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# Analysis of linear and cyclic oligomers in polyamide-6 without sample preparation by liquid chromatography using the sandwich injection method
## II. Methods of detection and quantification and overall long-term performance

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**Abstract**

By separating the first six linear and cyclic oligomers of polyamide-6 on a reversed-phase high-performance liquid chromatographic system after sandwich injection, quantitative determination of these oligomers becomes feasible. Low-wavelength UV detection of the different oligomers and selective post-column reaction detection of the linear oligomers with *o*-phthalic dicarboxaldehyde (OPA) and 3-mercaptopropionic acid (3-MPA) are discussed. A general methodology for quantification of oligomers in polymers was developed. It is demonstrated that the empirically determined group-equivalent absorption coefficients and quench factors are a convenient way of quantifying linear and cyclic oligomers of nylon-6. The overall long-term performance of the method was studied by monitoring a reference sample and the calibration factors of the linear and cyclic oligomers. 

*Keywords:* Sandwich injection method; Injection methods; Polyamide-6; Cyclic oligomers

## 1. Introduction

Nylon-6 is produced by polycondensation of caprolactam [1]. Due to its stability, the seven-membered ring monomer is present in unwashed nylon-6 in relatively large amounts [2]. Higher cyclic oligomers are present at lower levels and the amounts of linear oligomers are even less. The structures of these oligomers are depicted in Fig. 1.

The amount of oligomers present in unwashed nylon-6 can be minimized by hot-water extraction or vacuum heating [3–5]. The residual amount of oligomers influences the molar mass distribution and, for some fields of application, the amount of oligomers in the end product is of major importance [4,5].

In order to develop a quantitative analytical method, the linear and cyclic oligomers of nylon-6 have to be detected selectively. When the polyamide sample is injected with the sandwich injection meth-

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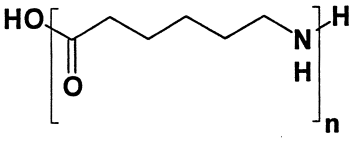
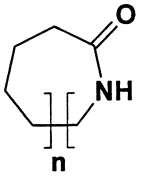



**Linear oligomer of 6-aminocaproic acid : Ln**




**Cyclic oligomer of caprolactam : Cn**

Fig. 1. Chemical structures of linear and cyclic oligomers of nylon-6.

od [6,7] on a reversed-phase column, the cyclic and linear oligomers can be separated and detected selectively in the mobile phase.

As linear oligomers are only present in relatively low concentrations compared to cyclic oligomers, selective detection after separation enhances accuracy. The most selective detection method is mass spectrometry and this is the first choice for identification purposes [8]. Soto et al. [9] used off-line LC–MS to identify the cyclic oligomers and Barkby et al. [10] demonstrated the presence of extracted cyclic oligomers in a water matrix with an on-line LC–FAB-MS configuration.

Selective detection can also be performed by pre-column derivatization of a functional group of a particular oligomeric series. The linear oligomers of nylon-6, nylon-6,6 and nylon-12 were derivatized with 2,4-dinitrofluorobenzene [11]. The well-known *o*-phthalic dicarboxaldehyde was used to derivatize Versamid, which is a polyamide based on di- or tri-ethylene-poly amines and dimerized diacids [12]. Both derivatizations were performed prior to size-exclusion chromatographic (SEC) separation. Pre-column derivatization of the amine-terminated linear nylon-4,6 oligomers with naphthalene dicarboxaldehyde was performed prior to reversed-phase separation in order to amplify the sensitivity and to study the influence of this attached group on chromatographic behavior [13].

Other less-selective detectors have been used. With isocratic reversed-phase HPLC conditions the refractive index detector [14–16] and low-wavelength UV detector [14–23] have been applied. Using multiple detection techniques simultaneously is very popular in SEC. UV and RI detection [24–26] and also an RI detector with a viscometer and a multi-angle light-scattering detector have been used in SEC analysis of nylons [27,28].

Although the evaporative light-scattering detector can detect the oligomers of polyamide-4,6 [29], UV-absorbance detection is the first choice for the determination of polyamide oligomers in combination with gradient elution [9,30]. The cyclic and linear oligomers do not have specific chromophore groups, but the amide function absorbs some energy in the low-wavelength UV region. We present a dual detection system with a UV-absorbance detector in combination with a post-column reactor where the relatively high levels of cyclic oligomers are detected with UV and the low amounts of linear oligomers are derivatized post-column with *o*-phthalic dicarboxaldehyde and determined with a fluorescence detector. We then demonstrate the long-term performance of the sandwich-injection-based method in combination with UV detection and post-column derivatization

## 2. Experimental

All polyamides used were synthesized at DSM. Cyclic and linear oligomers were obtained by preparative (HPLC) experiments. The linear oligomers are abbreviated $L_n$, and the cyclic oligomers $C_n$, where $n$ is the number of $COC_5H_{10}NH$ units (Fig. 1). The cyclic oligomers were pure, but the linear oligomers were contaminated with the corresponding carboxylic acid amide oligomer: $HO(OC–C_5H_{10}N)_nH–CO–H$. The purity of the oligomers was determined with H-NMR.

