Fourier transform infrared spectroscopy with a sample deposition interface as a quantitative detector in size-exclusion chromatography

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Abstract

The use of a state-of-the-art commercial solvent-elimination interface for liquid chromatography–infrared spectroscopy is discussed from the perspective of quantitative analysis. The effect of eluent flow-rate is investigated with respect to the homogeneity of the deposit and the trace width along the deposition trace. Low flow-rates (50 μl/min or less) turn out to be favorable for obtaining a good trace and a high sensitivity. The trace width decreased from 2.20 to 1.13 mm when the flow-rate was reduced from 500 to 25 μl/min. Preservation of chromatographic detail during deposition was evaluated at different substrate moving speeds. The additional (extra-column) band broadening that is inherent to nebulizer-deposition interfaces, causes a loss in resolution in size-exclusion chromatography (SEC)–Fourier transform infrared (FTIR) spectroscopy in comparison with SEC–UV. The repeatability of the deposition is evaluated by SEC–FTIR analyses of polystyrene standards (peak molar-masses: 1250–2 950 000 g/mol) and the RSD is found to range from 3.2 to 5.8% in response and from 0.21 to 0.47% in retention time. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Size-exclusion chromatography (SEC) is often used in the characterization of polymers and co-polymers. Because SEC only separates according to hydrodynamic volume, the effects of molar-mass and chemical composition cannot be distinguished. Thus, for non-homogeneous polymers, neither the molar-mass distribution (MMD), nor the chemical-composition distribution (CCD) or the functionality-type (FTD) distribution can be determined from SEC

alone. The detection methods most commonly used in SEC, such as differential refractive index (dRI) detection and evaporative light scattering detection (ELSD), are non-specific. Though UV–Vis detectors are more selective, many polymers do not show any UV activity at all, so this type of detector cannot be generally used for polymer-composition analysis.

Fourier transform infrared (FTIR) spectroscopy is a very powerful tool for analyte identification and obtaining detailed chemical (functional-group) information. In many cases it is therefore preferred to the previously discussed detectors. Thus, the most widely accepted method to obtain better insight in the chemical (micro-)structure of synthetic polymers is the coupling of SEC with FTIR. Combining liquid chromatography (LC) with FTIR spectroscopy will

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increase the amount of information obtained from chromatographic data. Such information is essential in the development of new polymers or in product-failure analysis.

A large number of interfaces between LC and FTIR have been described and two approaches can be distinguished, viz. techniques that use flow cells and techniques involving solvent elimination. In on-line flow-cell based LC–FTIR interfaces [1–3] spectra are acquired on-the-fly. However, applications are limited to IR transparent solvents and this approach shows rather poor detection limits. Because of these limitations, solvent-elimination based LC–FTIR interfaces are more successful. These make use of thermospray [4–6], particle beam [7,8], electrospray [9], ultrasonic [10–13], or pneumatic [14–20] nebulizers. The resulting interfaces produce mid-IR spectra free of solvent interferences and show lower detection limits than the flow-cell-based LC–FTIR interfaces. Nowadays, the most widely used pneumatic nebulizer is commercially available and such an instrument has been used in this study.

While the identification power of solvent-elimination interfaces has been amply demonstrated [12,19,21], quantitative aspects have hardly been investigated in polymer analysis. Provder et al. [20] studied the effects of specific instrument settings (viz. substrate scanning speed and number of spectra collected) on the reconstructed (Gram–Schmidt) SEC–FTIR chromatograms, which were only visually compared to the obtained SEC–dRI chromatogram. The effect of varying the substrate moving speed during deposition was not investigated. Schunk et al. [22] investigated the location and distribution of deposited polymer films by optical microscopy imaging of deposited polymers. Liu and Dwyer [13] noticed an inhomogeneous deposition, but accepted the inherent variance without optimizing the LC–FTIR conditions because IR absorption band ratios within FTIR spectra remained constant. Recently, quantitative analysis of polymers was investigated by Schunk and co-workers [23,24]. Their research focused on the development of FTIR calibration models and they discussed various aspects, including quality of the polymer film, molar-mass effects and data pre-processing.

