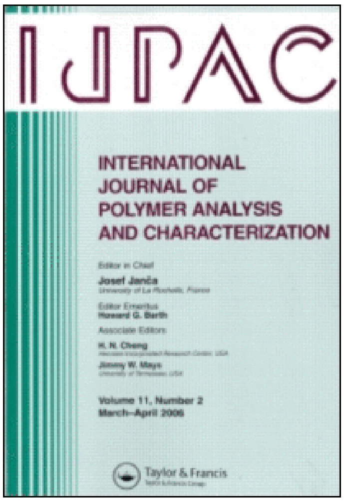

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A New IR Detector Cell with Optimized Optical Path Length for High-Temperature SEC of Polyolefins†

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A commercially available infrared detector cell suitable for high-temperature size exclusion chromatography was improved by new cell windows, reduction of the cell volume, temperature control and optimization of the optical path length. The theory for the optimization of the optical path length is presented, as well as the results of test measurements with solutions of polyethylene and polypropylene at different optical path lengths. The results obtained are in good agreement with the calculations which proves that the resolution of chromatograms can be improved and the detectable range of molar mass slightly extended by correct selection of the optical path length.

Keywords: Size exclusion chromatography, infrared detector, optical path length, polyethylene, polypropylene

INTRODUCTION

In high-temperature size exclusion chromatography (SEC) of polyolefins, infrared (IR) detectors have the advantage of being influenced less by fluctuations of temperature and pressure than refractive index detectors; however, IR detectors usually have a lower response and a larger detector cell volume.

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*Corresponding author.

†Dedicated to Prof. Dr. Peter Zügenmaier on the occassion of his 60th birthday

During a series of experimental studies on high-temperature SEC of polyolefins [1–3], a commercially available detector cell was improved by the use of cell windows with enhanced stability and by reduction of the cell volume. Since the performance of this modified detector cell was still unsatisfactory with respect to temperature control and its tendency to leakage, a new detector cell was built to eliminate these sources of error. In the course of testing this new cell, its optical path length was systematically varied and finally optimized for high-temperature SEC of polyolefins in 1,2,4-trichlorobenzene at 135°C.

This paper presents the new detector cell, the theory for optimization of the optical path length, and the results of test measurements with sample solutions of polyethylene and polypropylene, including a comparison with the calculated dependence of the detector response on the optical path length.

IR DETECTOR CELL

The schema of the new detector cell is depicted in Figure 1; Figure 1a shows the exploded view of the actual flow-through cell, Figure 1b shows the mounting this cell within a cylindrical thermostated metal block together with the ends of the connecting capillaries. The area of the cell cross section, that is, the area of the slit in the insert (cf. Fig. 1a), was chosen to be 11.5 mm^2, slightly larger than the cross section of the collimated IR beam of the IR detector, which was used in this study (model 830110.902, Du Pont Instruments). The volume of the detector cell thus depended on the thickness of the insert, that is, the optical path length l, and is 11.5 μL for $l = 1$ mm and 18.4 μL for $l = 1.6$ mm. The cell windows consist of a custom-made Suprasil^{R}300 (Hellma, Müllheim, Germany), each with a diameter of 15.8 mm and a thickness of 2.0 ± 0.05 mm (transmittance of 87 % of wavelength $\lambda = 3.42$ μm).

The insert (cf. Fig. 1a) is made of stainless steel and is centered within the cylindrical metal block by tongue and groove (cf. Fig. 1b, front view). The inlet and outlet capillaries are each precisely flush joined to the narrow channels which are drilled through the insert from the side to the lower and upper end, respectively, of the slit in the insert; the capillaries are mounted on the cylindrical metal block by nut and ferrule (cf. Fig. 1b, front view).

The cylindrical metal block is heated by a heating strip which covers the whole circumference area except the space required for mounting the

