	User friendly	Time-consuming optimization
Application area	SEC	SEC (gradient) HPLC

For a detailed explanation, see text and experimental description.

optical path length. Good signal-to-noise ratios (SNR) can be obtained when the eluent absorbance is approximately 0.4. Consequently, there is no universal path length for all solvents used in LC [13]. Based on this criterion, the optimum cell thickness can be calculated for every single LC eluent, as shown by Vidrine [7]. For example, typical optical path lengths are 0.01–2 mm for organic solvents. This strongly limits the sensitivity of this technique, as the solvent absorption becomes the limiting factor. Usually, a path length is chosen such that functional groups of interest can be detected within a transparent region of the eluent and only a few bands are opaque.

Commonly used IR flow-cell volumes are much smaller than required to minimize band broadening. The small detector cell volumes render flow-cell FTIR compatible with microbore-LC [14,15], where the chromatographic peak volumes are several orders of a magnitude smaller than in conventional LC. However, the sample capacity of LC columns decreases in proportion to their cross-sectional area. When combining interactive LC with IR, gradient elution cannot be applied, as accurate background subtraction with changing eluent composition is virtually impossible.

Despite all the above arguments, the use of flow-cell LC–FTIR is not completely impractical. The low cost, instrumental simplicity, ease of operation, low maintenance, and the possible use of non-volatile buffers stimulate the use of flow cells. Furthermore, detection in real-time makes it a potential detector for on-line reaction monitoring and rather fast IR detection. The analyte can be studied without any orientation or crystallization effects [16,17], oxidative degradation [6], or evaporation, which might occur upon collection and storage in solvent-elimination interfaces. A (limited) number of specific applications exist in which a flow cell can be extremely valuable. Specifically, this is the case when the separation is not strongly affected by the choice of eluent, as in SEC with organic eluents. Therefore, flow-cell SEC–FTIR can be used in rapid, selective and quantitative analysis to obtain structural information on major constituents of mixtures across the molecular mass distribution (MMD) [18].

The second approach utilizes a heated nebulizer, often aided with nebulizer gas, to evaporate the effluent and to deposit analytes on an infrared-transparent substrate, such as ZnSe, Ge, or CaF₂. FTIR spectra are acquired on-the-fly or (shortly) after deposi-

tion in transmission or reflection–absorption (R–A) mode. Major advantages of solvent-elimination interfaces are (i) the absence of interfering eluent absorption bands, (ii) increased off-line scanning time for signal-to-noise-ratio improvement and (iii) that spectra can be searched against commercially available KBr-disk libraries. This makes solvent-elimination interfaces more favorable than flow-cell interfaces if qualitative information has to be obtained. Nonetheless, their use as quantitative detectors is limited [19]. To gain maximum sensitivity, as needed for example in environmental analysis, the use of an FTIR microscope is a prerequisite [20]. By varying the nebulizer temperature during the chromatographic run mobile-phase gradients can be used, while maintaining a constant deposit quality. However, optimization of the deposition is time consuming and the deposit quality depends on the nature of the sample (viscosity, tendency to crystallize, molecular mass, affinity to the eluent, etc.) and on the evaporation capacity of the interface used.

In this paper, a comparison is made between a recently introduced flow cell and a solvent-elimination interface. Both systems are commercially available for coupling of SEC with infrared spectroscopy. By using two model polymer systems consisting of a polycarbonate/aliphatic polyester (PC/APE) blend and a polycarbonate-*co*-polydimethylsiloxane (PC-*co*-PDMS) copolymer, a comparison is made between the two interfaces on the basis of the peak shape integrity and the qualitative and quantitative performance (sensitivity, linearity, detection limits) in SEC–FTIR. The merits and disadvantages of both techniques in polymer analysis are discussed.

2. Experimental

2.1. Chemicals

HPLC-grade dichloromethane (DCM) was obtained from J.T. Baker (Deventer, The Netherlands). Polystyrene standards were purchased from Polymer Laboratories (Church Stretton, Shropshire, UK). PC ($M_w = 45$ kg/mol), APE ($M_w = 95$ kg/mol) and PC-*co*-PDMS (M_w , unknown) were obtained from General Electric Plastics (Bergen op Zoom, The Netherlands). Polymer-stock solutions were prepared by weighing and dissolution in DCM. Blends, i.e.

solutions of polymer mixtures consisting of 50:50% (w/w) PC/APE, were prepared by combining the stock solutions. Standard solutions of the copolymers and blends were prepared by dilution in DCM to final concentrations in the 0.2–4 mg/ml range for each standard. All standard solutions were stored in the dark at 6 °C.

2.2. Chromatography

In the flow-cell set-up, an Agilent (Waldbronn, Germany) chromatographic system model 1100, with a vacuum degasser, and thermostatted column compartment was used with an on-line photo-diode array (PDA) UV detector (Agilent 1100 series DAD) set at 264 nm. A computer operating Agilent Chemstation software (version 09.01) was used for instrument control.

A Waters 2695 Separations Module (Milford, MA, USA), equipped with a vacuum degasser and a thermostatted column compartment, was used in conjunction with a solvent-elimination interface. On-line UV-detection was performed with a Waters PDA model 996 at 264 nm. A computer using Waters Millennium 32 (version 3.2) software controlled the system and was used to monitor the detector signals.

All separations were carried out on two 300 mm × 7.6 mm i.d. PL gel columns (porosity: 10³ and 10⁵ Å; particle diameter: 5 µm; Polymer Laboratories) at 21 °C and DCM as eluent. A rather high flow rate of 1 ml/min was used as DCM is readily evaporated. The injected sample volume was 50 µl.

2.3. Interfacing liquid chromatography and FTIR spectroscopy

The flow cell (Polymer Laboratories) consisted of two 4 mm thick KBr windows with a clear aperture of approximately 8 mm and a 1 mm diamond-shaped stainless steel spacer (incorporated in the cell body), resulting in a cell volume of 70 µl.