To obtain quantitative data from solvent-elimination based LC–FTIR interfaces, it is necessary that the FTIR spectra represent all (or a given constant fraction) of the material deposited on the substrate. However, spreading of the deposit outside the area covered by the FTIR beam is a phenomenon inherent to the pneumatic spray nebulizers commonly used for interfacing LC–FTIR. Deposit spots spread out due to the convection of evaporated eluent and nebulizer gas across the substrate when both impinge on the deposition substrate. In addition, the sample trace may not be completely homogeneous (i.e., it may not have a constant thickness and composition throughout the spot). Finally, the performance parameters of the FTIR system (e.g., beam diameter and beam positioning) are of great importance. To study these effects, an exploratory study into quantitative aspects and settings of a commercially available LC–FTIR interface has been carried out with the aim to improve the quantitative interpretation of data obtained from LC–FTIR systems. To study fundamental aspects we focused only on LC where the solvent composition was not changed during the analysis. New findings are presented which allow a better understanding of the performance of pneumatic nebulizers. In particular, deposition effects are documented that occur with a commercially available solvent-elimination interface, used in conjunction with an FTIR sampling accessory and using an FTIR microscope. The trace widths proved to depend on the eluent flow-rate, affecting the quantitative figures of merit. After optimization of the eluent flow-rate, the chromatographic resolution obtained for the SEC–FTIR analysis of a mixture of polystyrene standards has been compared to that obtained with conventional SEC–UV. From triplicate collections and FTIR analysis of the polystyrene mixture, the repeatability of deposition was determined across a broad mass range.

2. Experimental

2.1. Chemicals

Unstabilized tetrahydrofuran (THF; HPLC grade) from Labscan (Dublin, Ireland) was used for all experiments. Polystyrene standards were supplied by Polymer Laboratories (Shropshire, UK) and polycarbonate standards were obtained from Scientific

Polymer Products (Ontario, NY, USA). Stock standard solutions of polystyrene and polycarbonate were prepared by weighing and dissolution in HPLC-grade THF. A mixture of polystyrene standards with peak molar-masses (M_p) of 1.25, 34.5, 465 and 2950 kg/mol, was prepared by combining the stock solutions and dilution with HPLC-grade THF to final concentrations of ca. 0.4 mg/ml for each standard. All standard solutions were stored in the dark at 6°C.

2.2. Size-exclusion chromatography

The chromatographic system consisted of a Waters 2690 Separations Module (Milford, MA, USA), equipped with a vacuum degasser and a thermostatted column compartment. This system was used for flow-injection experiments, in which a 50-μl sample plug was introduced into the eluent stream without using any separation column, and SEC experiments. On-line UV detection was performed with a Waters photodiode array detector Model 996 at 260 nm. A computer using Waters Millenium32 (version 3.2) software controlled the system and was used to monitor the detector signals.

SEC separations were carried out on two 300 mm×7.5 mm I.D. PLGel linear MixedB columns (particle diameter 10 μm; Polymer Laboratories) using THF at a flow-rate of 0.5 ml/min. The injected sample volume was 50 μl. During all analysis the column compartment was maintained at 35°C and the sample compartment was set at 20°C. An Acurate Model ICP-04-20-CR (LC Packings, Amsterdam, The Netherlands) flow splitter was used for measuring the chromatographic resolution and the repeatability. One-twentieth of the total flow through the column (i.e., 25 out of 500 μl/min) was diverted to the LC–FTIR interface.