Dissolution of the polyamides in formic acid (98–100% p.a., Merck, Darmstadt, Germany) was performed in a Bransonic Ultrasonic Cleaner, Model 5210 (Danbury, CT, USA).

The HPLC system consisted of a HP1050 quartenary pump and a HP1050 variable injector with an extended capacity of 115 vials (Hewlett-Packard,

Waldbronn, Germany). All samples were injected using the sandwich injection procedure [6,7]. Six microlitres of the polyamide solution in formic acid was sandwich between two zones of 2 μl formic acid to prevent the polymer precipitating before the column. The aqueous (MilliQ, Waters, Milford, MA, USA) mobile phase A contained 1% acetonitrile (Lichrosolve, gradient grade, Merck) and 10 m*M* phosphoric acid (prepared with phosphoric acid 85% p.a., Baker, Deventer, The Netherlands) and mobile phase B was pure acetonitrile. Using a programmed gradient, the pump changed the percentage of mobile phase B from 0 to 50 in 22 min with a flow-rate of 1.2 ml/min. The pressure drop ($\Delta P$) along the 250× 4 mm Nucleosil 120-5C18 column (Machery-Nagel, Düren, Germany) was approximately 200 atm. UV detection at $\lambda = 200$ and 220 nm was performed with a Linear 204 programmable dual-wavelength detector (Linear Instruments, Reno, NV, USA) and the fluorescence signal was generated with a Waters 474 fluorescence detector (Waters, 16 μl detector cell, $\lambda_{ex} = 330$ nm, $\lambda_{em} = 420$ nm, excitation and emission bandwidth 18 nm). Post-column reagents were prepared as follows: 50 g boric acid (p.a., Merck) was dissolved in 1 l MilliQ water by adding potassium hydroxide pellets (p.a., Merck) until a pH of 10 was reached. *o*-Phthalic dicarboxaldehyde (OPA, 0.8 g, p.a., Acros Chemica, Geel, Belgium) was dissolved in 10 ml ethanol (Lichrosolve, gradient grade for liquid chromatography, Merck) and together with 1 ml 3-mercaptopropionic acid (Fluka Chemika, Buchs, Germany) the solutions were added to the borate buffer solution. The post-column flow obtained with a Gilson 302 pump, a 5 WSC pump-head and a Gilson 802 pulsation damping unit (all from Gilson, Villiers-le-Bel, France) was 0.5 ml/min. The UV and fluorescence detector signals were collected with the X-Chrom/Windows NT 3.51 version 2.11b data management system (LAB-systems, Manchester, UK)

## 3. Results

### 3.1. Detection

Oligomers of polyamide-6 are hard to detect as they do not have strongly conjugated groups. The amide function absorbs some energy in the low-UV region ($\lambda \leq 220$ nm). The cyclic oligomers do not have any functional groups to be derivatized, so eluents with very good UV transparency have to be used to perform UV detection. The wavelength where the cyclic oligomers are usually detected is $\lambda = 200$ nm, however when very high concentrations of caprolactam are present, dual-wavelength detection can be used at $\lambda = 200$ and 220 nm ($\varepsilon_{\text{caprolactam at 200 nm}}/\varepsilon_{\text{caprolactam at 220 nm}} = 9.7$).

The linear oligomers are commonly present at relatively low levels, but they have, in addition to the carboxylic acid group, a primary amine group, which opens the possibility of easy, selective and sensitive post-column reaction detection.

A set of chromatograms from a typical polyamide-6 sample is given in Fig. 2.

Ramert-Lucas et al. found that if two or more methylene groups separate chromophores the absorption spectrum is just a summation of the two chromophores [31]. Roa called this principle insulation of chromophores [32].

Many researchers have studied the UV absorbance of cyclic oligomers [16,17,20] and stated that only the amide function contributes to the total UV absorption [33]. By defining the boundary conditions, this could be captured in an equation by using an equivalent absorption. If conjugated groups are separated by non-conjugated alkyl chains, when the influence of intramolecular interactions is negligible compared with intermolecular interactions with the surrounding environment, and if gradient changes of the mobile phase do not modify group-equivalent absorption coefficients, the equivalent absorption of a given oligomer can be summed. For the cyclic oligomer $C_n$ with $n$ equivalent amide groups, this results in:

$$A_{C_n} = cl\varepsilon_{C_n} = cln\varepsilon^{eq}_{\text{amide in chain}} \quad (1)$$

where $A_{C_n}$ is the absorbance of a cyclic oligomer (absorbance units, Au), $c$ is the concentration of the oligomer (mol $l^{-1}$), $l$ is the length of the detector cell (m), $n$ is the number of backbone units, $\varepsilon_{C_n}$ is the molar absorption coefficient of the cyclic oligomer (Au $mol^{-1}$ l $m^{-1}$) and $\varepsilon^{eq}_{\text{amide in chain}}$ is the equivalent absorption coefficient of an amide group in a chain (Au $eq^{-1}$ l $m^{-1}$). For the higher cyclic oligomers (with $n > 2$), Eq. (1) gives a reasonable fit.