A solvent-elimination interface LC-Transform Model 500 (Lab Connections, Northborough, MA, USA), based on the principle described by Gagel and Biemann [21–23], was used to evaporate the eluent. The eluting analytes were collected on a 60 mm diameter rear-surface-aluminized germanium (Ge–Al) substrate, continuously moved at a speed of 6 mm/min. The interface parameters were set to obtain an opti-

imum solute deposit and included: 135 °C nebulizer temperature, 7 mm nebulizer height and 172 kPa nebulizer gas (nitrogen) pressure. Labcon 1.0 software (Lab Connections) operated the interface. After sample deposition, the collection substrate was manually transferred to an automated optical IR accessory comprising two three-times-focussing mirrors and a stepper motor for substrate rotation. The accessory was controlled by LCT 1.6.1 software (Lab Connections), and R–A spectra were acquired by stepwise rotation of the substrate. The observed shift in retention time at the peak maximum for all interfaces in Figs. 1, 2, 4, 6 and 7 is due to minor differences in the internal volumes, which were difficult to correct for.

2.4. Spectroscopy

A Perkin-Elmer (Norwalk, CT, USA) spectrometer model Spectrum GX, equipped with a medium-band mercury/cadmium/telluride (MCT) detector was used for the acquisition of FTIR spectra. Each spectrum consisted of 8 accumulated scans and the resolution was set at 8 cm⁻¹. In the flow-cell experiments, a spectrum was acquired every 6 s. The sample and detector compartments were continuously purged with dried nitrogen gas to minimize interference from water vapor and carbon dioxide present in the atmosphere. Data acquisition was performed using Perkin-Elmer Spectrum 3.0 software. Background spectra were obtained from blank eluent before each flow-cell experiment or at unused positions on the substrate (solvent elimination). Selected IR absorption bands for detection of APE and PC were the carbonyl-stretching vibrations at 1724 and 1774 cm⁻¹, respectively. For PDMS, the Si–O stretching vibrations (1054 cm⁻¹) were selected. Measurements of the peak areas of baseline-corrected absorption bands as a function of retention volume were performed by Perkin-Elmer Timebase 1.1.

3. Results and discussion

3.1. Band broadening

For the assessment of the flow-cell and solvent-elimination interfaces, their effects on the peak asymmetry factor and on the chromatographic resolution were studied as measures for peak shape integrity.

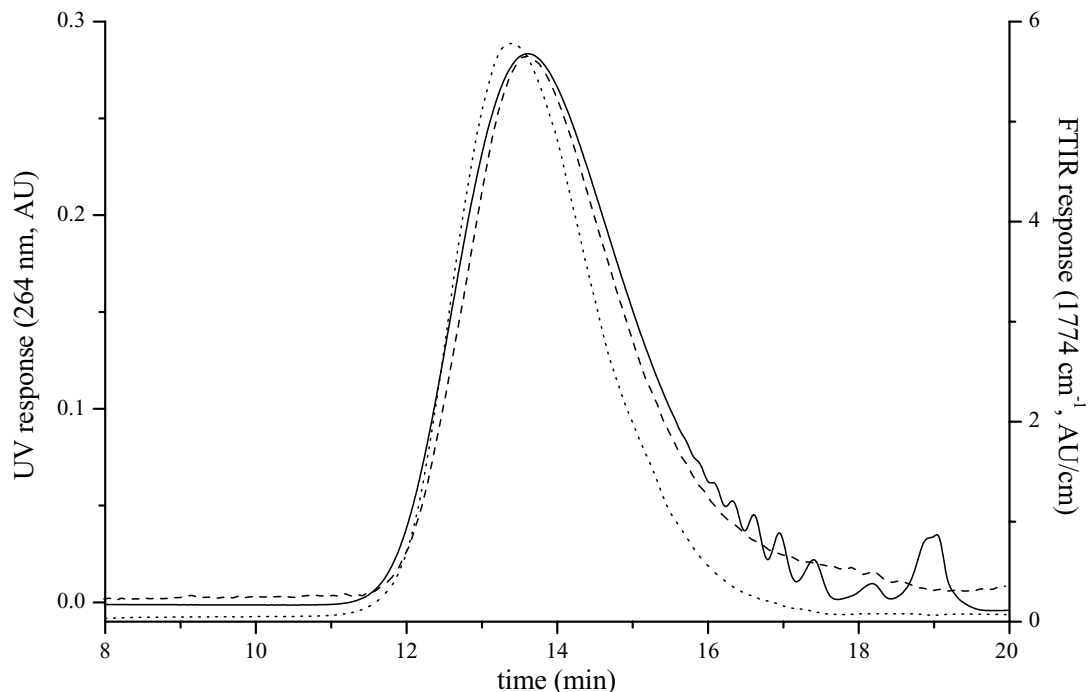


Fig. 1. Overlay of SEC-UV chromatogram (continuous line) and SEC-FTIR functional-group chromatograms for flow-cell (dashed line) and solvent-elimination (dotted line) interfaces obtained for PC ($c = 4$ mg/ml). UV detection was performed at 264 nm and functional-group chromatograms were constructed from the integrated absorption at 1774 cm^{-1} . (For comparison reasons, the flow-cell FTIR response has been multiplied by a factor 5.)

The peak asymmetry (A_s), the distance from the center to the tail of the peak divided by the distance from the center to the front of the peak at 10% of the peak height, was determined from the peak obtained for the analysis of a 4 mg/ml PC solution using a UV detector or either interface directly connected to the separation columns. Under these circumstances, the additional contribution of band broadening introduced by the flow cell and solvent elimination interface can be determined under the specific analysis conditions. At low sample loads, the peak-start and peak-end can merge into the baseline below the detection limit, prohibiting accurate determination of peak tailing. Therefore, a high sample load was chosen for these experiments.