2.3. Interfacing liquid chromatography with FTIR spectroscopy

An LC-Transform Model 500 (Lab Connections, Marlborough, MA, USA) interface, based on the principle described by Gagel and Biemann [14–16], was used to evaporate the eluent and to collect the chromatogram on a 60×2 mm (diameter×thickness) rear-surface-aluminized germanium substrate. The interface was controlled by Labcon 1.0 software (Lab Connections). For flow-injection and continuous-flow injection experiments (i.e., where a continuous flow of polystyrene containing THF was delivered to the LC–FTIR interface) by means of a syringe pump and SEC analyses, the conditions are summarized in Table 1. Nitrogen was used as nebulizer gas. The substrate moving speed was 1.7 mm/min in the experiments described in Sections 3.1 and 3.2. Collection of the analytes on the substrate was delayed until the actual elution of the samples. The LC–FTIR interface was triggered via an electronic pulse from the chromatographic system. The substrate movement during sample deposition was controlled by an x,y-stepper motor. In deposition-homogeneity and response-optimization studies, a Harvard Apparatus 22 (Holliston, MA, USA) syringe pump was used to deliver a constant flow of 25 μl/min of THF containing 0.2 mg/ml of polystyrene to the LC–FTIR interface. The syringe pump and the chromatographic system were connected to the LC–FTIR interface via a T-piece and a make-up flow of pure eluent was added by the chromatographic system to obtain a total flow-rate of 500, 250, 100, 75, and 50 μl/min. In flow-injection studies, the LC–FTIR interface was coupled directly to the injector of the chromatographic system. In other experiments the interface was operated in parallel with the UV detector via a flow splitter.

After sample deposition, the collection substrate was manually transferred to a three-times focusing optical FTIR accessory, controlled by LCT 1.6.1 software (Lab Connections), and spectra were acquired by stepwise rotation of the substrate.

Table 1
Experimental LC–FTIR interface conditions used to obtain a dry deposit at various THF flow-rates

Flow-rate (μl/min)	$h_{nebulizer}$ (mm)	$T_{nebulizer}$ (°C)	$p_{nitrogen}$ (kPa)
25	8	40	138
50	6	50	172
75	6	55	138
100	6	55	172
250	7	95	172
500	8	110	172

2.4. Spectroscopy

FTIR spectra were acquired using a Perkin-Elmer (Norwalk, CT, USA) spectrometer model Spectrum GX, equipped with a medium-band mercury–cadmium–telluride (MCT) detector. The scan resolution was set at 4 cm^{-1} and for each spectrum eight scans were accumulated. The sample and detector compartments were continuously purged using nitrogen gas, which was dried using a Zander Adsorbtion Dryer, Type KM5 TE (Essen, Germany). Data acquisition was performed using Perkin-Elmer Spectrum 3.0 software. Background spectra were obtained at unused positions on the germanium substrate. FTIR functional-group chromatograms were constructed using Perkin-Elmer Spectrum TimeBase 1.1. For the construction of these chromatograms, the total area of the absorbance or the maximum peak height from the selected IR absorption band in each spectrum was used.

FTIR microscopy experiments were performed in the reflectance mode on a Perkin-Elmer System 2000 spectrometer, equipped with a Perkin-Elmer Autoimage microscope with a beam spot size of 100×100 μm and 100-μm steps. A narrow-band MCT detector was used and the microscope was controlled by Autoimage 4.1 software. The acquisition parameters were identical to the settings used for the Perkin-Elmer Spectrum GX.

3. Results and discussion

3.1. Homogeneity of deposits

To evaluate the regularity and homogeneity of deposition along the trace, a constant flow of a solution of polystyrene in THF was directed at 0.5 ml/min to the LC–FTIR interface without chromatography. The polystyrene was deposited as an arc-wise, continuous trace of constant mass and composition from 25 to 340°. After obtaining the FTIR spectra of the deposit, the maximum IR absorption band heights at 698 and 3026 cm^{-1} were calculated against the disk angle. As shown in Fig. 1 (only profile at 698 cm^{-1} shown), the functional-group profile turned to be sine-wave shaped and the
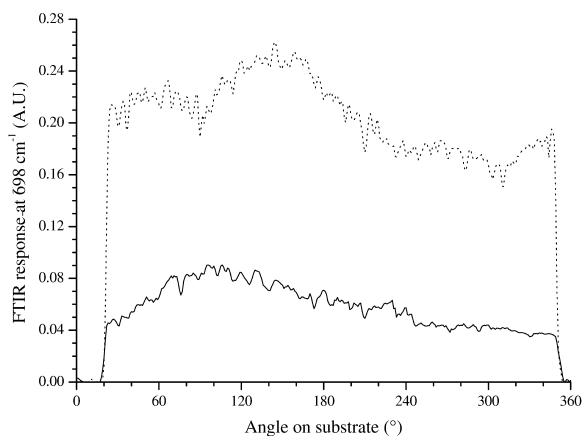