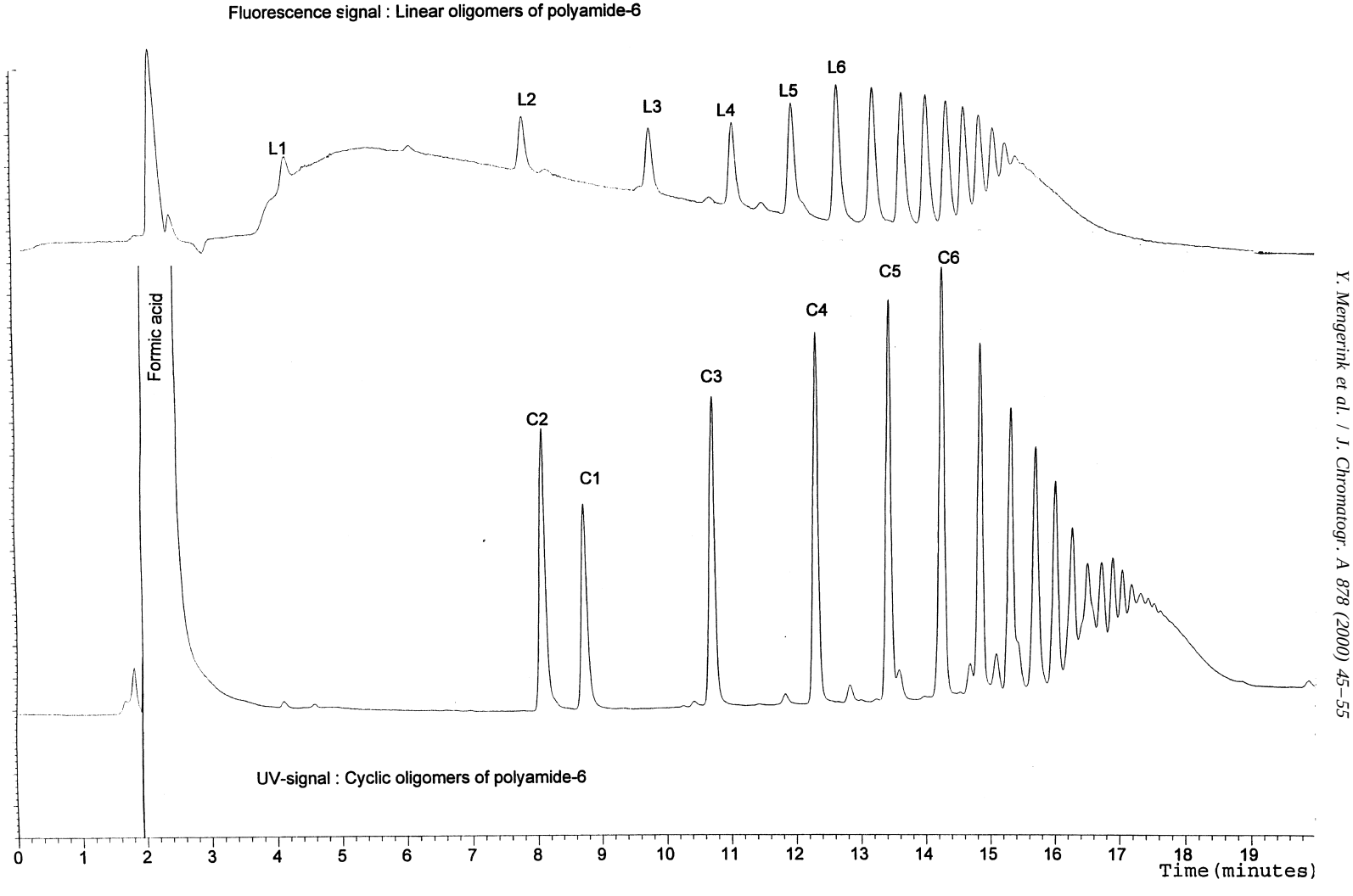



Fig. 2. Typical set of chromatograms of a polyamide-6 sample. (a) UV detection of the cyclic oligomers ($\lambda = 200$ nm). (b) Fluorescence detection of the derivatized linear oligomers. Gradient, 1 to 50.5% acetonitrile in 22 min; aqueous phase, 10 m*M* $H_3PO_4$ in water; flow-rate, 1.2 ml/min.

Table 1
Calibration factors at 200 nm (mAu l $m^{-1}$ $g^{-1}$) for the cyclic and linear oligomers

| Cyclic oligomer | $\varepsilon'$ (200 nm) | Linear oligomer | $\varepsilon'$ (200 nm) | |
|---|---|---|---|---|
| | | | Theoretical, Eq. (3) | Experimental |
| $C_1$ | 5050 | $L_1$ | – | <15 |
| $C_2$ | 3050 | $L_2$ | 1625 | 1725 |
| $C_3$ | 3375 | $L_3$ | 2300 | 2300 |
| $C_4$ | 3475 | $L_4$ | 2500 | 2450 |
| $C_5$ | 3475 | $L_5$ | 2700 | 2450 |
| $C_6$ | 3475 (=$C_5$) | $L_6$ | 2825 | 2600 |

However, when our results (Table 1) and the results of other research groups [16,17,20,33] are fitted in Eq. (1), UV absorbance for caprolactam and the cyclic dimer do not fit so well: the absorbance for caprolactam is much higher and the absorbance for the cyclic dimer is a little lower than expected. The discrepancies in UV absorbance for the cyclic dimer can be explained by the fact that a very stable intramolecular hydrogen bond is possible [34]. The rigid ring or the absence of intramolecular interactions of the cyclic monomer caprolactam could explain its relatively high UV absorbance.