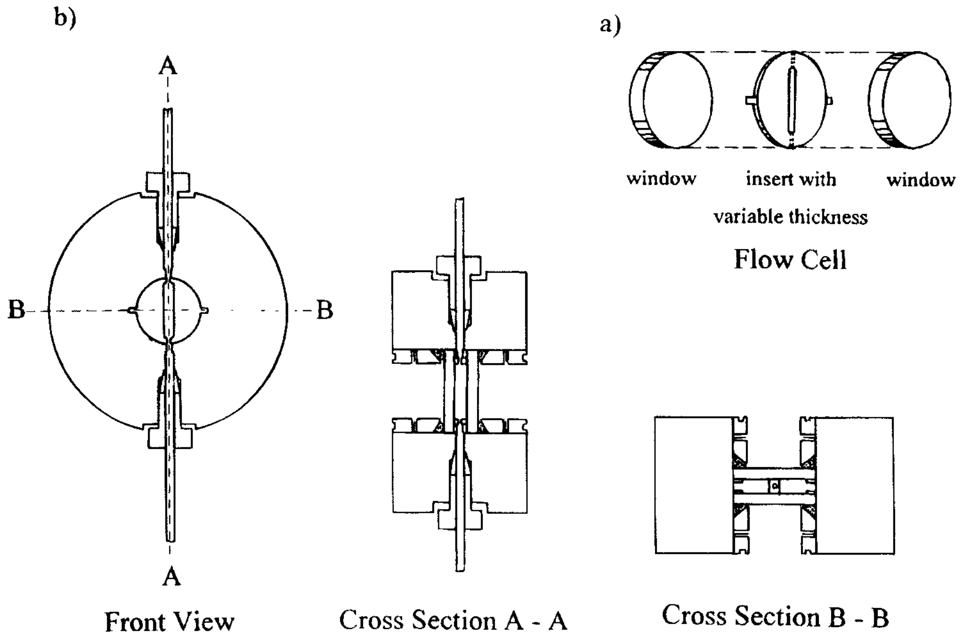

FIGURE 1 Schematic drawing of the new infrared detector cell. a) cell geometry, b) cell mounting.

capillaries. The connecting capillaries are heated by heating wires. The temperature of the metal block and of the connecting capillaries are controlled independently by two temperature control units (model KS40, Philips, Hamburg, Germany), temperature operating range from ambient temperature to 145°C.

OPTIMIZATION OF OPTICAL PATH LENGTH

For the calculation of the optical path length, that is, the thickness of the insert (cf. Fig. 1a), which leads to the highest response of the IR detector, the following assumptions were made:

(i) the light is a parallel and monochromatic beam,
(ii) the beam enters and leaves the cell perpendicular to the cell face,
(iii) dispersion or scattering effects inside the cell are neglected,
(iv) no interactions between the molecules or the molecules and the solvent.

According to Beer's law [4], the intensity of the light transmitted through a sample solution I_{out} can be expressed as the exponential function

$$I_{out} = I_{in} \cdot \exp[-\alpha \cdot c \cdot l] \tag{1}$$

where I_{in} is the intensity of light transmitted through the pure solvent, α is the specific absorption coefficient of the solute ($cm^2 \cdot g^{-1}$), c is the concentration of the solution ($g \cdot cm^{-3}$), and l is the optical path length (cm).

The intensity of the beam transmitted through a cell filled with solvent (I_0) and a cell filled with solution (I) can be expressed according to Equations (2) and (3):

$$I_0 = P \cdot \exp[-\alpha_s \cdot l] \tag{2}$$

$$I = I_0 \cdot \exp[-\alpha \cdot c \cdot l] \tag{3}$$

where P is the intensity of the primary beam attenuated by the windows of the cell and α_s is the absorption coefficient of the pure solvent (cm^{-1}).

Inserting Equation (2) into (3) leads to Equation (4):

$$(I_0 - I) = P(\exp[-\alpha_s \cdot l] - \exp[-l \cdot (\alpha_s + \alpha \cdot c)]) \tag{4}$$

Considering P, α_s, c and α as constant, the highest detector response (I_0 – I) dependent on the optical path length can be found by the criterion:

$$\frac{d(I_0 - I)}{dl} \tag{5a}$$

Substitution of Equation (4) into (5a) leads to:

$$\begin{aligned}\frac{d(I_0 - I)}{dl} &= P \cdot (-\alpha_S \cdot \exp[-\alpha_S \cdot l] \\ &+ (\alpha_S + \alpha \cdot c) \cdot \exp[-l \cdot (\alpha_S + \alpha \cdot c)] = 0\end{aligned} \tag{6}$$

Dividing this expression by $exp(-\alpha_s \cdot l)$ and rearrangement leads to

$$l = \frac{1}{\alpha \cdot c} \cdot \ln\left(1 + \frac{\alpha \cdot c}{\alpha_S}\right) \tag{7}$$

When applying a constant optical path length during an entire SEC run, it is appropriate to choose the optical path length which leads to the highest detector response at the lower and upper end of the chromatographic peak. The respective optical path length can be determined from Equation (7) as the limiting value for $c \rightarrow 0$:

$$\lim_{c \to 0} \frac{1}{\alpha \cdot c} \cdot \ln\left(1 + \frac{\alpha \cdot c}{\alpha_S}\right) \tag{8a}$$