Fig. 1. Response of functional-group profiles obtained by continuous, arc-wise depositions of polystyrene from 25 to 340° at a flow-rate of 500 μl/min (——) and 25 μl/min (·····). The response was constructed from maximum absorption band heights at 698 cm^{-1}. The total mass deposited was kept constant.

intensity of the response varied from 0.0350 to 0.0904 AU. The stability of the response, expressed as the relative standard deviation (RSD) of the response along the deposit, was 26.6% (see Table 2). Such a variation will not impart the use of this LC–FTIR interface for qualitative purposes (spectrum identification), but it will jeopardize quantitative interpretation of the absorbance intensities.

A combination of two interface-related factors provides a plausible explanation for the observed deposition pattern. Firstly, the actual contour of the spray leaving the nozzle was oval rather than circular. This is often observed in LC–FTIR solvent-elimination interfaces [25]. Secondly, the movement of the deposition substrate is determined by an x,y-stepper motor. In other designs of deposition interfaces, the substrate is rotated around its center, while the position and orientation of the nozzle (and thus of the spray) relative to the substrate surface is constant. When, in case of moving the complete substrate in the x,y-plane, at a disk angle of 0° a part of the spray is pointing to the center of the substrate, it will be pointing to the outside of the substrate after a rotation by 180°. A combination of these two factors results alternately in narrow traces, where the deposited mass is concentrated on a small area of the substrate, and broad traces, where the deposited mass is spread over a larger area.

Table 2
Response, stability of the response (expressed as RSD), and response-ratio for arc-wise depositions of polystyrene from 25 to 340°, calculated from maximum absorption band heights at 698 and 3026 cm^{-1}

Flow (μl/min)	Response 698 cm^{-1}		Response 3026 cm^{-1}		Response ratio of 696 cm^{-1} and 3026 cm^{-1}	
	Average (AU)	RSD (%)	Average (AU)	RSD (%)	Average (–)	RSD (%)
500	0.0601	26.6	0.0253	31.7	2.424	7.9
250	0.0955	27.2	0.0389	22.8	2.433	6.5
100	0.0978	27.2	0.0427	26.4	2.286	3.4
75	0.1184	25.2	0.0497	24.8	2.382	2.4
50	0.1278	23.0	0.0504	19.1	2.520	6.2
25	0.2056	13.5	0.0768	11.1	2.674	4.7

Similar experiments were carried out by Liu and Dwyer [13]. However, they used an ultrasonic nebulizer interface, in which the substrate movement was different from that used in our system, in that it was rotated under the nozzle. The FTIR optics accessory was similar. At a flow-rate of 1 ml/min, Liu and Dwyer obtained an average spectral peak area of 9.4 AU/cm and a response stability, expressed as RSD, of 4.6% for the 700 cm^{-1} absorption band, calculated from a 62° arc-wise deposition (start position unknown) on the substrate. In our experiments, the response stability was 14.9% (RSD) over a similar angle (rotation angle, 40–102°; flow-rate, 500 μl/min). This is more evidence that the substrate-to-nozzle position and its orientation is an important factor for obtaining a homogeneous deposition of long, circular traces. Ideally homogeneous traces are obtained. If not, it is essential that the scanning conditions are adapted to the deposition conditions so as to obtain the best possible results, i.e., both deposition and scanning should either take place linearly or by a rotation around the center of the substrate.