The UV chromatogram shows a typical separation of PC with an A_s value of 1.8, including separation of the oligomers in the low molecular mass range (Fig. 1). The peak asymmetry is not affected by the flow cell, as indicated by the calculated A_s value ($A_s =$

1.8). However, the chromatographic resolution for the oligomers is partly lost. From the UV chromatogram, it can be calculated that the peak volume ($\sigma_{V(\text{col})}$) for an oligomeric peak (eluting volume, $V_e = 16.9$ ml) is $272\ \mu\text{l}$ ($\sigma_{\text{peak}} = 68\ \mu\text{l}$). The extra-column band broadening introduced by the detector volume is thought to be insignificant when the flow-cell volume is less than about 10% of the peak volume [24]. In the present case, the flow-cell volume of $70\ \mu\text{l}$ represents 26% of the oligomer band width, thus affecting the typical oligomer separation pattern observed in the UV chromatogram. This discussion suggests the use of a smaller detector cell volume when oligomers are to be analyzed. The polymer peak ($V_e = 13.6$ ml, $\sigma_{\text{peak}} = 1.08$ ml) is not visibly affected by the large detector volume as $\sigma_{V(\text{col})} = 4.32$ ml. In principle, flow-cell SEC-FTIR has a much higher potential as a quantitative detector, because all of the sample is detected, providing accurate molecular mass data for polymers across a broad molecular mass range.

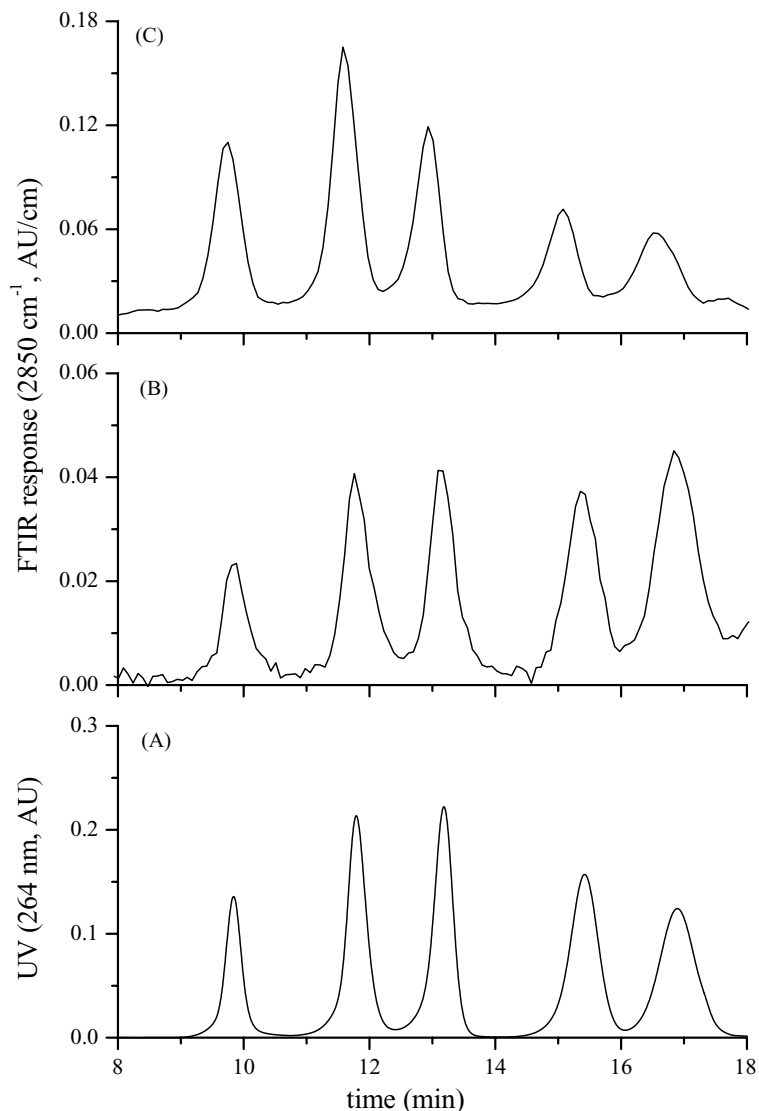


Fig. 2. (A) SEC-UV chromatogram and SEC-FTIR functional-group chromatograms for (B) flow-cell and (C) solvent-elimination interfaces obtained for a PS standard mixture ($c = 1 \text{ mg/ml}$). UV detection was performed at 264 nm and functional-group chromatograms were constructed from the integrated absorption at 2850 cm^{-1} . Peak molecular masses: 488.4, 76.6, 28.5, 5.0 and 1.27 kg/mol.

The peak asymmetry value obtained with the solvent-elimination SEC-FTIR ($A_s = 1.7$) was slightly smaller than the A_s calculated from the UV detector. As seen in Fig. 1, the tail of the distribution appears to be suppressed. As noted in Section 1, the success of deposition is affected by the nature of the polymer. Calibration with narrow PS standards shows that the molecular mass of the oligomers

is in the order of 1100 g/mol. These low molecular mass components can be pushed towards the edges of the deposit outside the IR scanning area during deposition. Despite careful optimization of the deposition-conditions, they may therefore remain undetectable, causing a suppressed peak tail. Consequently, the calculation of accurate MMD and statistical moments from solvent-elimination data for

certain low molecular mass polymers (M_n , M_w , M_z) is impeded. This makes the use of solvent elimination less practical for quantitative analysis and for the determination of M_n , M_w and M_z .

The chromatographic resolution was compared for a four-component polystyrene-standard mixture analyzed using UV detection. In a previous paper [19], we have shown that the chromatographic resolution in solvent-elimination interfaces depends mainly on the substrate moving speed. In addition, the tendency of the polymer to flow on the substrate upon evaporation of the eluent—influenced by the gas flow—affects the chromatographic resolution. This factor is determined by the physical properties of the polymer (i.e. crystallinity, viscosity) on the substrate. Consequently, there are no single conditions in terms of interface parameters or eluent flow rate that yield a consistent chromatographic resolution upon deposition. Time-consuming optimization procedures are therefore required for different samples or for different chromatographic conditions. To allow a fair comparison between the two SEC–FTIR interfaces, the substrate moving speed was optimized for the SEC-column set and the eluent flow rate.