A direct consequence of Eq. (1) is that the calibration factor is the same for all higher cyclic oligomers ($n>2$) if it is expressed in absorbance units divided by concentration in g $l^{-1}$ ($\varepsilon'$) instead of dividing it by the molarity ($\varepsilon$), as the molecular weight is directly proportional to the equivalent amount of amides (cf. Table 1). The number of amide functions divided by the molar mass is constant for all cyclic molecules.

Although we used a post-column reaction for the determination of the linear oligomers it is interesting to look at the UV absorbance for these kinds of oligomers. In Ref. [18] the linear oligomers eluted unretained and the total peak area was thought to indicate the total linear oligomeric content, ignoring the fact that the UV absorbance for each linear oligomer is different. Contrary to cyclic oligomers, the number of amide functions divided by the molar mass is not constant for the linear oligomers. The UV absorbance can be reformulated as:

$$\varepsilon_{L_n} = lc\{\varepsilon^{eq}_{acid} + \varepsilon^{eq}_{amine} + (n-1)\varepsilon^{eq}_{amide\ in\ chain}\} \qquad (2)$$

where $A_{L_n}$ is the absorbance of the linear oligomer $L_n$ (Au), $c$ is the concentration of the oligomer (mol $l^{-1}$) and $\varepsilon^{eq}$ is the equivalent absorbance coefficient (Au $eq^{-1}$ l $m^{-1}$) of the carboxylic acid group, the primary amine group and the amide group in the chain, respectively.

The response of the acid and amine groups is very low and can be neglected, but it can also be determined by injecting commercially available 6-aminocaproic acid, the monomer of this series of linear oligomers. The $\varepsilon^{eq}_{amide\ in\ chain}$ is the same as for the higher cyclic oligomers, so the absorption coefficient for a linear oligomer is given by:

$$\varepsilon'_{L_n} = \frac{113(n-1)\varepsilon'_{C_n} + 131\varepsilon'_{6-aca}}{131 + 113(n-1)} \qquad (3)$$

where $\varepsilon'_{L_n}$, $\varepsilon'_{C_n}$ and $\varepsilon'_{6\text{-aca}}$ are the absorption coefficients of a linear oligomer, a higher cyclic oligomer and of the linear monomer 6-aminocaproic acid, respectively (Au $g^{-1}$ l $m^{-1}$), 113 is the molar mass of one backbone unit (g $mol^{-1}$) and 131 is the molar mass of the monomer 6-aminocaproic acid (g $mol^{-1}$).

To validate Eq. (3), the absorption coefficients of the linear oligomers were calculated with the absorption coefficients of the cyclic oligomers and compared with the experimental data. The results, given in Table 1, correlate well.

Because the linear oligomers are commonly present at low levels compared to the cyclic oligomers, we coupled a post-column reactor behind the UV detector. With the use of the well-know OPA–3MPA (*o*-phthalic dicarboxaldehyde and 3-mercaptopropionic acid) [35–40] reaction, primary amines are derivatized into isoindoles, which can be selectively detected with fluorescence, as the coeluting cyclic oligomers do not interfere.

The material and the reaction time in the capillary

were investigated by changing the length, the volume and the material of the post-column reactor. With three different reactors and a total flow of 1.7 ml $min^{-1}$ [coiled stainless-steel capillary 1 (5 m×0.25 mm=0.5 ml=0.3 min reaction time), coiled stainless-steel capillary 2 (6 m×0.35 mm=1 ml=0.6 min reaction time) and crocheted PEEK capillary 3 (11 m×0.35 mm=2 ml=1.2 min reaction time)] the response factors did not change by more than 6%.

By changing the eluent flow (0.5–1.5 ml/min) and the post-column flow proportionally, different reaction times can be investigated at constant reaction pH. Fig. 3 shows that, with the exception of 6-aminocaproic acid, the response of all linear oligomers tends to change minimally on increasing the reaction time, and even the coefficient of variation of the mean response of 6-aminocaproic acid is less than 6%. Although the response increases at higher pH, the noise from the post-column pump increases exponentially above pH 10, which is the optimum with respect to the signal-to-noise ratio (Fig. 4)

The absolute calibration factor for the fluorescence signal of the linear monomer is stable, as with all OPA reagents prepared within 9 months, this factor gives a coefficient of variation of less than 10% (Fig. 5). Also, the content of the linear oligomers in a reference sample is stable (Fig. 6), so the degrees of conversion of the different linear oligomers are reproducible.