One needs to be aware of this phenomenon in case the commercial LC–FTIR interface used in this paper is applied as a detector for quantitative purposes. Scanning the entire deposit rather than small spots, by surface mapping with FTIR microscopy might overcome the present problems [26], at the expense of a much-increased complexity.

FTIR microscopy experiments were performed to confirm our hypothesis of oval deposition by acquiring FTIR spectra across polystyrene depositions which were deposited by moving the substrate in the

x or y direction only. This will also unravel any inhomogeneity across the deposition trace. To this end, a polystyrene (M_p, 195 900 g/mol; ca. 0.1 mg/ml) solution in THF was linearly deposited at a flow-rate of 500 μl/min. FTIR absorption band heights at 2924 cm^{-1} showed significant differences in the deposited mass perpendicularly across the trace, as can be seen in Fig. 2. The deposition pattern observed when depositing in the x-direction is asymmetrical and depositing in the y-direction results in a symmetrical pattern. However, in both cases, little material was deposited in the center of the trace. Previously published results [22], where FTIR microscopy scans were taken across a
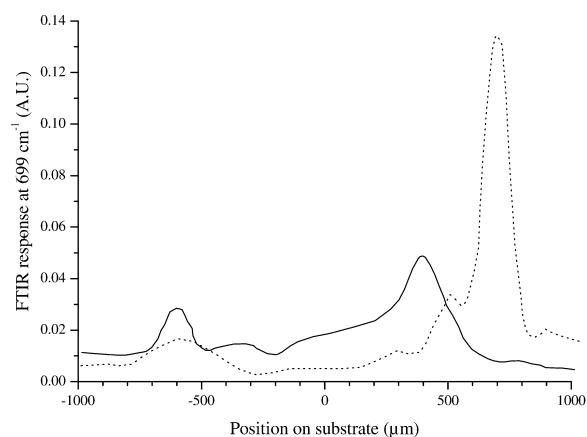

Fig. 2. Response of functional-group profile perpendicularly to the trace obtained by linearly deposited polystyrene and subsequently scanning by FTIR microscopy. The response was constructed from absorption band heights at 2924 cm^{-1}. [Deposition flow-rate, 0.5 ml/min; x-direction (····) and y-direction (——)].

poly(methyl methacrylate) deposit, showed the left and the right part of the trace to be of almost equal intensity.

To eliminate a faulty nozzle as the cause of our observations, the gap where the capillary protrudes into the nozzle and where the spray is surrounded by sheath gas was verified to be circular. Furthermore, the stainless steel nozzle capillary was replaced by a perfectly circular and perpendicularly cut fused-silica capillary of 200 μm I.D. to eliminate distortion at the edges of the original mounted capillary as a possible cause. This still resulted in the previously described deposition pattern. Until now, many parameters may influence the spray shape, and an exact correlation between these parameters and the spray shape are not known. Data produced by other workers (cited above) indicated that the way in which the substrate is moved under the nozzle is of major importance for producing a continuous trace. Because the principle of deposition movement of the LC–FTIR interface used in this study cannot be changed, it was investigated whether the trace inhomogeneity can be overcome by changing the operating parameters as described below.

3.2. Determination of trace width and optimization of the response

In addition to a high-response, a stable and constant response (i.e., low RSD) is desired to obtain quantitative results from LC–FTIR data, independent of the deposit position on the substrate. In principle, a maximum response with a small variation around arc-wise depositions can be obtained by producing a deposition trace sufficiently narrow for it to be fully contained within the IR beam. In that case, small variations in the deposition pattern will be obscured. The main factor responsible for the trace width is the eluent flow-rate, while other parameters, such as the nitrogen pressure and the interface temperature, must be simultaneously optimized to obtain a dry deposit.