For both SEC–FTIR interfaces, the chromatographic resolution decreases equally (Fig. 2) compared to the UV chromatograms as a result of an increased peak width at half-height. As discussed previously, band broadening arising from an excessive detector cell volume may reduce the chromatographic resolution. However, if flow-cell FTIR is to be used in chromatographic systems, the detector volume is a compromise between sensitivity and the chromatographic resolution. Increasing the detector volume while keeping the aperture constant will reduce the energy throughput, give rise to higher background absorption (if opacity is not obscuring absorption bands of interest) and the acquired spectra will cover a larger elution volume reducing the acquired spectral information and chromatographic resolution. Conversely, if beam-condensing optics are used to obtain a smaller beam diameter, the detector cell volume can be reduced without losing sensitivity [14]. However, oblique rays caused by the optics can be partially lost by window reflectance. The decreased SNR observed in the flow-cell SEC-IR chromatogram can be ascribed to the high eluent absorption in the C–H stretch region (cf. Fig. 3).

Despite optimization of the substrate moving speed in solvent-elimination SEC–FTIR, band broadening is introduced during the deposition process caused by the nebulizer spray-shape characteristics [19,25]. The resolution was most clearly affected by this process. This is in contrast with the peak asymmetry data obtained from a PC sample. Probably, PC is more easily spread out on the deposition substrate, thereby producing broader traces and pushing deposited analyte away from the scanning area. This leaves a clean substrate behind, resulting in an apparently narrower peak. In contrast, PS remains at the position where it is deposited. Even under optimized interface conditions the nature of the analyte influences the deposition efficiency and this demonstrates the inherent complexity of LC-solvent-elimination FTIR.

3.2. Repeatability and linearity

The IR transparent regions of DCM are found in the region 2000–1600 cm^{-1} prohibiting the use of (aromatic) C–H stretching vibrations for detection of the model polymers (Fig. 3). Therefore, the absorption band positions arising from carbonyl-stretching vibrations for PC and APE, separated by 50 cm^{-1} , were selected for detection. A challenging detection problem was found in the analysis of PDMS, where the Si–O vibration (1054 cm^{-1}) was in a region where DCM has a strong sloping background, which could introduce errors, raise detection limits and result in an inaccurate calibration.

The repeatability of the response at the peak maximum, expressed in terms of the relative standard deviation (R.S.D.), was determined for the blend and for the copolymer from four analyses at the 1 mg/ml level at all the detection wavenumbers previously indicated. The repeatability was significantly better when using a flow cell but was still acceptable for the solvent-elimination interface (see Table 2). This can be assigned to the well-defined optical path length of the flow cell. Solvent elimination and subsequent sample deposition is subject to irregularities in the deposit, leading to a larger variance in the observed absorption band intensity for repeated depositions and affects the repeatability as is obvious from the error bars in Fig. 4.

The linearity of the response for the blend and copolymer was studied by injecting concentrations

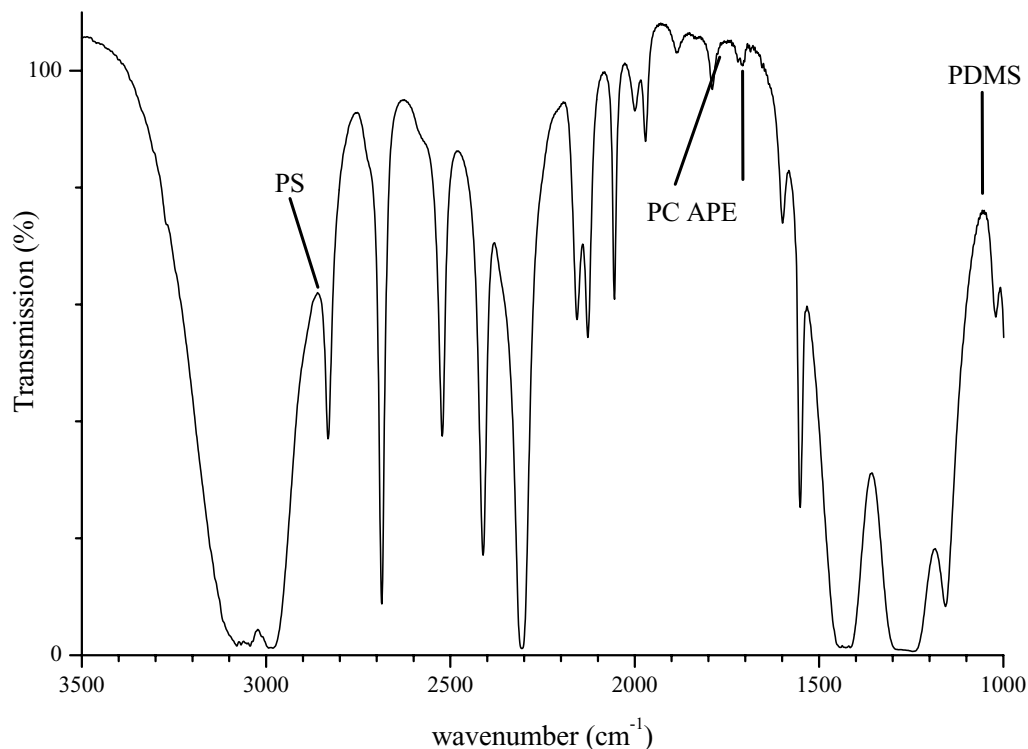


Fig. 3. Transmission spectrum for DCM obtained from blank eluent in a 1 mm path length KBr-flow cell. Detection regions for PC, APE, PDMS and PS are indicated in figure.