A small drawback of this post-column reactor is the long-term instability of the OPA reagents as recently described by Molnar-Perl et al. [35]. After several days, an as yet unknown precipitate appears. When the reaction capillary is not cleaned well daily with the aqueous mobile phase after each analysis sequence, a precipitate builds up inside the capillary,

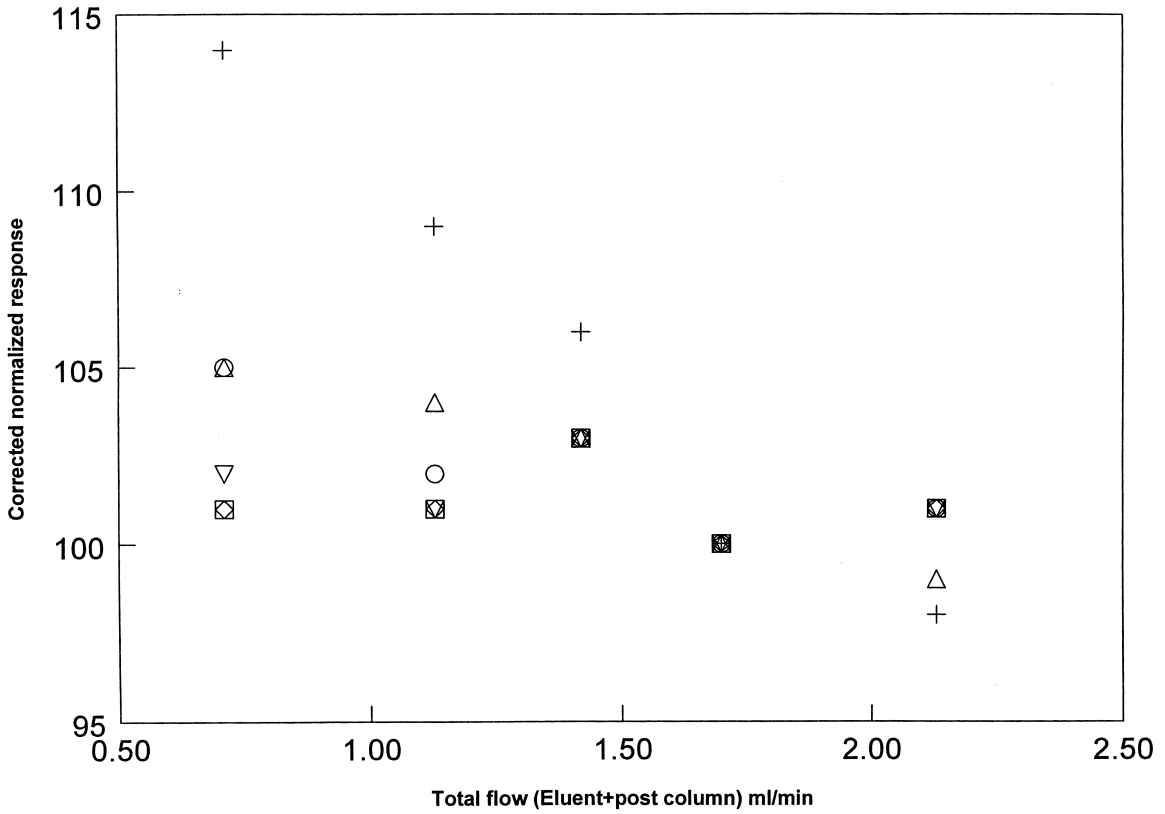



Fig. 3. Influence of the total flow, and thus the reaction time, on the corrected normalized response of the linear oligomers in a (6 m×0.25 mm=0.6 ml) capillary. Cross, linear monomer $L_1$; triangle up, $L_2$; circle, $L_3$; triangle down, $L_4$; diamond, $L_5$; square, $L_6$.

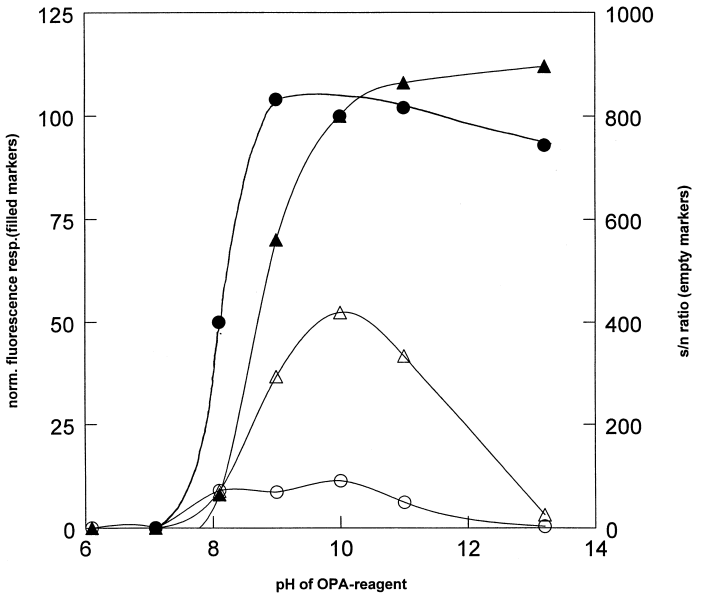



Fig. 4. Influence of the pH of the OPA/3-MPA substrate on the post-column reaction. Buffer concentration, 0.4 *M* boric acid; pH adjusted with KOH to establish pH. Triangle, linear monomer $L_1$; circle, $L_6$. Filled symbols indicate normalized fluorescence response; empty symbols indicate signal-to-noise ratio.

which causes a small but broad peak in the chromatogram, making integration at low levels of the eluting linear oligomer derivatives harder to perform correctly (see Fig. 2).