The trace width was measured at several flow-rates, viz. 500, 250, 100, 75, 50, and 25 μl/min with the interface temperature and the nitrogen pressure being adjusted to obtain a dry deposit. Polycarbonate (ca. 1.0 mg/ml) was used as test compound and was deposited in linear traces in the flow-injection mode. Subsequently, FTIR microscopy scans were obtained

perpendicularly across the polycarbonate trace and concentration profiles were constructed of the carbonyl absorption band height at 1776 cm^{-1}. Upon decreasing the flow-rate from 500 to 100 μl/min the trace width was significantly reduced from 2.20 to 1.24 mm. No carbonyl absorption was observed in the center of the trace at flow-rates of 500 and 250 μl/min. At 75, 50, and 25 μl/min flow-rates, the trace width decreased to 1.17, 1.15, and 1.13 mm, respectively (see Fig. 3) and carbonyl absorption appeared in the center of the trace.

In order to investigate the response and the stability of the response expressed as RSD along the trace, arc-wise depositions of polystyrene (M_p, 465 kg/mol) were prepared in the constant-flow mode (no column) at the eluent flow-rates listed earlier. During all depositions, the mass flow (5 μg polystyrene/min) and the total mass deposited were held constant. The polystyrene deposit was scanned from 25 to 340°, resulting in 316 spectra. The average response and stability of the response (expressed as RSD) were calculated by averaging the response from functional-group profiles constructed from maximum IR absorption band heights at 698 and 3026 cm^{-1} (see Table 2 and Fig. 4). An example of the response along the trace at 698 cm^{-1} is given in Fig. 1. As expected, at low flow-rates (25 μl/min)
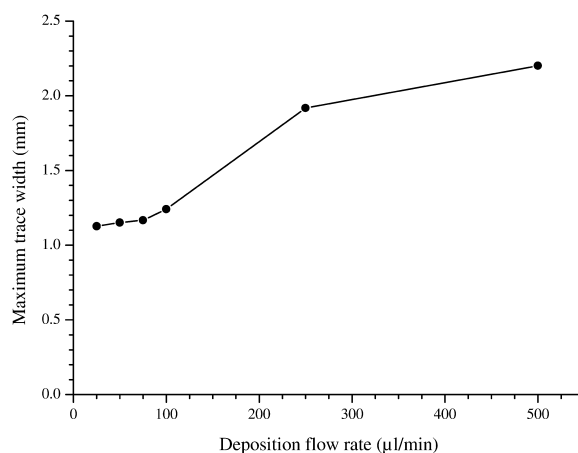

Fig. 3. Trace width (in mm) obtained after linear deposition of polycarbonate at different eluent deposition flow-rates. The trace width was calculated from the carbonyl absorption band height at 1776 cm^{-1} obtained from FTIR microscopy scans perpendicularly across the trace. For details, see text.
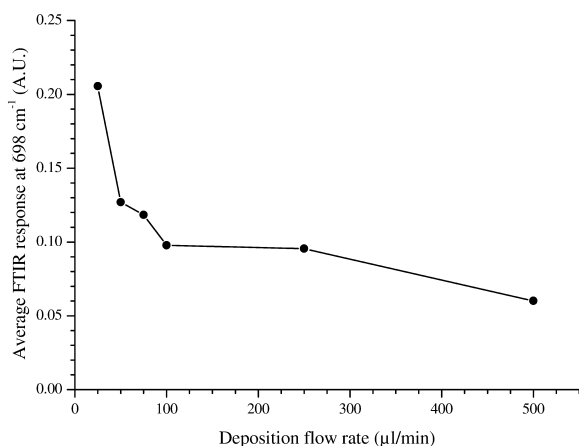
Fig. 4. Average response of functional-group profiles obtained by continuous, arc-wise depositions of polystyrene from 25 to 340°. The response was constructed from maximum absorption band heights at 698 cm^{-1} at various flow-rates. For details, see text. The total mass deposited was kept constant. The total number of spectra averaged was 316.

the sensitivity for the IR absorption band at 698 cm^{-1} has increased significantly (by a factor of 3.4) compared with the response at a flow-rate of 500 μl/min. At the same time, the RSD decreased from 26.6 to 13.5%. Apparently a more compact deposition was produced and the trace width was reduced to a value more in line with the FTIR beam diameter, obscuring some of the fluctuations in the deposition. In addition, in spectral-band-ratio analysis, where concentration effects are cancelled out, the standard error was of the order of 2 to 6% at all flow-rates smaller than 250 μl/min (see Table 2).