ranging from 0.2 to 4 mg/ml and plotting the FTIR response at the eluting peak maximum versus the concentration. For all selected detection wavenumbers, linear calibration curves were obtained ($r > 0.994$). Typical functional-group chromatograms and calibra-

tion curves for the PC/APE blend are presented in Fig. 4 and the results for all analyses are summarized in Table 2. For the R–A spectra obtained from deposits on Ge–Al, a shift in the carbonyl absorption band maximum of 5 cm^{-1} towards higher wavenumbers was

Table 2

Statistical parameters, limit of detection (SNR = 3) and repeatability ($n = 4$; calculated as R.S.D.) of the FTIR response for the SEC–FTIR analysis of a PC/APE blend and of PC-co-PDMS using a solvent-elimination interface (SE) and a flow cell (FC)

	PC/APE blend				PC-co-PDMS			
	PC (1774 cm^{-1})		APE (1724 cm^{-1})		PC (1774 cm^{-1})		PDMS (1054 cm^{-1})	
	SE	FC	SE	FC	SE	FC	SE	FC
a	2.08	0.0741	2.84	0.105	1.12	0.0570	0.0178	0.00758
b	−0.37	−0.0013	−0.44	0.0048	−0.074	5.8×10^{-6}	−0.0035	0.00033
r	0.997	1.000	0.994	1.000	0.999	1.000	0.996	1.000
LOD (mg/ml) ^a	0.0070	0.051	0.0070	0.034	0.028	0.056	0.14	0.37
Repeatability (%)	4.2	0.48	3.7	0.63	2.9	0.45	4.4	0.73

Model: $Y = aX + b$; concentration (mg/ml) vs. FTIR response (AU/cm); r , correlation coefficient.

^a The S and N were determined from the lowest calibration standard and the LOD was the extrapolated concentration at which the SNR was 3.

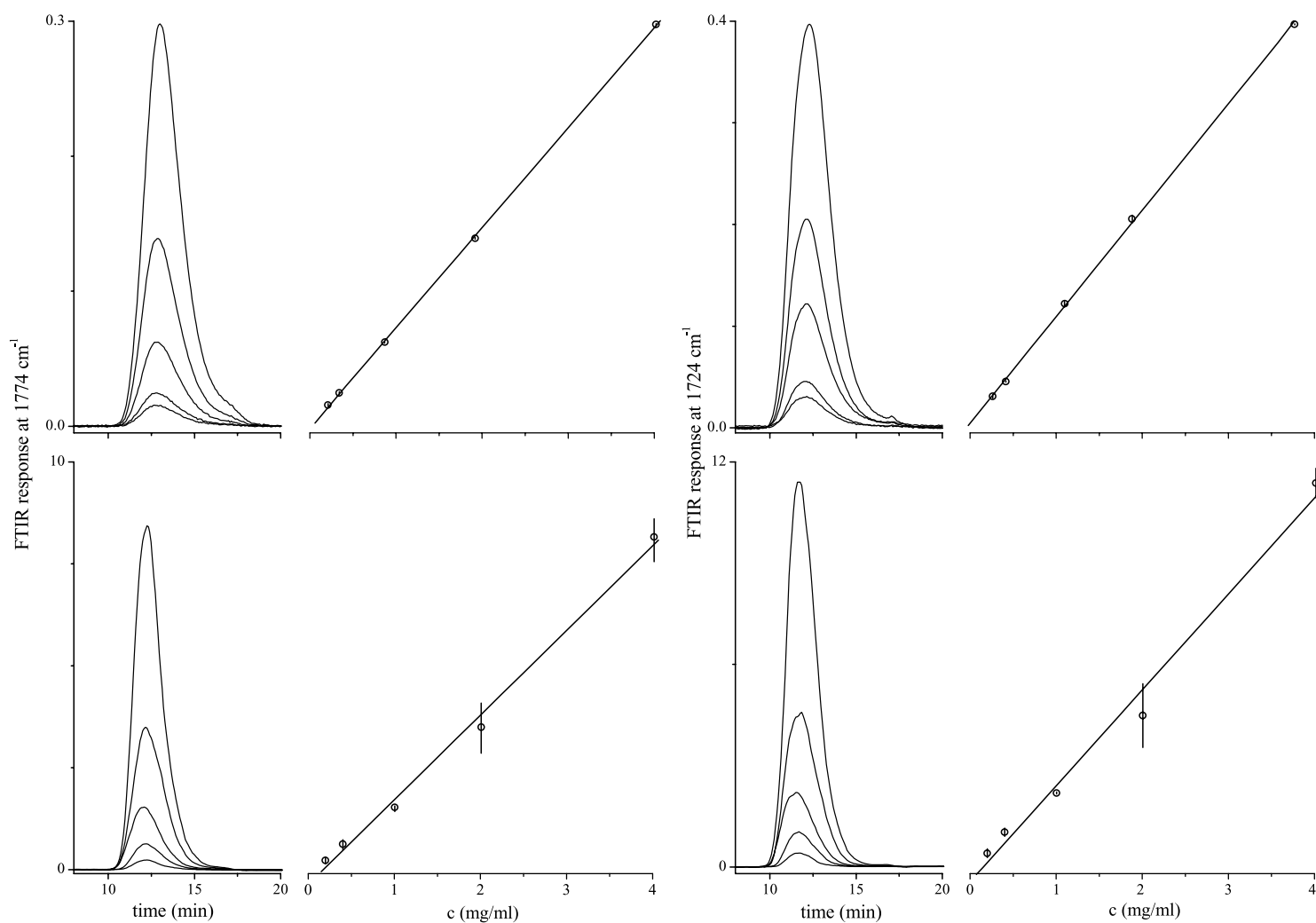


Fig. 4. SEC-FTIR functional-group chromatograms and calibration curves for PC (left) and APE (right) in a 50:50% (w/w) PC/APE blend obtained from flow-cell SEC-FTIR (top) and solvent-elimination SEC-FTIR (bottom) including error bars ($n = 2$). For experimental details, see text. Linear regression details are presented in Table 2.

observed, caused by the absence of solute-solvent interactions in solvent-elimination SEC-FTIR. The response at the absorption band maximum was used for detection in solvent-elimination SEC-FTIR.