Applying the rule of de L'Hopital, we arrive at Equation (8b):

$$\lim_{c \to 0} \frac{1}{1 + \frac{\alpha \cdot c}{\alpha_S}} \cdot \frac{1}{\alpha_S} = \frac{1}{\alpha_S} \tag{8b}$$

IR DETECTOR CELL EVALUATION IN HIGH-TEMPERATURE SEC OF POLYOLEFINS

Materials

The polymers used were a linear polyethylene NBS 1475 Standard Reference Material (U.S. Department of Commerce, N.I.S.T., Washington DC) with a weight average molar mass of 52 000 g/mol, determined by light scattering as given by the distributor, and a sample of isotactic polypropylene Daplen PT 55 (M_w = 206 000 g/mol, determined by SEC coupled with light scattering in our laboratory [5]), kindly supplied by PCD Polymer GmbH (Linz, Austria). The solvent, 1,2,4-trichlorbenzene (TCB), "pro synthesis" grade, was purchased from Merck (Darmstadt, Germany) and further purified by distillation. 2,6-di-tert-butyl-(4-methylphenol) "purum" grade was from Fluka (Buchs, Switzerland).

The nitrogen supplied from a pressure cylinder had a purity of 99.999 vol% ($O_2 \leq 3$ ppm, $H_2O \leq 5$ ppm, $C_nH_m \leq 0.2$ ppm) and was further purified by a molecular sieve (Oxisorb® cartridge, Messer-Griesheim, Frankfurt, Germany).

Methods

The absorption coefficient of the solvent α_s and the specific absorption coefficient of the solute α (polyethylene NBS 1475 and polypropylene Daplen PT55, see above) were measured with the IR detector (model 830110.902 of Du Pont Instruments) set at a wavelength of 3.42 µm (C-H stretching) using the new detector cell with an optical path length of l = 1.0 and of l = 2.2 mm. Since the Du Pont IR instrument (Wilks-Miran) may not be available, instrument modification described in the paper may be applicable to similar models of flow-through IR spectrometers. The calculation of α_s and α was carried out by Equations (2) and (3).

SEC was carried out with a self-assembled apparatus consisting of a L-510 pump (Waters Corp., Milford, MA), a sixport injection valve 7010 (Rheodyne, Cotati, CA) with a 305-µL sample loop, and the infrared detector described above. The flow of the eluent was measured by a mass flow meter (Liqui Flow L1) in combination with an analog channel module (E-5611, Bronkhorst, Ruurlo, Netherlands). A combination of three linear columns was used: TSK-Gel GMH6-HT, 13-µm particle size, 300 mm × 7.5 mm i.d. (Toyo Soda, Tokyo, Japan) and LiChrogel PS40000 and PS4, 10-µm particle size, 250 mm × 7 mm i.d. (Merck, Darmstadt, Germany). The measurements were performed at 135°C with TCB as eluent, and the flow rate was 0.5 mL/min. Sample solutions were prepared by dissolving between 10 and 40 mg of the polymer in 20 mL TCB at 160°C within 45 min. The solvent contained 0.5 g/L 2,6-di-tert-butyl-(4-methylphenol) and was flushed with nitrogen for 15 min to prevent thermal degradation.

RESULTS AND DISCUSSION

The linearity of the detector was demonstrated by recording the infrared signal of solutions of polyethylene and polypropylene with varying concentrations (0.5–2.0 mg/mL) and then plotting the peak areas versus the concentration. The calibration curves are linear and run through the origin.

The absorption coefficient α_s for TCB and the specific absorption coefficient α for polyethylene and polypropylene (α_{PE} and α_{PP}) measured at two optical pathlengths were averaged and are given in Table I.

For highest detector response at low polymer concentrations, an optical path length of $l = 1/\alpha_s = 0.16$ cm should be chosen according to Equation (8b). This result was experimentally tested by SEC measurements using three different optical path length of 1.0, 1.6 and 2.2 mm, both in the case of the polyethylene and the polypropylene samples.

Figures 2 and 3 clearly reveal that an optical pathlength of $l = 1.6$ mm leads to the highest detector response for both low and high polymer concentration. Furthermore, it can be seen from Figures 2 and 3 that, in the region of high polymer concentrations, the deviation of the detector response from the highest values for $l = 1.6$ mm is less with $l = 1.0$ mm than with $l = 2.2$ mm. The corresponding deviation in the region of low concentrations is, however, less with $l = 2.2$ mm than with $l = 1.0$ mm (cf. detail plot in Fig. 3).

Discrete values from the data shown in Figures 2 and 3 are given in Tables II and III to give a precise measure of the enhancement of the IR detector response accomplished by optimized optical path length in these measurements. In Tables II and III, also the concentration of the eluted solutions are given, which were calculated from the normalized chromatogram (peak area = 1) and the injected mass of the solute (concentration of sample solution × volume of sample loop).