3.3. Chromatographic resolution

Working with off-line detectors or spectrometers, after immobilizing or fractionating chromatograms, can have adverse consequences on the chromatographic resolution. While in fractionation the chromatographic resolution is limited by the number of fractions collected, in solvent-elimination LC–FTIR the chromatographic resolution is affected by the substrate moving speed [22]. In order to find deposition conditions at which FTIR chromatograms show comparable resolution as chromatograms obtained with in-line detectors, substrate moving speeds of 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0 mm/min were selected to collect and subsequently analyze a polystyrene standard mixture. Resolution from the UV chromatogram was compared with that from the total areas of the absorption band at 698 cm^{-1}. From Table 3 it can be seen that the most significant increase of SEC–FTIR resolution is observed when increasing the substrate moving speed from 1.0 to 2.0 mm/min. Furthermore, it can be seen that even at a high substrate speed, it is hard to preserve the chromatographic resolution for polystyrenes of relatively low molar-mass due to molar-mass effects [24].

An undesirable consequence of a high substrate speed is a loss in sensitivity, because less mass is deposited on the same area of the substrate. This can be seen from Fig. 5, where the response of low-molar-mass polystyrene (M_p, 1250 g/mol) decreases more strongly with increasing moving speed compared to polystyrenes of higher molar-mass.

For polystyrene with peak molar-masses of 2 950 000 and 465 000 g/mol, SEC–FTIR resolution is nearly as good as SEC–UV resolution at a rather high substrate moving speed of 3.5 mm/min. Thus, chromatographic resolution is not only determined by the substrate moving speed, but also by the molar-mass of the deposited polymer [24]. This is

Table 3
Chromatographic resolution determined from SEC–UV and SEC–FTIR at different substrate moving speeds

Peak[a]	Chromatographic resolution							
	UV detection (260 nm)	FTIR detection at various substrate moving speeds (mm/min)						
		1.0	1.5	2.0	2.5	3.0	3.5	4.0
A–B	2.2	1.0	1.4	1.6	1.8	2.0	2.1	1.9
B–C	3.3	1.5	1.9	2.4	2.5	2.9	2.8	3.1
C–D	3.3	1.9	2.2	2.7	2.9	3.2	3.0	3.1

[a] Peak molar-masses (in kg/mol): A, 2.95·10^3; B, 465; C, 34.5; D, 1.25. For chromatograms, see Fig. 5.
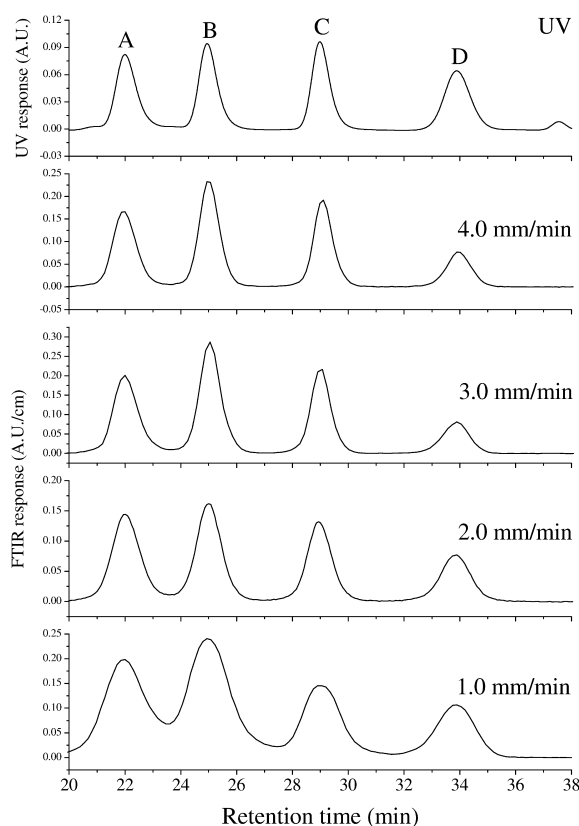
Fig. 5. SEC–UV chromatogram and SEC–FTIR functional-group chromatograms obtained after deposition of a polystyrene standard mixture at various substrate moving speeds. Functional-group chromatograms were constructed from the total area of the absorbance at 698 cm^{-1}. Peak molar-masses (in kg/mol): A, $2.95 \cdot 10^3$; B, 465; C, 34.5; D, 1.25.