Usually, in IR the minimum identifiable quantity (MIQ) is reported. This is the minimum concentration for which at least six absorption bands are discernable [26]. However, several absorption bands in spectra obtained using a flow cell are obscured by the eluent ab-

sorption, prohibiting full qualitative information. For this reason, we only focussed on the specific absorption bands and report the limit of detection (LOD) here (expressed as injected concentration). For both interfaces the LOD based on a signal-to-noise ratio of three was satisfactory.

The sensitivity (slope of the calibration curve) obtained with the solvent-elimination interface was found to be higher than the sensitivity for the flow cell and the LOD was better for solvent-elimination

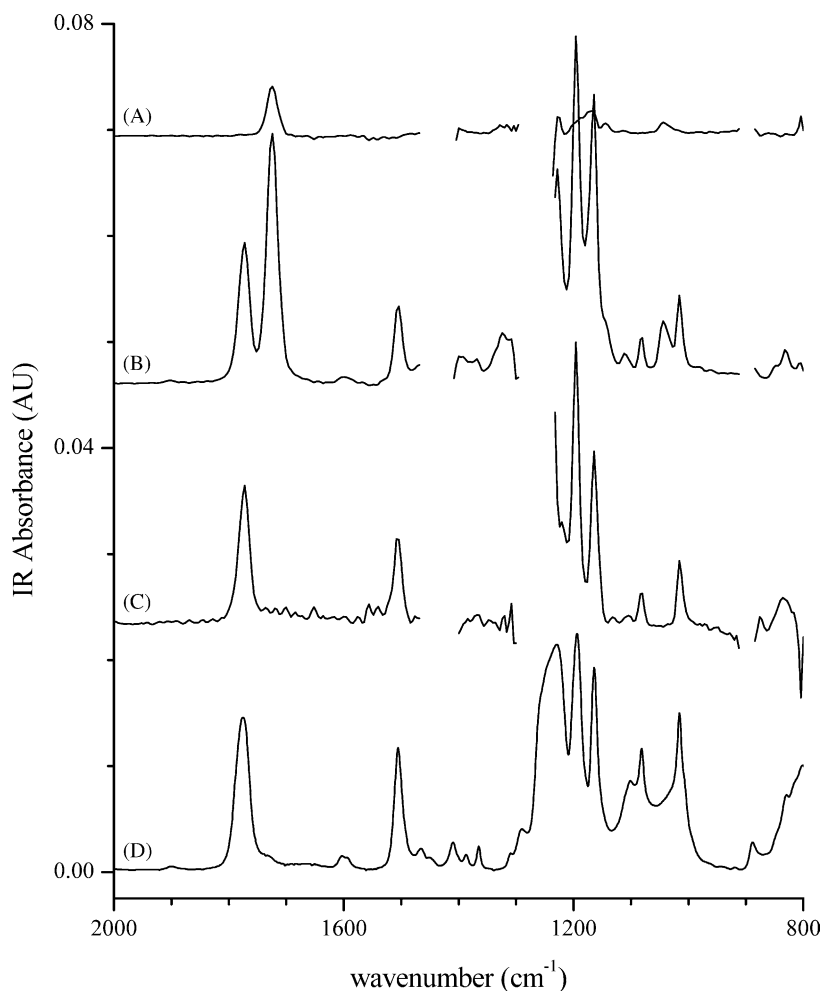


Fig. 5. Spectra subtraction: (A) spectrum obtained from the high molecular mass region of Fig. 4 at $t_r = 10.2$ min; (B) spectrum at the peak maximum of the APE functional-group chromatogram from Fig. 4 at $t_r = 12.3$ min; (C) difference spectrum (middle minus top) indicating the presence of PC; (D) KBr reference PC spectrum. The regions of 2000 cm^{-1} and higher do not contain any information and are omitted and opaque regions are blanked.

SEC–FTIR then for flow-cell SEC–FTIR. An improvement of the flow-cell LOD can be expected when a larger optical path length (up to approx. 3 mm) is used.

3.3. Qualitative analysis

Isocratic on-line SEC–FTIR using the flow-cell detector produces IR spectra that are well suited for