With the data in Table II, the expected detector response ($I_o - I$) was calculated by Equation (4). The result is shown in Figure 4. Comparison of

TABLE I Absorption coefficients at λ=3.42 μm of 1,2,4-trichlorobenzene (α_S) and polyethylene NBS 1475 (α_{PE}) and polypropylene Daplen PT 55 (α_{PP}) in 1,2,4-trichlorobenzene at 135°C determined with different optical path lengths.

Absorption coefficients	$\ell = 1.0$ mm	$\ell = 2.2$ mm	average value
α_s / (1/cm)	6.3	6.0	6.2
$\alpha_{PE} \cdot 10^3$ / (cm^2/g)	10.1	9.7	9.9
$\alpha_{PP} \cdot 10^3$ / (cm^2/g)	20.3	26.6	23.4

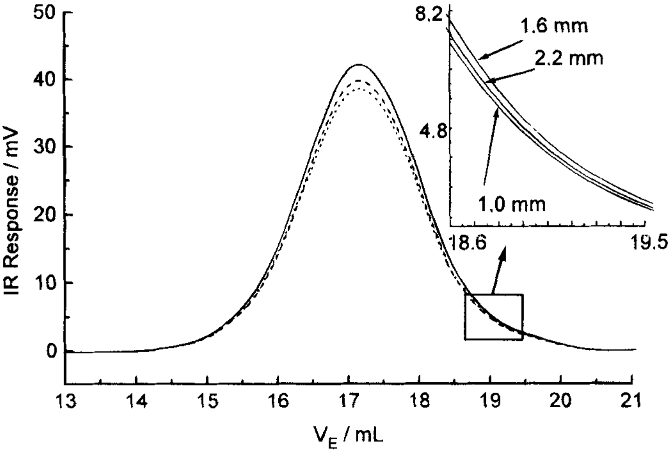

FIGURE 2 SEC elution curves of polyethylene NBS 1475 sample solution (c = 0.98 mg/mL) in TCB at 135°C detected by the IR detector at 3.42 μm with optical path lengths of 1.0 mm (dashed line), 1.6 mm (continuous line), and 2.2 mm (dotted line).

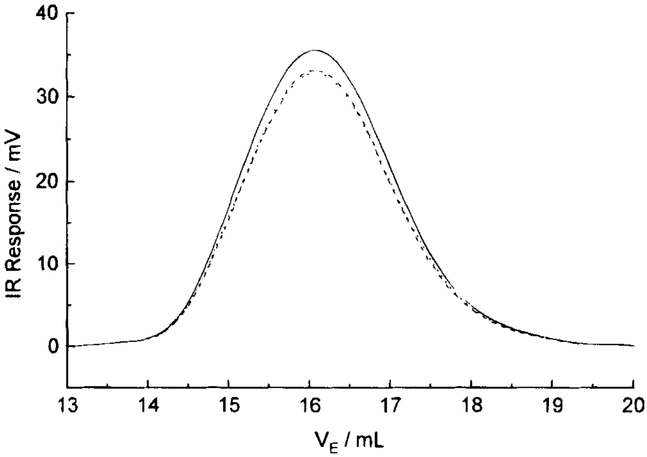

FIGURE 3 SEC elution curves of polypropylene Daplen PT55 sample solution (c = 0.73 mg/mL) in TCB at 135°C detected by the IR detector at 3.42 μm with optical path lengths of 1.0 mm (dashed line), 1.6 mm (continuous line), and 2.2 mm (dotted line).

TABLE II Difference of infrared detector response curves Δ recorded with path lengths of 1.0 and 2.2 mm compared to response curve obtained with a path length of 1.6 mm for polyethylene NBS 1475 at 135°C at various elution volumes V_e and concentrations c.

V_e/mL	c10^3/(g/L)	Δ/% 1.0 mm	Δ/% 2.2 mm
14.44	0.87	−9.3	−5.2
14.96	3.89	−9.2	−5.3
15.43	11.96	−9.0	−5.6
15.91	29.12	−8.5	−6.0
16.38	62.83	−7.6	−7.0
16.85	107.74	−6.4	−8.2
17.32	136.78	−5.6	−8.9
17.79	124.71	−5.9	−8.6
18.26	83.16	−7.1	−7.5
18.73	41.13	−8.2	−6.4
19.21	19.07	−8.8	−5.8
19.68	9.32	−9.1	−5.5
20.15	4.12	−9.2	−5.3
20.49	0.70	−9.3	−5.2

TABLE III Difference of infrared detector response curves Δ recorded with path lengths of 1.0 and 2.2 mm compared to response curve obtained with a path length of 1.6 mm for polypropylene Daplen PT55 at 135°C at various elution volumes V_e and concentrations c.