Without good calibration standards the same assumptions as with UV detection can be made. Only the isoindole group is responsible for the fluorescence intensity and this would mean that 1 mol of linear oligomer would give a constant response, independent of the specific oligomer. As 6-aminocaproic acid is commercially available this is a convenient way of calculating the calibration factors of the higher, non-available, linear oligomers.

Although the fluorescence intensity is defined as [32,41–43]:

$$I_F = \Phi I_0(1 - 10^{-\varepsilon c l}) \quad (4)$$

where $I_F$ is the fluorescence response in quanta per second, $\Phi$ is the quantum yield, $I_0$ the intensity of the incident light in quanta per second, $\varepsilon$ the molar absorption coefficient (Au l $mol^{-1}$ $m^{-1}$), $c$ the concentration (mol $l^{-1}$) and $l$ the path length of the cell (m), the use of the intrinsic fluorescence sensitivity (IFS) has been proposed [42,44]. The IFS can be defined as $\Phi\varepsilon/BW$. For $\varepsilon cl < 0.02$, $(1 - 10^{-\varepsilon cl}) = 2.3\varepsilon cl$ and Eq. (4) can be reformulated as:

$$I_F = 2.3 I_0 IFS'_{6\text{-aca}} BWCl \quad (5)$$

where $IFS'_{6\text{-aca}}$ is the intrinsic fluorescence (Au $g^{-1}$ l), $BW$ is the band width at half height of the emission spectrum ($m^{-1}$), $C$ is the concentration (g $l^{-1}$) and $l$ is the path length of the detector cell (m). Due to this reformulation, the units of Eq. (5) do not fit.

With the insulation of chromophores rule in mind, the intrinsic fluorescence of the higher linear oligomers is given by:

$$IFS'_{L_n} = \frac{131 IFS'_{6\text{-aca}}}{\{131 + 113(n-1)\}} \quad (6)$$

where $IFS'_{L_n}$ is the intrinsic fluorescence of linear oligomer $L_n$ and $IFS'_{6\text{-aca}}$ is the intrinsic fluorescence of 6-aminocaproic acid. In Eq. (6) it is assumed that the degrees of conversion of all linear oligomers are the same and that the quantum yield of all linear oligomers is the same. This is unlikely, so Eq. (6) is improved by the introduction of an empirical quench factor:

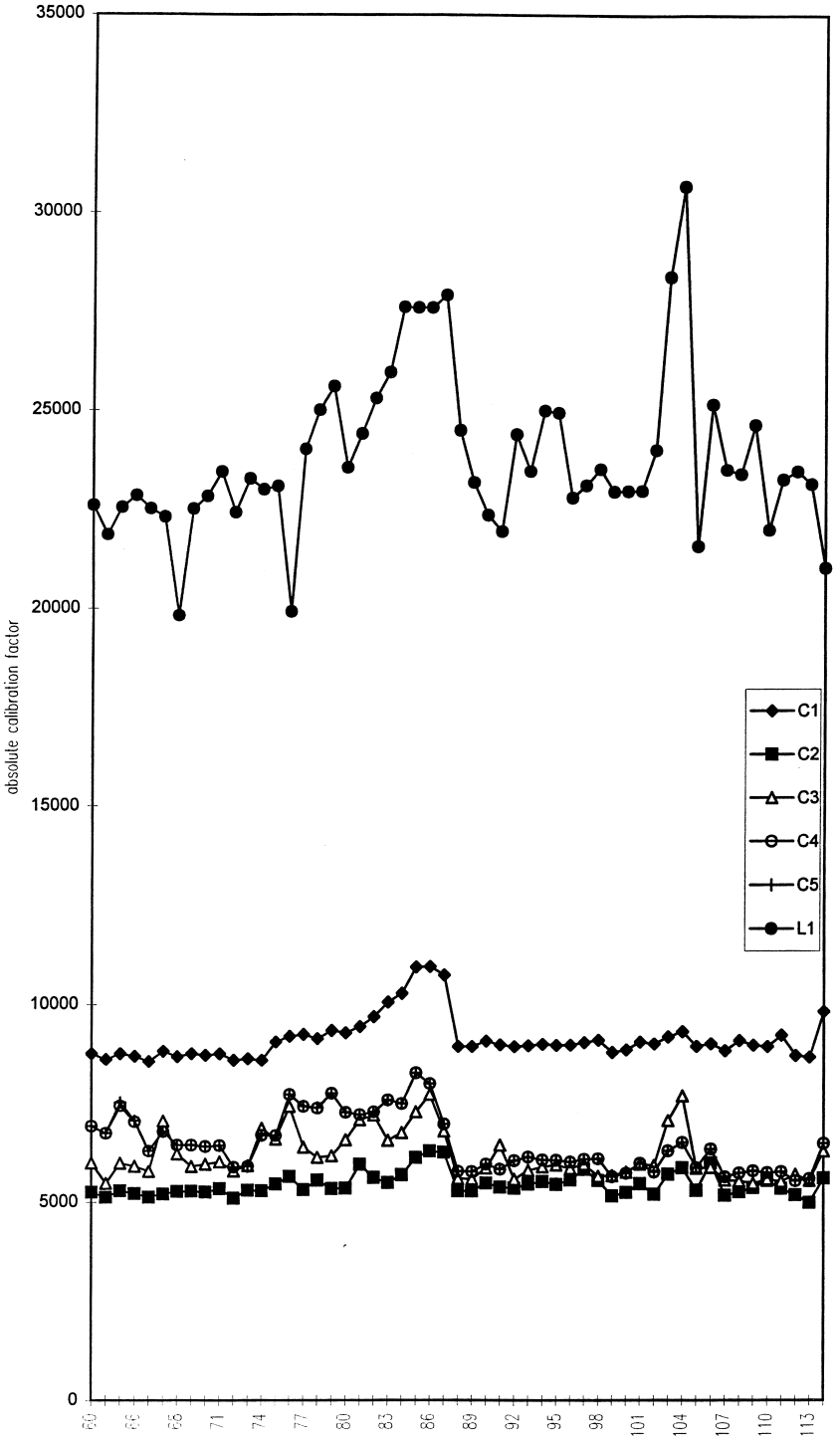



Fig. 5. Control chart of the calibration factors of 6-aminocaproic acid ($L_1$) and of the first five cyclic oligomers ($C_1$–$C_5$).