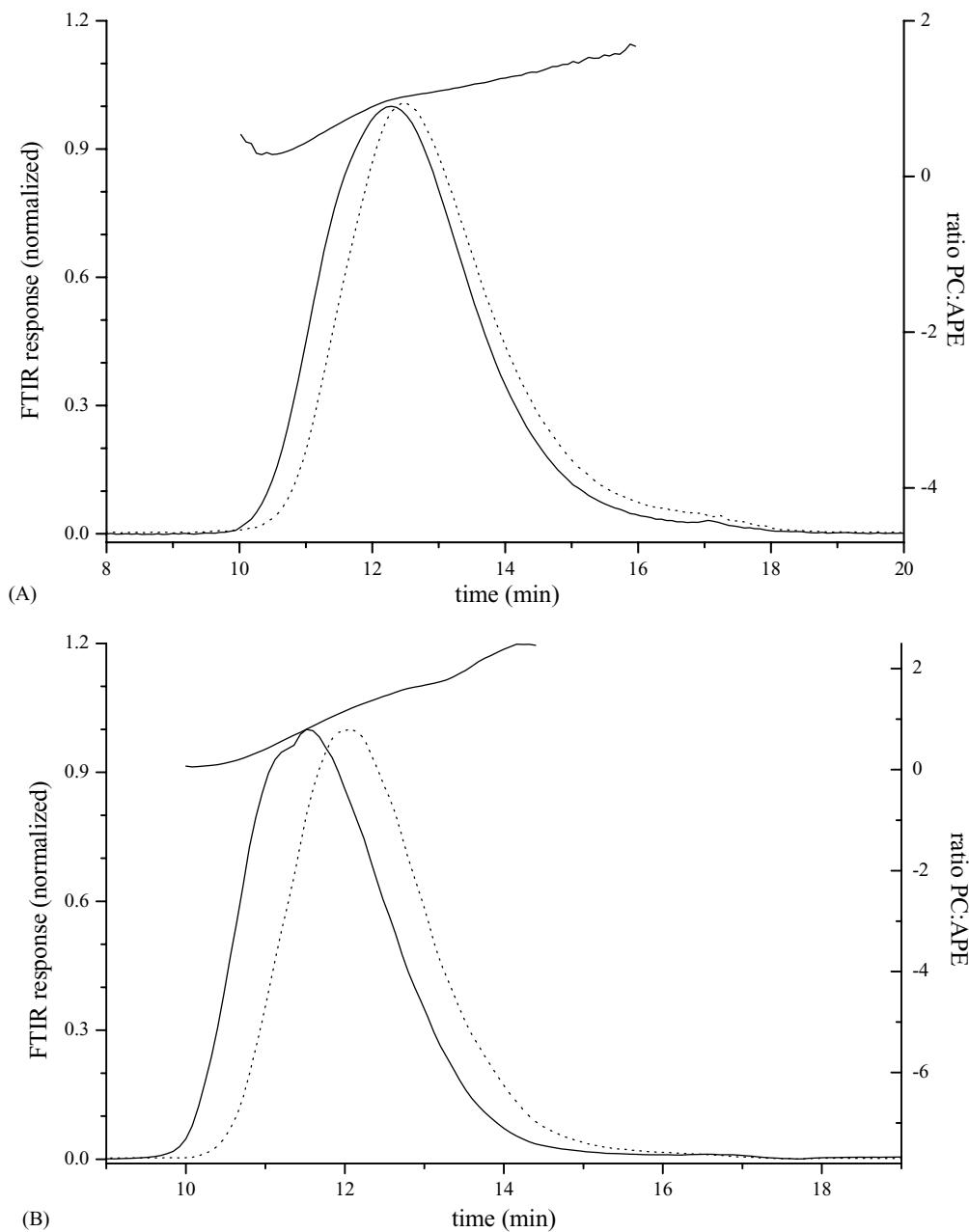


Fig. 6. SEC separation of a PC/APE blend (ca. 1.0 mg/ml). Functional-group chromatograms obtained from (A) flow-cell and (B) solvent-elimination SEC–FTIR. Functional-group chromatograms were constructed from the integrated absorption at 1774 cm^{-1} (PC, dashed line) and 1724 cm^{-1} (APE, continuous line). The absorption band ratio (PC:APE) is indicated above the chromatograms.