V_e/mL	c10^3/(g/L)	Δ/% 1.0 mm	Δ/% 2.2 mm
13.78	1.18	−9.3	−5.3
14.25	3.32	−9.3	−5.3
14.73	15.42	−8.9	−5.7
15.20	44.14	−8.2	−6.4
15.67	76.40	−7.3	−7.3
16.14	95.13	−6.8	−7.8
16.61	91.98	−6.9	−7.7
17.08	68.88	−7.5	−7.1
17.56	40.45	−8.3	−6.3
18.03	19.57	−8.8	−5.8
18.50	9.07	−9.1	−5.5
18.97	4.24	−9.2	−5.3
19.44	1.60	−9.3	−5.3
19.68	0.63	−9.3	−5.2

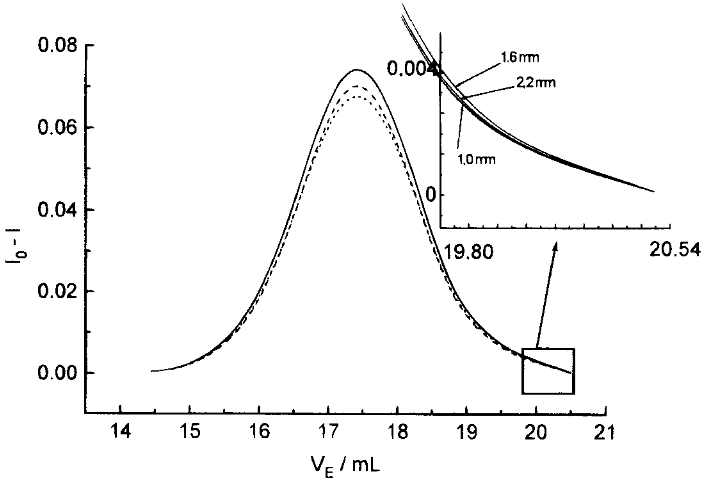

FIGURE 4 Calculated IR attenuation ($I_0 - I$) as a function of the elution volume (V_e) of polyethylene NBS 1475 in TCB at 135°C and 3.42 μm for optical path lengths of 1.0 mm (dashed line), 1.6 mm (continuous line), and 2.2 mm (dotted line) according to Equation (4). Concentrations as in Table II; $\alpha_s = 6.2\ \text{cm}^{-1}$; $\alpha = 9.929 \cdot 10^{-3}\ \text{cm}^2/\text{g}$.

Figures 4 and 2 suggests very good agreement between the calculated and the measured dependence of detector response on optical path length.

Although these findings clearly demonstrate the value of using an IR detector with optimized optical path length, the actual gain in the signal-to-noise ratio is rather limited (cf. Table IV). The noise of all baselines showed a uniform distribution using the chi-square test[6,7] and had similar mean square noise values.[8]

In the case of our SEC experiments with polyethylene NBS 1475, the use of an optimized optical path length (1.6 mm instead of 1.0 mm and 2.2 mm) resulted only in a slight extension of the detectable range in molar mass. Setting the threshold for the acceptance of a point on the elution curve to a signal-to-noise ratio of 1.5, the detectable range of molar mass at the high-molar-mass end was extended by about 20%, but only by about 6% at the low-molar-mass end.

Acknowledgements

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TABLE IV Signal-to-noise ratio (s/n) of the measurements of polyethylene NBS 1475 (PE) and polypropylene Daplen PT55 (PP) at different optical path lengths (ℓ) and elutionvolumes V_e; T=135°C.

Polymer	V_e/mL	s/n ratio		
		ℓ=1.0 mm	ℓ=1.6 mm	ℓ=2.2 mm
PE	17.15 (Peak max.)	40.8	42.2	40.4
	13.75	1.0	1.0	1.0
	14.0	1.1	1.2	1.1
	14.25	1.2	1.3	1.2
	14.5	1.4	1.5	1.4
	14.75	1.6	1.8	1.7
	15.0	2.1	2.3	2.2
	15.25	3.6	4.0	3.8
	19.25	3.4	3.7	3.5
	19.5	2.6	2.8	2.7
	19.75	1.7	1.8	1.7
	20.0	1.2	1.3	1.2
	20.25	1.1	1.1	1.1
	20.5	1.0	1.0	1.0
PP	16.09 (Peak max.)	33.3	34.4	32.0
	14.25	2.3	2.7	2.4
	18.5	2.2	2.6	2.3

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