true for polystyrene, but similar results are anticipated for other types of polymers, probably depend-

ing on the physical properties, such as crystallinity and viscosity. This needs to be explored through future experiments. A substrate moving speed of 2 mm/min was used in further experiments and offers a good compromise between chromatographic resolution, sensitivity, and the time needed to collect FTIR spectra.

3.4. Repeatability

Validation of the repeatability of deposition was performed by analyzing a polystyrene standard mixture by SEC–FTIR in triplicate and by comparing the data with those obtained from UV detection. Peak areas and retention times of all four polystyrene standards were calculated from FTIR functional-group chromatograms (absorption band area at 698 cm^{-1}) and from UV chromatograms at 260 nm. The latter data were used to estimate the conventional chromatographic repeatability.

The repeatability of chromatographic peak areas over a broad molar-mass range varied between 3.2 and 5.8% and the repeatability of retention times varied between 0.21 and 0.47% (see Table 4). This is in agreement with data obtained using the in-line UV detector. Interfacing LC to FTIR with the present type of interface will produce reliable data that can be compared with those from in-line detectors. In addition, SEC–FTIR provides structural information throughout the chromatogram.

4. Conclusions

SEC–FTIR is a mature technique for obtaining

Table 4
Repeatability of peak area and retention time for SEC–FTIR analyses of a mixture of polystyrene standards ($n=3$), calculated from UV detection at 260 nm and FTIR absorption band areas at 698 cm^{-1} (M_p, peak molar-mass)

M_p polystyrene (kg/mol)	Peak area				Retention time			
	Average (AU/min)		RSD (%)		Average (min)		RSD (%)	
	UV	FTIR	UV	FTIR	UV	FTIR	UV	FTIR
$2.95 \cdot 10^3$	4.74	1.02	2.44	4.0	22.13	23.2	0.15	0.47
465	4.59	1.13	2.35	3.5	25.06	26.2	0.13	0.42
34.5	4.53	0.91	1.26	3.2	29.11	30.2	0.11	0.22
1.25	4.46	0.64	0.86	5.8	34.03	34.8	0.09	0.21

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qualitative (spectral) information. A few quantitative studies have been performed in research environments using laboratory-built interfaces, but the application of commercial LC–IR interfaces for the quantitative analysis of polymeric samples has hardly been explored. It has been demonstrated that the eluent flow is a critical factor in obtaining a homogeneous deposition in commercially available solvent-elimination interfaces, in which the deposition substrate is moved by an *x,y*-stepper motor. The trace width was reduced from 2.20 to 1.13 mm by reducing the eluent flow-rate through the LC–FTIR interface from 500 to 25 μl/min. Much of this effect is reached by relatively small reductions in the flow-rate (e.g., down to 100 μl/min). Upon a reduction in the flow-rate, the depositions of polystyrene showed an improvement in response by a factor of 3.4, while the stability of the response, expressed as RSD was reduced from 26.6 to 13.5%. The chromatographic resolution in SEC–FTIR is not only affected by the substrate moving speed, but also by the molar-mass of the polymer to be analyzed. The repeatability of three consecutive depositions with a polystyrene standard mixture was found to be 4.0% in response and 0.47% in retention time for high-molar-mass polystyrene and 5.8% in response and 0.21% in retention time for low-molar-mass polystyrene.

Acknowledgements

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