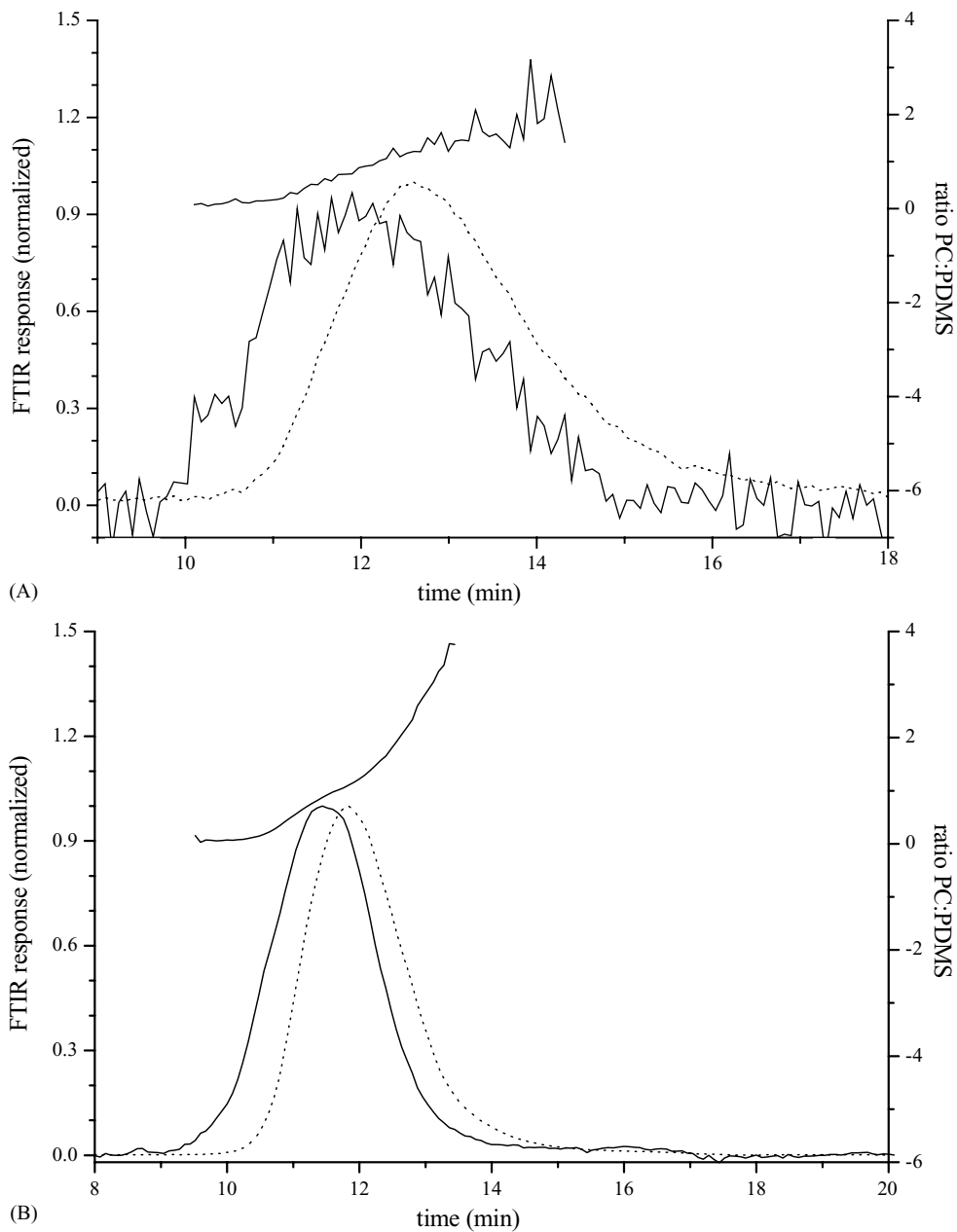


Fig. 7. SEC separation of a PC-co-PDMS copolymer (ca. 1.0 mg/ml). Normalized functional-group chromatograms constructed from the integrated absorption at 1054 cm^{-1} (PDMS, continuous line) and 1774 cm^{-1} (PC, dotted line) obtained from (A) flow-cell and (B) solvent-elimination SEC-FTIR. The absorption band ratio (PC:PDMS) is indicated above the chromatograms.

absorption subtraction, because analytes are present in dilute solutions in a constant matrix. Generally, this eliminates IR band shifts, which may arise from differing matrix effects, and from spectrometric data in FTIR being measured on an extremely precise wavenumber scale [6]. However, one must always be aware of spikes in the region where the eluent is completely opaque, which can lead to a false-positive detection of analyte absorption in the corresponding spectral region. By subtracting the IR spectrum extracted from the high molecular mass region ($t_r = 10.2$ min) from the spectrum extracted at the peak maximum ($t_r = 12.3$ min) of the APE functional-group chromatogram (Fig. 4), one can quantitatively analyze the differences on the PC/APE blend. Fig. 5 shows the result of the subtraction revealing carbonyl (1774 cm^{-1}), aromatic C–H (1505 cm^{-1}) and C–O ($1200, 1180\text{ cm}^{-1}$) absorption bands for PC. It is obvious that spectra acquired from solvent elimination SEC–FTIR contain full spectral information for interpretation and for library searches (spectra not shown).

3.4. Compositional analysis

IR is extremely useful in obtaining chemical composition information. Hence, SEC–FTIR can be of great value in the selective quantification of (non-UV active) blended polymers or copolymers and this will be demonstrated by the compositional analysis of a PC/APE blend (50:50% (w/w)) and a PC-co-PDMS (80:20% (w/w)). Typical functional-group chromatograms for a 1.0 mg/ml blend and for 1.0 mg/ml copolymer analysis are presented in Figs. 6 and 7.

The selective detection of PC and APE in the blend indicates that APE has a higher molecular mass compared to PC (Fig. 6) and the PC:APE ratio of these functional-group chromatograms shows an increase towards the low molecular mass. However, a change in the slope of the ratio is observed in flow-cell SEC–FTIR when passing the APE peak maximum, indicating a smaller MMD for PC than for APE. Furthermore, in the low molecular mass tail the oligomers show up as fluctuations in the PC:APE ratio (Fig. 6A). As for reasons discussed previously, both phenomena are not observed when using the commercial solvent-elimination interface (Fig. 6B).

Functional-group chromatograms for PC and PDMS and their intensity ratios PC:PDMS reveal a compositional drift (Fig. 7). The high noise level in the Si–O functional-group chromatogram is probably caused by the decreased energy throughput in the low wavenumber region, where solvent absorption is strong. Inspection of the functional-group chromatograms from both interfaces shows a shift in co-monomer distributions for PC and PDMS where PDMS is present largely in the high molecular mass region, while the PC component is present in the low molecular mass region. It must be noted that an average chemical composition is obtained as the separation is based on hydrodynamic volume.

For both interfaces, an offset between the peak maxima in the time-direction from the functional-group chromatograms can be observed as depicted in Figs. 6 and 7. Unfortunately, this offset is not consistent for the blend or copolymer on a particular interface. For example, the offset between the peak maximum of PC and APE functional-group chromatograms in the solvent-elimination experiments is larger than the offset found for the corresponding functional-group chromatograms in the flow cell experiments (Fig. 6). Possibly, this can be ascribed to phase segregation of the blend during the deposition process. Especially in the case of solvent-elimination interfaces, these shifts cannot be corrected for. Although the trend in composition can be easily observed in the data from both interfaces, the strong suppression of oligomer signals and the possible occurrence of phase segregation jeopardizes the compositional analysis using a solvent-elimination interface (Figs. 6 and 7).

4. Conclusions

Commercial flow cells offer a suitable (cheap) alternative to expensive commercial solvent-elimination interfaces for use in SEC–FTIR of synthetic polymers with respect to peak shape integrity, chromatographic resolution and quantitation. The chemical compositions of a polycarbonate/aliphatic polyester blend and a polycarbonate-co-polydimethylsiloxane copolymer were successfully revealed and the performance of the two types of interfaces was comparable. The conditions for the solvent-elimination interface were

optimized based on considerable experience with this device. Little time was spent on optimizing the flow-cell interface. Careful and proper selection of the eluent, to make the most use of the spectral windows, can extend the application area. To maintain the chromatographic resolution for peaks eluting as narrow peaks, such as oligomers or other small molecules, the flow-cell volume should be reduced. In general, the use of larger columns (e.g. 7.6 mm or 7.8 mm internal diameter) is recommended with the current flow-cell design. Additionally, flow-cell FTIR interfaces may provide reliable chemical composition data across the molecular mass distribution in a single analysis, thanks to the high accuracy and reasonable detection limits. Flow-cell SEC–FTIR can provide structural information to some extent. However, complete spectral information without solvent interference is still best obtained with solvent-elimination SEC–FTIR.

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