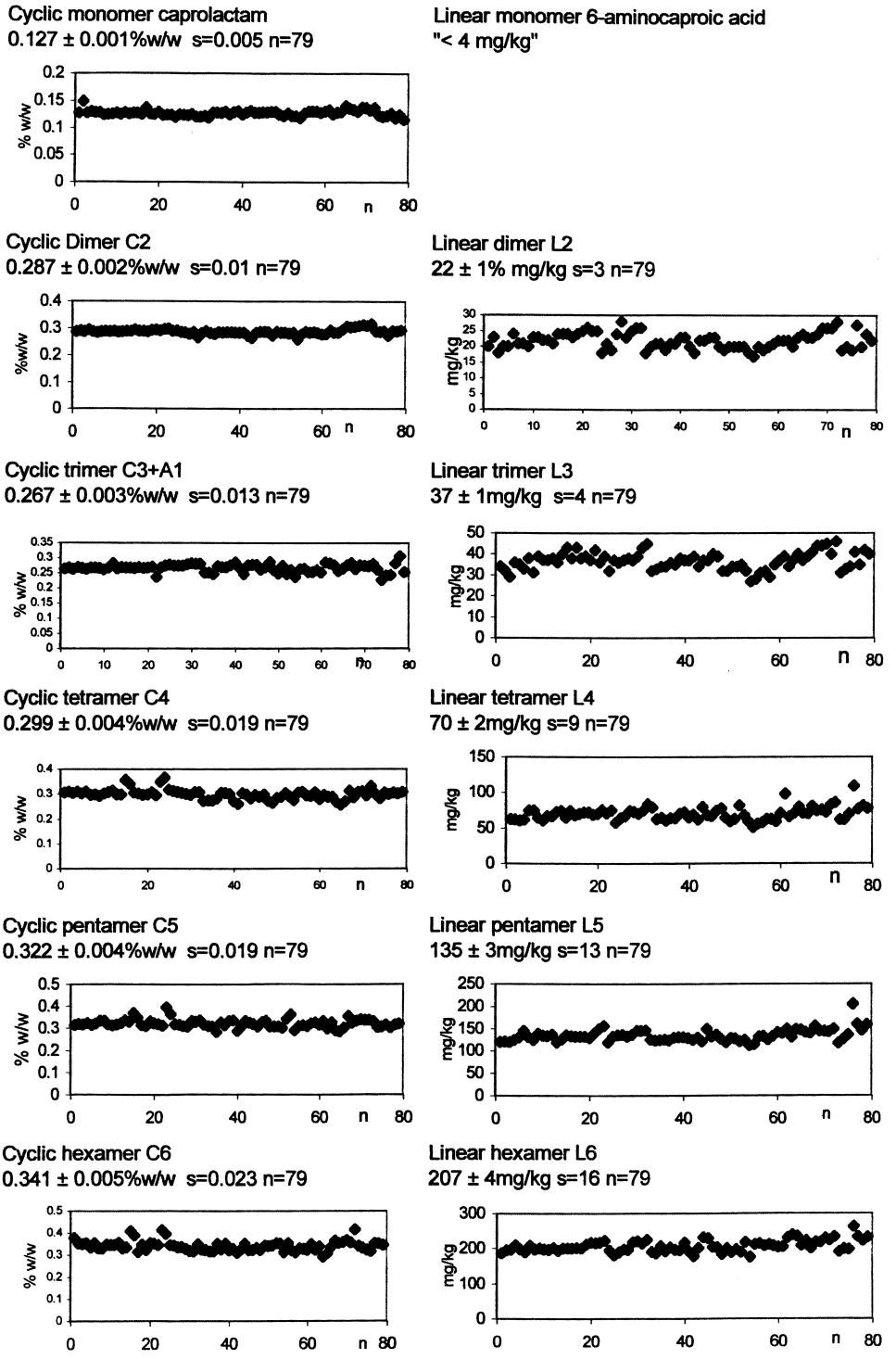



Fig. 6. Precision of the content of linear and cyclic pentamers in a reference sample.

$$IFS'_{L_n} = \frac{Q_{L_n} 131 IFS'_{6\text{-aca}}}{\{131 + 113(n-1)\}} \quad (7)$$

where $Q_{L_n}$ is the quench factor.

To determine the empirical quench factors for the respective linear oligomers we isolated a few milligrams of each linear oligomer by preparative HPLC. The results are given in Table 2. As isolated linear oligomers are scarce, for routine use Eq. (7) is utilized with the quench factors of Table 2 to calculate the calibration factor with the experimentally determined calibration factor of the linear monomer 6-aminocaproic acid.

A comparison of the detection principles yields that, with UV absorbance, the detection limit is approximately 100 mg $kg^{-1}$ and with the post-column OPA/3–MPA reactor the detection limits of the derivatized linear oligomers are in the range 5–20 mg $kg^{-1}$. For the cyclic oligomers, the detection limit does not increase on increasing the backbone units as it does for the linear oligomers in nylon-6.

### *3.2. Method performance*

With the sandwich injection method, polyamide can be injected into an HPLC system without problems. About 100 injections can be made before the column has to be cleaned or replaced [6]. With the use of the absolute calibration factor in a control chart, instrument performance can easily be monitored (Fig. 5). When the calibration factors of the linear and cyclic oligomers drift in the same direction, this is probably caused by a pump or injection problem. Only once did we observe a slow increase of all calibration factors, up to 20% higher than the normal values, which could be traced back to injector problems (Fig. 5, $n = 74$–$86$). When only the calibration factors of the linear or cyclic oligomers drift, this is obviously caused by the corresponding detection system. In Fig. 6 the accuracy of the contents of the linear and cyclic oligomers is given in a control chart of a representative reference polyamide sample [6]. For the representative polyamide-6 reference sample with low oligomer concentrations the coefficient of variation of the cyclic oligomers is 3–7% and for the linear oligomers the coefficient of variation is 8–13%. At higher concentrations of oligomers the coefficient of variation decreases. For an unwashed polyamide-6 reference sample the coefficient of variation of caprolactam (amount 8%) is less than 1%.

Table 2
Quench factors for the linear oligomers

| Linear oligomer | Quench factor |
|---|---|
| $L_1$ | 1 |
| $L_2$ | 0.8 |
| $L_3$ | 0.66 |
| $L_4$ | 0.66 |
| $L_5$ | 0.66 |
| $L_6$ | 0.66 |

As expected, the above deviation of the injection volume did not affect the contents of the reference sample (Fig. 6; compare experiments 1–73 with 74–80).

With the described method, the oligomer content of a nylon-6 sample can be analyzed by dissolving the polymer in formic acid (during 1 h with ultrasonic agitation), and analysis, including column equilibration for the next injection, takes 33 min. As more samples can be dissolved simultaneously and calibration and reference samples have to be run also, approximately 60 polymer samples can effectively be analyzed within 2.5 days. This does not include data analysis if not fully automated, which is strongly dependent on the available hardware and software.

## 4. Discussion/conclusion

Applying the equivalent group absorbance concept is very useful for research purposes and in semi-quantitative analysis of the oligomeric determination of all kinds of different polymers. When the chromophores of these oligomers are insulated, the calibration factor of many higher non-available oligomers can easily be estimated.

The concentration of linear oligomers in our samples was much lower than the concentration of cyclic oligomers, the latter being detected properly by low-UV absorbance detection. Because UV absorbance is mainly governed by the amide function, the absorption coefficients of non-available oligomers can be calculated. At the usual low level of linear oligomers compared to cyclic oligomers, UV detection is not feasible for these linear oligomers,

but they can be selectively determined with a post-column reaction detector. Their primary amine group reacts with *o*-phthalic dicarboxaldehyde and 3-mercaptopropionic acid to form a fluorescent isoindole. Again, the calibration factors can be calculated, although an empirical correction factor, the so-called quench factor, is necessary to improve accuracy. Detection limits of 100 mg of each cyclic oligomer and 5–20 mg of each linear oligomer in 1 kg polyamide are obtained. In real nylon-6 samples, the precision for cyclic oligomers is approximately 6% and for linear oligomers the precision is 10% or better.

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